

Modern Hypothesis for Physical Adsorption

Modern Hypothesis for Physical Adsorption

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

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

Dedicated to
Dr. E. Loren Fuller, Jr.
(1930-2007)

He had wisdom, knowledge and truth.

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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 physical adsorption-quantum mechanics calculations. They are written for anyone with a modest background in quantum mechanics and the most elementary aspects of the theory of physical adsorption.”¹ I had, of course, made some substitutions:

- for “A.W.” (Augmented Plane Wave) \Rightarrow “physical adsorption”
- For “Bloch electrons in an ideal crystal” \Rightarrow “quantum mechanic”

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 some physical adsorption isotherms to get a sample’s “surface area,” you should be able to understand what is written in this book.

Unfortunately, the 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 very 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. I have tried to address this problem head-on, pointing out flaws in the theory, without success. However, there are many attempts by others to “correct” the BET theory. For example, some have used multiple additions of BETs. Some others 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 leads to a 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. For those who just get on with it expecting to find a way to make the information useful, I have not included 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, so one can get started right away using the information. For the curious, the derivations are 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 roles did the personnel in the Oak Ridge National Laboratories play in the discovery of the quantum mechanics application?” This is explained in Appendix IV, which explained some of the history and the role that two researchers, Dr. Loren E. Fuller, analytical chemistry, and Dr. John Kirkpatrick, mathematics performed. Another appendix is my curriculum vita. It is quite boring reading but perhaps is needed to lend credence that I am indeed a believable scientist and the ad hominem statements are false.

Back to the equations - they are used for physical adsorption-quantum mechanics and are provided up-front. This is 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. The reader who has some experience with Physical Adsorption will be astonished at the precision obtained.

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 are second. Other symbols, being neither English nor Greek, are presented last. Some symbols are different from those commonly seen. However, as far as possible the SIO/IUPAC symbols or their approved alternative symbols are used. The reason for using the alternative conventions 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. There are some symbols that have never before been used anywhere except in the physical adsorption-quantum

mechanics and this is pointed out, for example the “threshold” symbols.

Following the introductory chapter, a list of possible experimental errors is addressed. This is **extremely important** because firstly, these are common errors. Secondly, these errors can radically change the answers. 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. These errors, by the way, have been used in the past to discredit the physical adsorption-quantum mechanics hypothesis. Very ironic. 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 hybrid pores, mesopores and mixed systems. These topics are in addition to the basic theoretical framework and can be confusing. So methodologies are given to follow. These methodologies should help to obtain the correct answer. The final chapters address two-gas adsorption (binary adsorption) and determining the heats of adsorption nonparametrically, by simply using the quantum mechanics results obtained from the isotherm.

The QM is not the only modern hypothesis for physisorption based on preexisting science. The hypothesis called 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 13 through 16.) QM and ESW can be derived from each other. Thus, they are mutually supportive and reinforce 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 other materials supporting the Modern Hypothesis has been largely performed by others. Most of these researchers either knew nothing about this modern hypothesis were hostile

toward it. Recent exceptions, by recent is meant the last 47 years, are more publications by Dr. Jürgen Adolphs in Germany and Dr. Loren E. Fuller and the Oak Ridge Laboratories' Analytical Divisions have been available. These tools are not widely used. Perhaps you can make a difference.

So, good luck and do not be discouraged by anything, including contrary advises either by authorities or by your own mind. - JBC - June 29, 2025

Purpose of the Book:

This book is not a review nor a compilation of previous works. This review/compilation is available in the 2nd edition of a book I wrote. (The book, however, is very expensive.) I have not referenced all the authors that one would consider as important. I have deliberately not included the BET equation, although I have included the BET transform. The transform is addressed in Appendix II. Appendix II critically evaluates "Henry's" laws (for which BET is one) and provides their disproof. There are several authors, such as deBoer, Polanyi, London and others who deserve acknowledgment and others such as the authors of the BET and Einstein who used their authoritarian position to embarrass and to squelch the motivation of the scientists of their time.

All of these considerations are inconsistent with the intent of this book, which is to allow the reader to learn about the quantum mechanics of physisorption. If there are objections about the lack of examples, these are available in the 2nd edition. Before obtaining the 2nd edition, try what is in this book to analyze new material using modern equipment that avoids the pitfalls of the second chapter.

Are you resistant? Why would you be? The method and analysis described in this book are easier and more intuitively interpretable than any of the classical techniques. So why work so hard to get the wrong answer when there is a better possibility, which is presented here, that is closer to the truth and much easier to do?

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1. The Ideal Equations with Examples:

The derivation of the equations is presented starting with the Hellmann-Feynman (HF) theorem (in Appendix III.) The HF theorem is not often used, but this is the simplest way to derive the equations. If the perturbation theory were to be used, the 1st approximation is good enough. This is due to the very small size of the perturbation compared to the surface aliquant. If you prefer other techniques, these equations have been derived in a book² using the perturbation and in a publication using the WKB approximation³. (WKB works, but is not advised due to discontinuity problems.) Digital calculations 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 the final resulting equations are based on solid theoretical grounds. If there is any question about this, consult with the nearest physicist at a University or College.

1.1 Simple two parameter case

Consider an adsorbent^a that is homogeneous^b, non-porous and not sterically hindered^{c,d}. This is referred to as “the simple case” and QM yields the following equations. The calculation starts with defining the quantities:

$$\Delta\chi := \chi - \chi_{\varsigma} \quad (1)$$

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

$$n_a/n_m := \theta = \Delta\chi \quad (2)$$

^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.”

and where n_a is the amount of the adsorbate^e, n_m is the monolayer equivalence^f and θ is classically called the “coverage.”

The following are the definitions of the QM quantities χ and χ_ζ . The subscript ζ (the Greek letter terminal sigma) indicates what is call a “threshold” quantity.

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

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

- P_{vap} = the vapor pressure of the adsorptive^h at the temperature of the adsorbent.
- P_ζ = the threshold pressure. The concept that the low end of the isotherm extrapolates to $(P, n_a) = (x, 0)$ 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, ε , to adsorptive pressure is

$$\ln(P_{\text{vap}}) = \bar{\varepsilon}/RT \quad (4)$$

Where the overlines indicate molar quantities (the alternative SI designator, “-”ⁱ, is used here to avoid conflict with “_m” for “monolayer equiv.”^j) After defining E_a as the threshold energy:

$$\ln \left(\frac{P_\zeta}{P_{\text{vap}}} \right) = -\frac{\bar{E}_a}{RT} \quad \text{or} \quad P_\zeta = P_{\text{vap}} \exp \left(-\frac{\bar{E}_a}{RT} \right) \quad (5)$$

^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

^g Why so many definitions? As you will soon see, the transform in the independent variable yields meaningful representations.

^h Def: Adsorptive: the gas phase in contact with the adsorbent. The adsorptive and adsorbate are the same thermodynamic component in QM theory and so in physical adsorption. They are not in the same state. See the next footnote

ⁱ Def: the overbar “-” is the IUPAC alternative for “per mole.”

^j equiv. = abbreviation for equivalence

From these equations the following is true:

$$-\ln(P) = -\frac{\bar{E}_a}{RT} e^{-\theta} + \frac{\bar{\epsilon}}{RT} \quad (6)$$

The thermodynamic internal energy function^{k,1} $\Delta_g^a \mathbf{E}$ is the energy change 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:

$$\Delta_g^a \mathbf{E}^\ominus := \Delta_g^a \mathbf{E}(n_a) = E_a \exp(-\chi) + \bar{\epsilon} \quad (7)$$

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

$$\Delta_i^a \bar{\mathbf{S}} = -RT \{1 - \exp(-\Delta\chi)\} \approx 0$$

This means that the entropy change is insignificant. It also means that the adsorbate is a liquid phase of a different average 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 yields are called the "Schichten"^m equations. A schicht in classical meanings as a "level," "layer," spot in a

^k $\Delta_g^a \mathbf{E}$ is the change in the internal energy of the system, the adsorbent plus adsorbate, from the liquid state. If it were compared to the standard (gas at 1 bar) to the adsorbed state this would be indicated by a symbol " \ominus " after the " \mathbf{E} ."

^l 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 1 vs. l. Can you blame them? It looks like a 1 pixel difference in Roman even in 24 pt.

^m 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.

“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 are some similar characteristics. So, the following are the Schichten equations. The subscripts indicate the schicht level:

$$\theta_1 = 1 - \mathbf{exp}(-\Delta\chi) \quad (8)$$

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

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

So for the $(n+1)^{\text{th}}$ schicht:

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

and it can be proved that:

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

Notice that the ratios are not arbitrary and for a flat surface the densities cannot be manipulated by adjusting equilibrium constants.

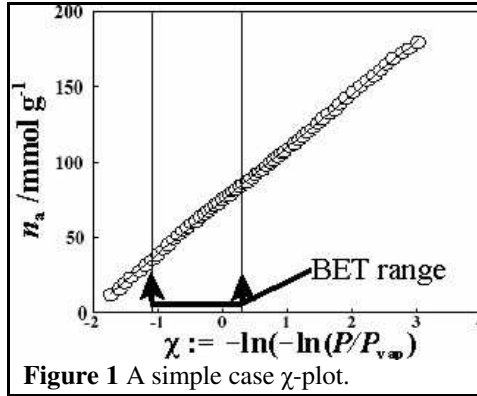
Obviously the schichten equations can be adjusted when steric hindrances are present. For example, if there is only room to stack one molecule in the normal direction from the surface, only equation, (8), will apply. All other schichten are sterically blocked. Equation (8) can be rearranged to:

$$n_1 = n_m + \frac{n_m RT}{\bar{E}_a} \ln\left(\frac{P}{P_{\text{vap}}}\right) \quad (13)$$

This is the log-law and is often observed. This plot 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 yields threshold pressure, P_ζ and when P is at P_{vap} then $n_1 = n_m$. That is, extrapolation to the ordinate axis yields the monolayer equivalence and the extrapolation to the abscissa yields P_ζ/P_{vap} , which yields $\mathbf{exp}(-E_a/RT)$, according to **Equation (5)** (p. 7.)

1.3 Calculating the unlimited multischichten case:

Using equation (1) with the definitions equation (2) and (3), one is able to find n_m and E_a from a straight fit of a curve n_a versus $-\ln\{-\ln(P/P_{\text{vap}})\}$. This is the plot which Le Saursure ⁴ determined in 1814 as an excellent fit to the isotherm. In this representation, the abscissa intercept is E_a/RT and the slope is n_m . This plot is called a χ -plot shown in **Figure 1**.



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

1. Calculate the n_m for an initial slope if it is straight enough. As will be seen later in section 4.2.2, there is an interesting phenomenon when the steric hindrance is such that a partial schicht is left over. This “last” schicht will start to fill and then “reverses” its densification to satisfy accommodate the lower schichten to fill in preference. This phenomenon is 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 apparent error can be corrected.

A total schichten filling is shown in **Figure 2**

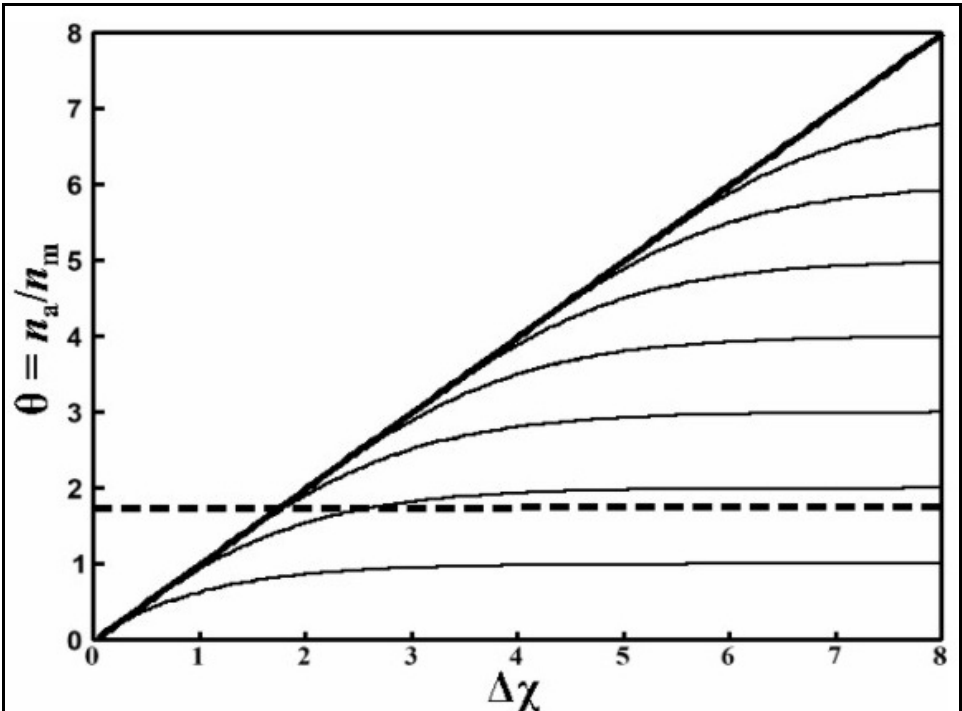


Figure 2 The addition of schichten with filling. If the maximum filling is designated by the dotted line Then when the 2nd schicht crosses the line it not only stops filling, but reverses (drops) to allow the 1st schicht to continue to fill to n_a .

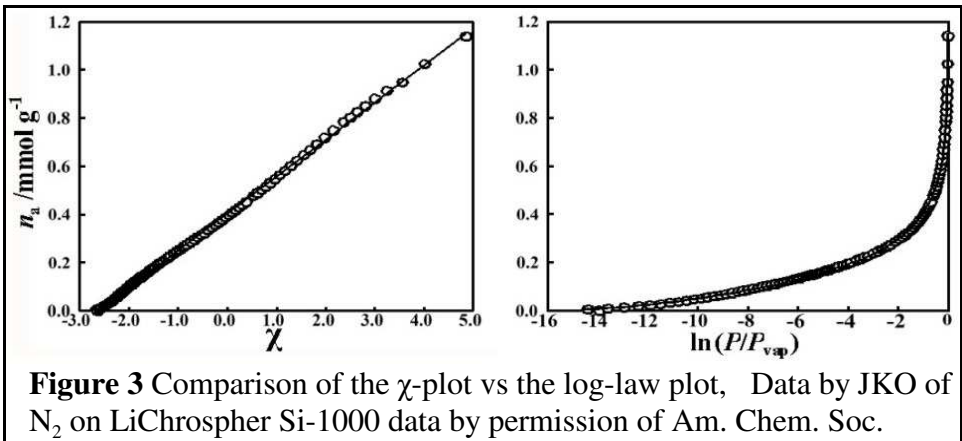
Since all schichten start to fill above P_c , there is a small amount to be sacrificed in the higher layer as well as the one that is above the main filling schicht. For example in the **Figure 2**, the 2nd schicht will have to give up some adsorbate for the 1st schicht to continuing to fill. 3rd one needs to release its adsorbates to the 1st and 2nd, but it might not be noticed due to experimental insignificance.

This graph demonstrates 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 χ -plot, log-law plot and $\Delta\chi$ -plot:

Below are some examples of a χ -plot and a log-law plot. It is important to be able to distinguish between a χ -plot and a log-law plot. A χ -plot is useful if there is no steric hindrance and the log-law is for porous material where only a single schicht is adsorbed. They look quite different. The $\Delta\chi$ -plot is the expression of equation (1).

1.4.1 Example χ -plot - Jaroniec, Krug and Olivier:



In **Figure 3** are plots by Jaroniec, Krug and Olivier⁵ (JKO) of N_2 on Si-1000 is plotted. (The last two points in the publication were Si-5000 were not used here since undoubtedly has a different surface composition.) On the left is a χ -plot and on the right is a log-law. The question is, 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 criterion must take into account the different amount of specific adsorbate. This criterion is specified by the letters “FDR” meaning “Full Date Range.” It is the standard error of the n_a , symbol s_n , 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

Table 1 Output parameters obtained by linear regression of JKO χ -plot

Name	Symbol	Value	Std. Dev.	units
monolayer equiv	$n_m^* =$	0.1593	$\pm 7.9 \times 10^{-4}$	mmol g ⁻¹
threshold χ	$\chi_c^* =$	-2.5917	$\pm 8.4 \times 10^{-3}$	
std. error for n_a	$s_n =$	0.0125		mmol g ⁻¹
% of data range	$s_{n\text{FDR}} =$	1.22 %		
starting energy	$E_a =$	-8.71	± 0.07	kJ mol ⁻¹
correlation	$r^2 =$	0.998		

* indicates the two output parameters.

(p12)

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 an increase in the n_a is very steep, which can cause an artificially highⁿ s_n in the steep zone. This is normal for mesopores and is discussed in the mesopore section.

It is obvious with the definition of FDR, that poorly scattered data might never qualify by this 1% rule. If the rule disqualifies the experiment, repeat experiments are recommended, check the error list and check for additional features. Notice in this case, the data is not highly scattered and the percent FDR is greater than 1%. Thus, some feature are present that have not been taken into account. In this case, later sections accounting for heterogeneity and a pressure correction improve the fit.

ⁿ s_n := standard error in the dependent variable n_a - different from original set symbol

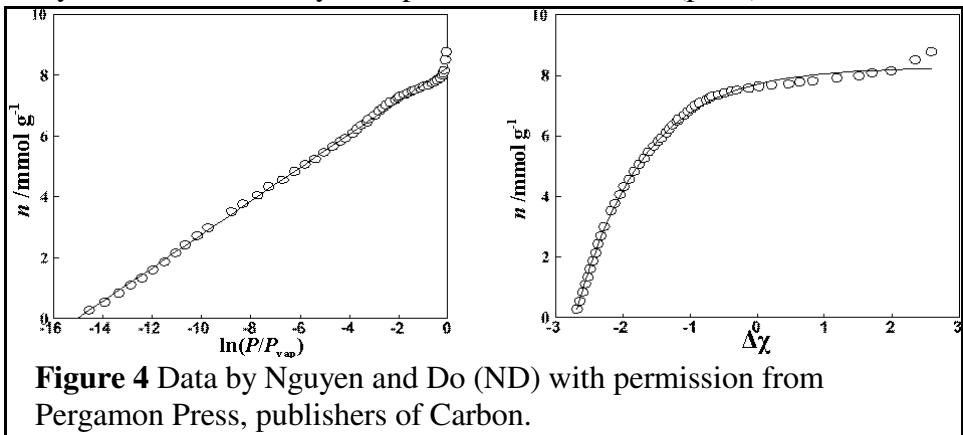
1.4.2. The $\Delta\chi$ -plot a scale for monolayer amount.

The $\Delta\chi$ -plot is similar to the χ -plot except the abscissa is given by $\Delta\chi = \chi - \chi_c$. In the simple case, $\Delta\chi$ becomes a measure of monolayer equivalence according to **Equations (1) and (2)** (p 6.) Some of the added features upset this convenient arrangement but it is still useful.

On the other hand, the χ -plot is an energy plot according to **Equation (7)** (p.8.) This is a plot which makes mesoporosity, hysteresis and thermodynamics intuitive.

1.4.3 Example log-law, data by Nguyen and Do:

Another isotherm for illustration is presented two ways in **Figure 4**. This data is by Nguyen and Do⁶ (ND) of N₂ on microporous carbon (Takeda ACF). On the left in **Figure 4** is the log-law and on the right the χ -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** (p.15.)



Both of these examples will be used again to point out some subtle features. (Notice that the normal isotherm has not been used so far. Why is that? Because it is useless except for the magic point, which is explained later.)

The lesson here is that is the χ -plot describes the isotherm then the

isotherm is not sterically hindered and if the log-law fits it is hindered to one schicht. You ask, “What about an intermediate case, for example, 1½ or 2 schichten?” This is presented later along with other interesting isotherms.

A more complete analysis drops the $s_{n,FDR}$ below 1% here as well. This is demonstrated in Appendix VII (A7.3) **Table 15** (p.113).

Table 2 Output parameters obtained by linear regression of ND log-law

Name	Symbol	Value	Std. Dev.	units
monolayer equiv*	$n_m =$	8.251	± 0.032	mmol g ⁻¹
threshold $\ln(P_\zeta/P_{\text{vap}})^*$	$=$	-15.0555	± 0.0459	
threshold P	$P_\zeta/P_{\text{vap}} =$	2.894×10^{-7}		
threshold χ	$\chi_\zeta =$	-2.7117		
starting energy	$E_a =$	-9.84	± 0.07	kJ mol ⁻¹
	$s_n =$	0.0196		mmol g ⁻¹
	$s_{n,FDR} =$	0.24 %		

* the 2 parameters obtain from the plot. Others are derived from these.

1.4.4 The Fuller “magic point”

According to QM, the point at which the isotherm’s inflection point occurs is when $P/P_{\text{vap}} = 0.3678\dots = 1/e$. At this value, $\chi = 0$ (and $-E/RT = 1$).

The slope of $X := P/P_{\text{vap}}$ may be determined so:

$$\theta = -\ln\{-\ln(X)\} + \chi_\zeta \quad (14)$$

(Where χ_ζ is a constant.) Differentiating yields and using the definition

$\theta = n_a/n_m$:

$$\frac{dn_a}{dX} = \frac{n_m}{X \ln(X)} \quad (15)$$

Substituting for X on the right with the values at the magic point:

$$\frac{dn_a}{dX} = \frac{n_m}{e^{-1} \ln(e^{-1})} \quad (16)$$

Rearranging and using $\ln(e^{-1}) = -1$:

$$n_m = -\frac{dn_a}{dX} e^{-1} \quad (17)$$

Thus, finding the slope at $X = 0.3678\dots$ yields the monolayer equivalence. The obviously works only for nonporous materials or where porosity begins after the value of the magic point.

The problem using this is obtaining the slope. Since the data is digital, there is an inherit error beyond the normal scatter in the data. In reference (2 p. 18) this is pointed out with some example determinations. The data is not symmetrical about the magic point. So, even though the selection of the two points opposite 0.3678... to determining the slope, there is this asymmetry problem. This is illustrated in the **Table 3**. However, data scatter may be a more serious problem.

Notice that whatever two points about the magic point are selected, the average of these two point are not equal to the answer in bold. This is true for both the column that is for the simulation directly, **Equation (17)**, and from a digitally generated slope.

Shortening this technique would increase the uncertainty. A general criticism is that only the n_m can be obtain. One could extrapolate to obtain the E_a , but this would certainly be pushing the limits of the technique. If the need for precision is not a problem, then perhaps it could be used as a quality control analysis.

Table 3 The relationship between the relative pressure, X , and the slope yielding n_m . n_m is set to 2 for illustration.

X	$-\chi$	formula	digital
0.267879	0.551044	2.085155	2.0856
0.277879	0.494607	2.067647	2.0680
0.287879	0.438614	2.052490	2.0529
0.297879	0.383003	2.039516	2.0399
0.307879	0.327716	2.028580	2.0289
0.317879	0.272700	2.019561	2.0199
0.327879	0.217905	2.012352	2.0126
0.337879	0.163282	2.006862	2.0071
0.347879	0.108786	2.003015	2.0033
0.357879	0.054372	2.000746	2.0010
0.367879	0.000000	2.000000	2.0002
0.377879	0.054372	2.000733	2.0010
0.387879	0.108784	2.002908	2.0031
0.397879	0.163274	2.006497	2.0067
0.407879	0.217881	2.011481	2.0117
0.417879	0.272642	2.017846	2.0181
0.427879	0.327595	2.025585	2.0258
0.437879	0.382777	2.034698	2.0349
0.447879	0.438225	2.045191	2.0454
0.457879	0.493978	2.057076	2.0573
0.467879	0.550072	2.070371	2.0706

1.5 Conclusion for the Ideal Equations:

At this point, you are probably wondering if this is really that simple. Well, it is and it isn't. At this point you can only analyze a simple nonporous, homogeneous samples and a purely microporous samples. You may be able to run some isotherms, or have some available, and if you do you will probably come across some that do not fit. So you need more information.

But first, the next chapter provides some very important information about the experimentation. These problems are very common, so take them seriously. After these problems are solved, it may be that things will fall into place with the rest of the book.

Oh, and by the way, get a good non-linear least squares routine for your computer. You need to get the output of *independent variable* (y) *standard error*, s_n . s_n needs to be minimized.

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 Number 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 intradisciplinary 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.^o

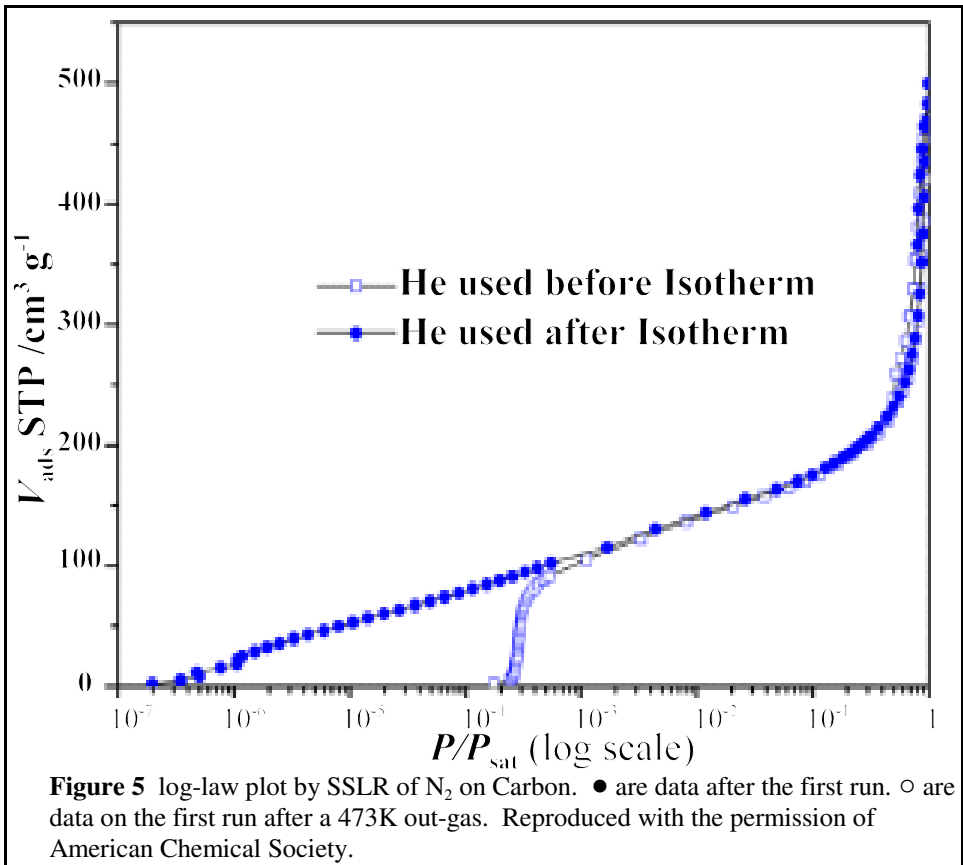
Why is this important? You have already learned the value of the quantity E_a , around which the entire calculation centers, is usually found in the HV or UHV range. Furthermore, the log-law, an important sub-law found in QM, is difficult to determine above $X = 0.01$. It is easily mistaken for the Langmuir isotherm, which is disproved and not a logical option. The log-law is also needed to determine if there is microporosity (as defined in section 1.) since it is more obvious with HV or UHV systems.

Another reason mentioned in the article by Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso⁷ (SSLR - read it!) is that out-gassing of the sample in HV appears to be a requirement for some adsorbent-adsorbate combinations^p. 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 5**.

Possible avoidance: If there is absolutely no porosity, then measurement above $X = 0.01$ will yield an average n_m 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.

^o 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 of any type using these theories..

^p The Oak Ridge Analytical group demonstrated that a hydrogen bake out for oxide and carbon adsorbents was required to get rid of contamination.



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 and some by deBoer^q. (deBoer with temperature correction.) 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, who indicated how to make a correction. However, 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

^q 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 are rather rare.

and recording the uncorrected atmospheric pressure. This is another quality control. Uncorrected changes in P_{vap} causes a wavy χ -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 handled with internal baffles in the tube and on the hang-down wire. A more thorough discussion is provided in the fore-mentioned book².

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 capacity.

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

^r A bend in one direction and then a bend back so to result in going in the same direction.

solved. For the best information on this problem see the Vacuum Technology book by Roth⁸.

With gravimetric systems the hang-down tube diameter and length can be increased to eliminate 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_c , 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 placed 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 the other classes of hysteresis. Not much research has been done on this but an excellent paper on this subject is the one by SSLR⁷. 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, is to do measurements 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. 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 which present different decay constants for a particular adsorbate-adsorbent pair is advised. This should 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, pressure and amount of weight gained but also P_{vap} readings, base vacuum, out-gassing procedure, instrument specifications, starting total mass, gas purity, adsorbent preparation or specifications from preparer, adsorbent characterization and the list of the readings of at least three experimental runs. Check to see if there are other important starting parameters that are needed. 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 as to why. It may be that the lack of information will disqualify the validity in the future. Put information in tables or lists for easy reading. Be kind to your colleagues and either list all the data in digital form or make it available to the public, somehow. Many journals provide a supplementary section available to the public. Check to see if this would be free to access. It's these details that determine if the publication is used or ignored as a reference.

The more information you provide, the better. If the journal restricts your length, or does not have archive ability, archive information somewhere else accessible to the public, for example in ResearchGate. - - 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_a , the dependent variable, for the ordinate for the isotherm plots. This means that for a variety of energy surfaces the n_a s add. For two n_a s, 1 and 2:

$$\{n_a(1) + n_a(2) \equiv n_a(1+2)\} \Big|_{F(P)} \quad (18)$$

as shown in **Figure 6**.

3.1 Using the insight of *Equation (14)* (p. 26):

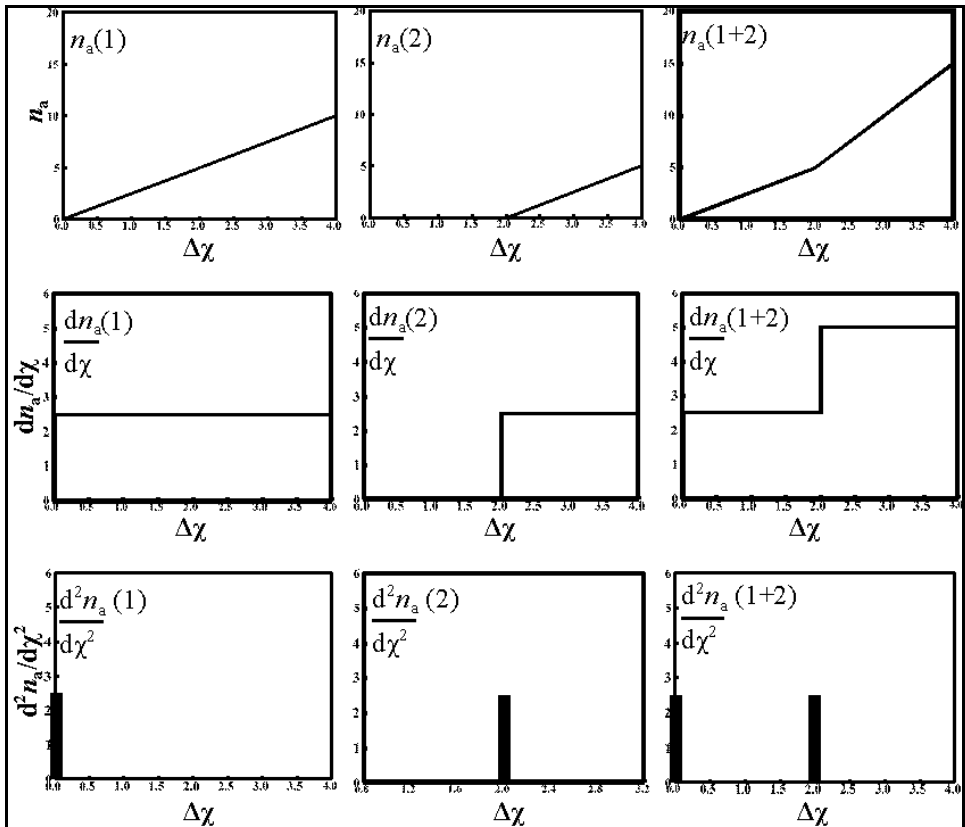


Figure 6 Simulation of the addition of two isotherms of differing E_a s. The two left columns are two isotherms, the 3rd column = 1st + 2nd. Top row - experimental n_a , middle - $dn_a/d\chi$ and the bottom row - $d^2 n_a/d\chi^2$.

The isotherms add even with the abscissa transformed, which is something most isotherm hypotheses, including the BET, are not capable of doing. Schematics of this situation this is illustrated in **Figure 6**. 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 added.
- 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, $P_{\zeta}s$ or energies, $E_a s$. The second derivatives also add.

Thus, a heterogeneity with two 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 another second line with a different E_a . This simple arrangement is not present in other analyzes.

This type of behavior does not seem to be common except for a log-law starting isotherm followed by a χ -plot for higher pressures. More common is the case where the χ -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.

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:

$$n_{\text{ads}} = n_m \mathbf{Z}(\chi, \langle \chi_{\zeta} \rangle, \sigma_c) \quad (19)$$

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

$$\mathbf{N}(x, \mu, s) = \frac{1}{\sqrt{2\pi s^2}} \exp\left(-\frac{1}{2}\left(\frac{x-\mu}{s}\right)^2\right) \quad (20)$$

$$\mathbf{D}(x, \mu, s) = \frac{1}{\sqrt{2\pi}s^2} \int_{-\infty}^{\tau=x} \exp\left(-\frac{1}{2}\left(\frac{\tau-\mu}{s}\right)^2\right) d\tau \quad (21)$$

$$\mathbf{D}(x, \mu, s) = \int_{-\infty}^{\tau=x} \mathbf{N}(x, \mu, s) d\tau \quad (22)$$

$$\mathbf{Z}(x, \mu, s) = \int_{-\infty}^{\tau=x} \mathbf{D}(\tau, \mu, s) d\tau \quad (23)$$

...and integration by parts yields:

$$\mathbf{Z}(x, \mu, s) = (x - \mu) \mathbf{D}(x, \mu, s) + \frac{2s^2}{\sqrt{\pi}} \mathbf{N}(x, \mu, s) \quad (24)$$

$$\therefore n_a = n_m \mathbf{Z}(x, \mu, s) \quad (25)$$

Where \mathbf{N} is the normal distribution and \mathbf{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 7** is an example of a $\mathbf{Z}(\chi, E_a, s)$ and the \mathbf{N} from which it is derived.

$T = 78 \text{ K}$:

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

$(n_m = 1.0)^*$

$s = 0.5^*$

* an output parameter.

The brackets $\langle \rangle$ indicates an average amount. The new parameters are: $\mu \equiv \langle \chi_s \rangle$, n_m and s . Notice that the extrapolated line from higher pressures intersects at the normal **max**. The $s = 0.5$ is unusual. Usually it is $s < 0.2$.

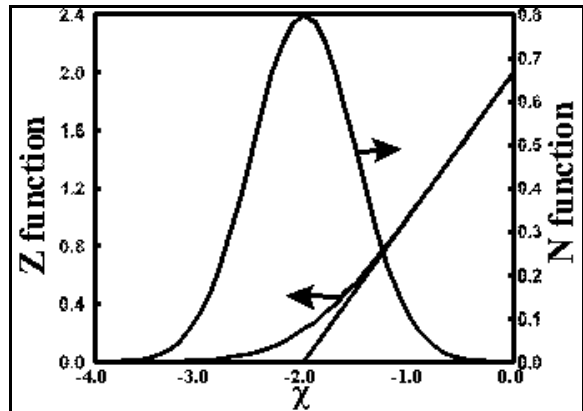


Figure 7 An example of the \mathbf{Z} function and the \mathbf{N} from which it is generated.

3.2 How do I fit the Z function for heterogeneity?

Two of the output parameters have basically the same meaning, See **Table 4**. The parameter s is added.

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 (25)** (p. 28.)

- 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 $n_m = m$,
- Let $\langle \chi_c \rangle = m/b$.
- Let $s = \sim 0$ not exactly 0, say 1×10^{-20} . (Setting s to exactly 0 will yield an error for most least squares routines.)

Table 4 comparing the Z function with linear fit

Z	single χ_c
$\langle \chi_c \rangle =$	χ_c
$n_m =$	n_m
$s =$	nonexistent

3.3 How to compensate for a bad vapor pressure reading

This output parameter is for 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 than 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:

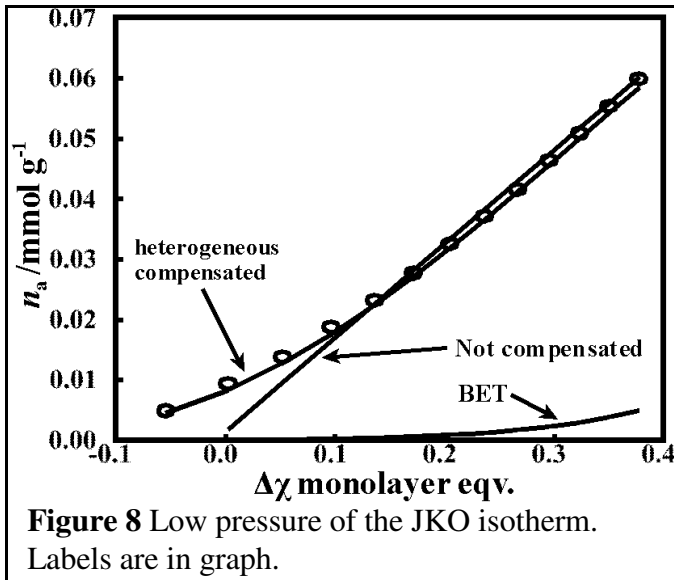


Table 5 The parameters of the JKO data compensated for heterogeneity.

Parameter	Symbol	Value	units
monolayer equiv.	$n_m =$	0.1596	mmol g ⁻¹
average χ_c	$\mu = \langle \chi_c \rangle =$	-2.5905	mmol g ⁻¹
Normal peak value	$s =$	0.2386	
	$E_a =$	-8.54	kJ mol ⁻¹
std. n_a error	$s_n =$	0.0124	mmol g ⁻¹
s_n / full data range	$s_{n \text{ FDR}} =$	1.21	%
correlation	$r^2 =$	998	

A low amount of heterogeneity was detected in the JKO's standard isotherm. Heterogeneity was not used in **Figure 3**(p.12) since in the view of the overall isotherm it was not obvious. However on closer inspection at low pressure, presented in **Figure 8**, it is clearly there.

The output parameters obtained from **Figure 8** are presented in **Table 5** for the heterogeneous compensated fit. Notice that this fit has one more parameter compared to the fit that is not compensated. (See **Table 1** on page 12.)

The parameters are present here. The parameter $\mu, = \langle E_a \rangle$ is similar to E_a except bra-kets ($\langle \rangle$) 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 χ_c or $-\ln(-E_a/RT)$ s .

Looking back at the linear regression, **Figure 3** (p. 12) and the listed values in **Table 1** (p. 12,) the improvement in the σ_{FDR} is at least a factor of 4, but the change was small for the output parameters.

3.4 The pressure correction - an ignored parameter^s:

The pressure correction is to compensate for the error in P_{vap} . This is the temperature of the adsorbent. If measured it is usually done with a liquid-gas thermometer. Assuming a liquid N₂ coolant bath, it is often simply stated to be 78K (to one part in ~80. Really?)

With a coolant bath, the temperature may be far from what one believes, due to the effect of atmospheric pressure. The connection, of course, can be calculated with the Clausius Clapeyron equation^t. The ΔH of vaporization of N₂ is well known, $\Delta_f^g H(\text{N}_2) = -7.1 \text{ kJ mol}^{-1}$. Thus, a one degree change in temperature yields a $P_{\text{vap}} = 1.47 \text{ bar}$! Or this is nearly a 50% error! DeBoer's correction was about 20%.

^s If one were to read the deBoer-Zeikker article carefully, one would realized that their third constant was a correction for temperature as indicated in the illustration.

^t Something my first year chemistry students would be very aware of !!

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, this creates a funneling problem. (2.3.)

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

One can correct for the pressure error après experiment, which will be demonstrated here with the JKO data. To do so, first run the program without the correction as a starting approximation. In **Figure 9** (33) on the right is fit which was found 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, $G \approx 1$.

$$P_{\text{vap,R}} = GP_{\text{vap,M}}, |G| - 1 > 0.010 \ \& \ \forall P < P_{\text{R}} \quad (26)$$

Where **R** stands for the real and **M** stands for the measured. The added parameter, G , is inserted into the equation by multiplying the assumed vapor pressure by it. The qualification for G means that any correction less than 1% is probably not significant, never-the-less it should be tracked and recorded as a function of n_a . The other qualification is that there is an error some place if a pressure reading goes above P_{R} , but the fitting program will show as an error anyway.

In **Figure 9** 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 6** are the output parameters. The changes in the first three output parameters are not significant.

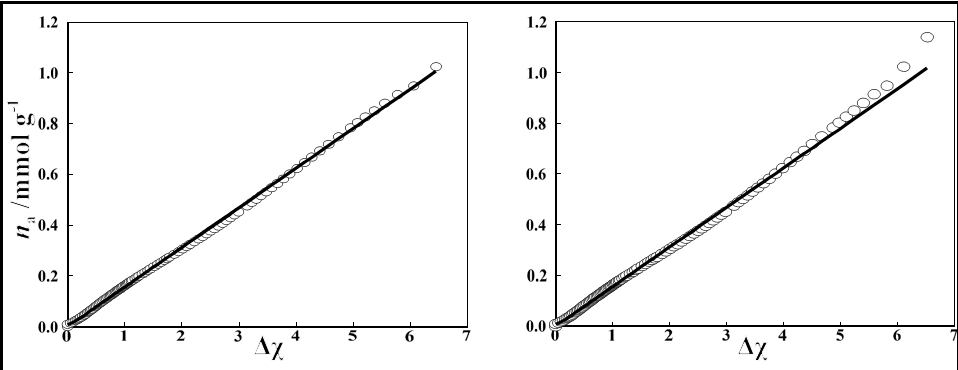


Figure 9 The pressure compensated isotherm on the left and the non-compensated isotherm on the right. The heterogeneous was previously compensated above in **Figure 8**.

Table 6 the output parameters for the 4-parameter fit for the JKO data for N_2 adsorption on Si-1000 .

		Value	Units
$-\ln\{-\langle E_a \rangle RT\} = \mu$	$\langle \chi_s \rangle =$	-2.6408	
monolayer equiv.	$n_m =$	0.1526	mmol g ⁻¹
normal peak	$s =$	0.1764	mmol g ⁻¹
$G \times P_M = P_R$,	$G =$	1.015	
n_a std. error	$s_n =$	0.00675	mmol g ⁻¹
s_n /full data range	$s_{n\text{FDR}} =$	0.659 %	
	$r^2 =$	9993	
	$E_s =$	8.98	kJ mol ⁻¹

Notice that there is still a little bit of waviness in the data relative to the fit. This is probably due to slight changes in temperature. As listed in the **Table 6**, the temperature correction was quite small and did not make much difference in the output parameters compared to **Table 5**, yet a big difference in r^2 and for s_n of a factor of about 2.7. The multiplying factor, G was barely under the the stated criterion of 1.01. So, for very careful work one should try to obtain the temperature to 0.001 K, which is hard to do without a gas thermometer.

By and large the JKO standard curve is ideal. ($\sigma_{\text{FDR}} = 0.38\%$ is unusual, which indicates how good the data is, with little scatter.) The problem, of course, is if it is used with the BET as a calibration it is useless, as are all standard curves. This is the normal use for the “standard curve,” but here it is an important test for the QM. In this context, it is being used as an example of a very carefully performed experiment with an excellent adsorbent. A very rare observation indeed! The next section reveals another set of isotherms of high quality.

3.4.1 Data by Calzaferri, Gallagher and Brühwiler⁹

The data by Calzaferri, Gallagher and Brühwiler (CGB) in **Figure 10** is another example of very good data that can be used to test hypothesis.

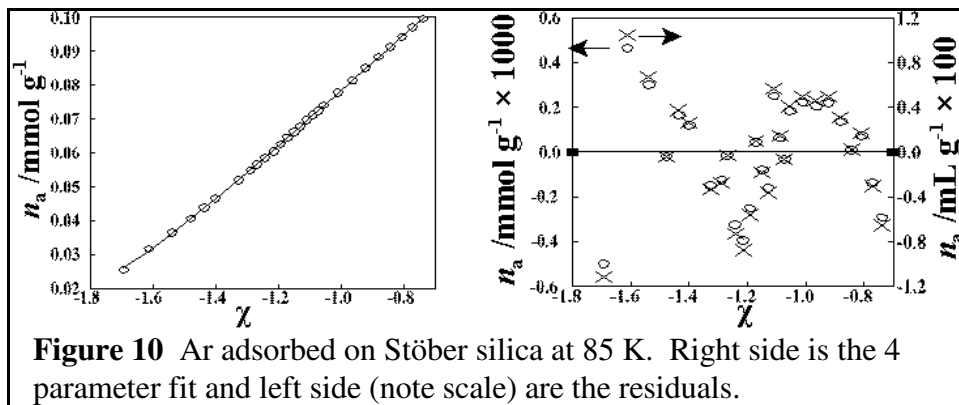


Figure 10 Ar adsorbed on Stöber silica at 85 K. Right side is the 4 parameter fit and left side (note scale) are the residuals.

Given that probably almost every adsorbent has some heterogeneity and perhaps at least a small pressure correction, it would be best to assume these exist and after an initial 2 parameter fit, add in the heterogeneity and lastly the P_{vap} correction.

To illustrate this, the excellent data by CGB is fit first with a simple linear regression and then with the 4 parameter fit. **Table 7** is the 4 parameter fit and **Table 8** is the linear regression. There is a small improvement by

Table 7 Data by CGB analysis using QM equation Ar on Stöber Silica

$\langle \chi_s \rangle^* =$	-1.9789	
$n_m^* =$	0.0813	mmol g ⁻¹
$s^* =$	0.5534	mmol g ⁻¹
$G(T)^* =$	1.043	
$s_n =$	2.38×10^{-4}	mmol g ⁻¹
$s_{n \text{ FDR}} =$	0.24 %	
$A^\ddagger =$	9.1	m ² g ⁻¹
<i>CGB estimated</i> $A_{\text{est}} =$	8.4	m ² g ⁻¹
$E_a =$	-4.99	kJ mol ⁻¹
% “error” in $d = 1 - d^\ddagger/d_{\text{est}} =$	-4 %	
* original parameters		
† IUPAC conversion of 0.143 nm ² at 77K		

going to the 4 parameter versus the linear regression in **Table 8**:

Table 8 Linear regression analysis of CGB data for Ar on Stöber SiO₂:

$$\begin{aligned}
 n_m &= 0.0788 \text{ mmol g}^{-1} \\
 \chi_\varsigma &= -1.9952 \\
 s_n &= 6.4 \times 10^{-4} \text{ mmol g}^{-1} \\
 s_{n \text{ FDR}} &= \mathbf{0.54\%}
 \end{aligned}$$

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. It was his knowledge of the QM derivation, but he had to tailor his publication to satisfy any potential reviewer. This may be why IUPAC at one time disallowed isotherms^u that were not “Henry’s Law”. (Although they allowed for the Dubinin group of isotherms and freundlich isotherms which do not follow the linearity of “Henry’s law” since they passed through (0,0). These last ones, however, in general do not usually obey the proportionality requirement.)

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 QM property that easily operates at this level is superposition

^u “Any proposed theory of physical adsorption must include in its resulting mathematics the Henry’s law limit or it is invalid.” The proposer of this requirement is lucky that his/her name is not given credit for this statement, because it is going down as infamous.

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. Furthermore, all the schichten ensembles are “seen” by all the others and are also indistinguishable. The indistinguishable is why the word “layers” is not used but the positions are referred to by density. These reasons may seem strange, but that is just the way QM works.

There may be more information of gleam from these data fits. The residuals definitely have clear trends. For example, the KJO residuals have very little random scatter as one can determine from the residuals in **Figure 11**. What the trend is due to is at the moment unknown. Perhaps temperature trends, kinetics settling rates or something else. Looks like a good research project.

If you have been convinced at this point, that there is some truth to the QM

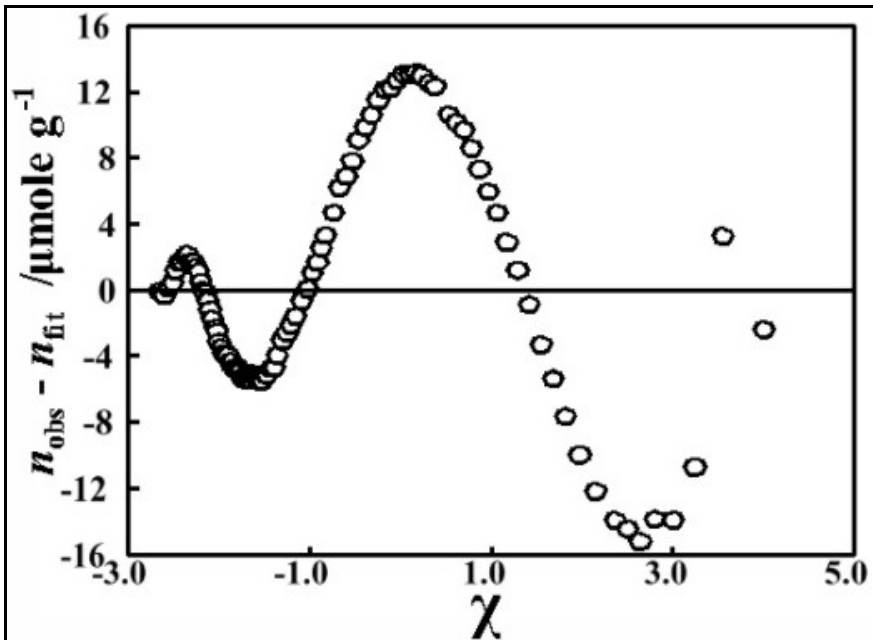


Figure 11 The residuals from the KJO fit. The smoothness hints of a real phenomenon. Perhaps, it is a slight temperature drift.

Modern Hypothesis for Physical Adsorption

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 review the section on schichten equations and then 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 1.4.3. Those are about the schichten equations and the log-law:

$$n_1 = n_m + \frac{n_m RT}{E_a} \ln \left(\frac{P}{P_{\text{vap}}} \right) \quad (27)$$

The data by Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso⁷ (SSLR), demonstrate the log-law and the threshold pressure. The fit is shown in **Figure 12**.

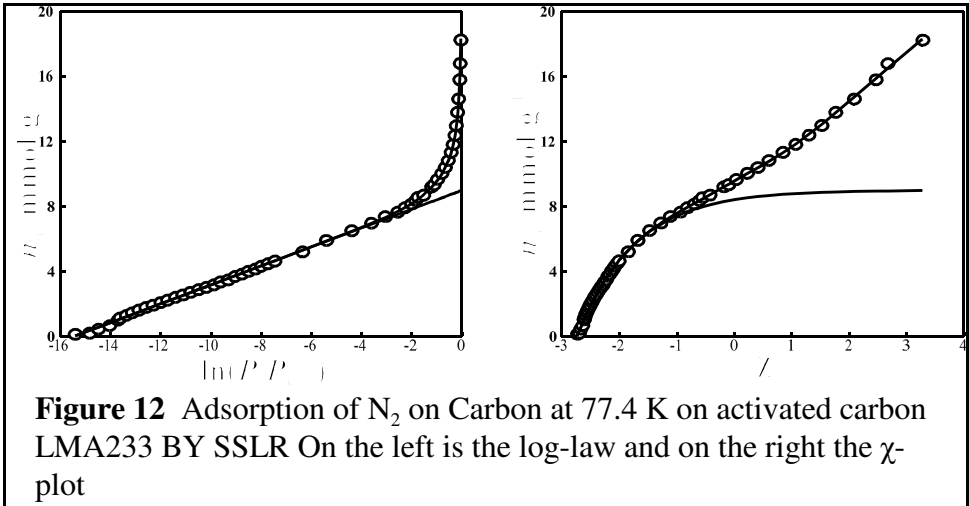


Figure 12 Adsorption of N₂ on Carbon at 77.4 K on activated carbon LMA233 BY SSLR On the left is the log-law and on the right the χ -plot

The linear fit looks good up to about $\ln(P/P_{\text{vap}}) \approx -4$, but 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 a non-linear least squares (NLLS) fit is used. The output parameters and the standard error for the n_a fit is presented in **Table 9**. 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 χ -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 9**. To get the ordinate of the 1st schicht line, the slope was multiplied by the abscissa intercept.

Table 9 Data for N₂ adsorption on microporous C by SSRL

quantity value	Units	Description/meaning
$m_{1,*} = 0.581$	mmol g ⁻¹	Slope (= m) of the 1st schicht line (homogeneous fit)
$\ln(P_{\zeta}/P_{\text{vap}})^* = -15.445$		abscissa intercept relative to reference state
$E_{a,1} = -10.02$	kJ mol ⁻¹	differential energy at the start, (Threshold energy)
$\chi_{\zeta,1} = -2.7379$		threshold for the 1st schicht monolayer equiv.
$n_{m,1,*} = 8.99$	mmol g ⁻¹	ordinate intercept for the 1st schicht monolayer equiv.
$n_{\text{ext}} = 2.967$	mmol g ⁻¹	monolayer equiv of the external area
$\chi_{\zeta,\text{ext}}^* = -0.6493$		position of threshold for external surface in the χ -plot
$\Delta\chi_{\zeta,\text{ext}} = -1.967$		position of threshold for external surface in the $\Delta\chi$ -plot
$\langle E_p \rangle = 4.1$	J mol ⁻¹	Average energy of the external peak value
$s_{\text{ext}}^* = 0.649$	J mol ⁻¹	The external “spread” parameter of the Z function, 1σ .
$G^* = 1.025$	K	Pressure correction due to higher than recorded T
$s_n = 0.0856$	mmol g ⁻¹	The standard n_a error for the entire isotherm, 1σ .
$s_{n,\text{FDR}} = 0.47 \%$		$s_{n,\text{FDR}} = s_n / \mathbf{max}(n_a)$
* ouput parameters all other values are derived from these.		

One might criticize the number of parameters being calculated here, but there are only 6. Two are for the log-law, three for the χ -plot which included heterogeneity and one for the pressure correction. The pressure

correction is of marginal significance.

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 then there is mesoporosity, if past $\chi = 0$ especially. In the above fit the onset was at $\chi < 0$. If there is hysteresis, it seems to be a slam dunk.

In this next example, the pore filling slightly past the monolayer filling. It has been postulate that mesoporosity is not possible below $\Delta\chi = 2$ 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 interphase.

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 χ 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

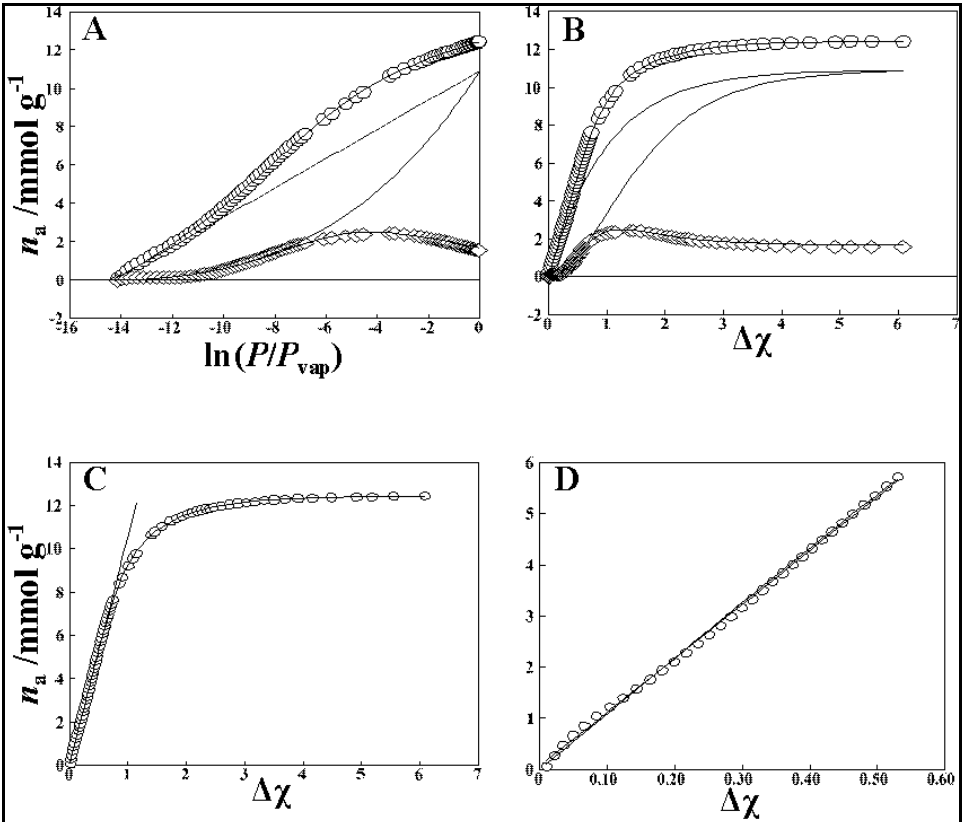


Figure 13 The data by graphed by low-law and $\Delta\chi$ to show how the analysis of this type of hybrid analysis can be accomplished. Original digital data and permission provided by Professors Madani and Pendleton. Digital data available from Prof. Madani.

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, Pendleton¹⁰ (MKR-RBP) and

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 13**.

In graphs A and B the dashed line (the top line not going through data) 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 monolayer coverage of the $\Delta\chi$ -plot. This is demonstrated by **C** and **D**. 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 χ -plot and the log-law plot are useful for this situation. The final least squares fit is a 4-parameter fit. There was no detectable pressure correction. Schicht 1 and 2, of course, have the same χ_c as required. The 4-parameters are in **Table 10** along with some derived quantities.

Table 10 Output parameter for the MKR-RBP data.

$\chi_c^* =$	-2.6591	$\ln(P_p/P_{vap})^* =$	-4.596
$\ln(P_\zeta/P_{vap}) =$	-14.283	$\langle\chi_p\rangle =$	-1.525
$E_a =$	-10.37 kJ mol ⁻¹	$\langle E_p\rangle =$	-53.7 J mol ⁻¹
$n_{m,1}^* =$	10.84 mmol g ⁻¹	$s^* =$	2.5410
$s_n =$	0.059 mmol g ⁻¹	*original fitting parameters. Others are derived from them.	
$s_{n\text{ FDR}}$	0.47%		

The following are the description of the input parameter:

χ_c = the threshold pressure for both schicht 1 and 2

$n_{m,1}$ = the monolayer equivalence for schicht 1

$\ln(P_p/P_{vap})$ = the χ^{-1} distribution peak for schicht 2 (similar too the normal distribution.)

s = the width of the 2nd schicht (denominator in arg of χ^{-1} .)

n_{ext} = external surface monolayer equivalence was ~ 0 in this case.

4.3 Conclusion about Microporosity

Although the title here says “Microporosity” there is really no criteria to make a firm definition of what is microporosity. Clearly if only one monolayer can adsorb one could use the word “microporosity.” Here we are stuck with the word “hybrid” to indicate there is more than just one the first schicht involved. How to interpret **Figure 13 C** above? ...Or what if there are multiple schichten, say 3 or 4? Without the mesopore interruption this question is a problem. Classically one would draw a straight line from the high values to the $\Delta\chi$ ordinate, but when does it flatten out sufficiently to do that? ...and what is the value for n_{ext} .

These questions probably can only be answered using a sophisticated spread sheet accounting for the various schicht densities. Luckily there is sufficient restrictions on what is the proper schichten density in the non-hindered case that it is possible to construct such a spread sheet and insert limits on the total amount (with a plethora of “if” statements.) Such spread sheets have been used, but at this point it seems to be a little too much material.

At any rate, it seems that the complex cases are not too common and this book should provide the solutions to the vast majority of isotherm possibilities. (Now there will be multiple investigators looking for these isotherms that “fall through the cracks.”)

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, although Fuller correlated the value of E_a to the adsorbate polarization. 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 what 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 χ -plot are clearly the monolayer equivalence and the measurement of the isotherm starting energy. Microporosity is also fairly clear.

We now come to a phenomenon where the meaning of the fit is not quite so clear. One can use the cumulative distribution or the inverse χ -function to characterize the mesoporosity. This has three parameters, the peak position of the normal distribution from which the cumulative distribution is derived. The cumulative distribution blends in with the low slope and finishes blending in with the upper slope. Thus the peak and the spread of the mesopore distribution is obtained along with the value of external monlayer coverage.

This seems to be a reasonable interpretation for the cumulative distribution. The question becomes what is the meaning of the three parameters, especially the peak value. Associated with the peak value is an energy, E_p , but that only gives on another way of locating the peak. The question is, "What is E_p ?" or "what determines it?" or "How can it be predicted?" "Can these parameters be predicted or are they just analysis parameters?" They would still be useful to characterize the isotherms precisely and efficiently.

Furthermore, these parameters change when the isotherm is reversed, yielding the hysteresis phenomenon. This needs 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 of pore wall separation. For the modern definitions, this is replaced by questions of what the interactions are between the adsorbent, adsorbate and adsorptive. This interaction is between E_p (\uparrow or \downarrow)^v for the pore radii and the $\Delta\chi^a\mathbf{E}$. It seems based upon competing energies that determine the classification of microporosity versus mesoporosity.

5.2 Recognizing Mesoporosity

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

Beyond the heterogeneity in the χ -plot, mesoporosity causes a positive curvature. This is followed by a negative curvature resolving in a final linear portion for the χ -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 χ -plot. These two need to be added.

The first case above is illustrated by the schematic in **Figure 14**. This is an idealized isotherm diagram of an adsorbent sample that involves the features of heterogeneity and mesoporosity. (The ordinate intercept of n_{ext} yields the anti-Gurvitsch rule for mesopore quantity.)

There has been much discussion about the origin of hysteresis in the physisorption literature. This section only provides a method of curve fitting to provide parameters to characterize the mesoporosity. This can fit both

^v \uparrow means adsorption and \downarrow means desorption.

branches of the hysteresis. Later are some tentative proposals for the origin for mesoporosity and hysteresis will be provided.

5.3 The **D** function again and a new function χ^{-1} :

The **D** function, commutative normal distribution. has been given above. The new function χ^{-1} describes the ending of the QM fitting. It is simply the inverse function, displaced and distributed. It is given in **Eq. (28)**.

$$\chi^{-1} = \mathbf{exp} \left\{ -\mathbf{exp} \left(\frac{\chi - \chi_p}{s_p} \right) \right\} \quad (28)$$

The analysis uses the following equations. These apply either the χ -plot or the $\Delta\chi$ -plot, depending upon preference. Here it is shown for the $\Delta\chi$ -plot. The bold **ns** are for the linear functions or if there is heterogeneity the corrected function for heterogeneity.

Using the **D** function to modify the χ or $\Delta\chi$ -plot is **Equation (29)^w**

$$\mathbf{n}_{a,\Sigma} = \mathbf{n}_{a,1} + (\mathbf{n}_f - \mathbf{n}_{a,1}) \mathbf{D}(\Delta\chi, \Delta\chi_p, s_p) \quad (29)$$

where: $\mathbf{n}_{a,1} = \Delta\chi n_m$ and $\mathbf{n}_f = \Delta\chi n_{\text{ext}} - n_p$

or using the χ^{-1} the function becomes **Equation (30)**:

$$\mathbf{n}_{a,\Sigma} = \mathbf{n}_{a,1} + (\mathbf{n}_f - \mathbf{n}_{a,1}) \left\{ -\mathbf{exp} \left(-\mathbf{exp} \left[\frac{\Delta\chi - \Delta\chi_p}{s_p} \right] \right) \right\} \quad (30)$$

(Obviously, the heterogeneity correction would apply to $\mathbf{n}_{a,i}$. The subscript Σ indicate the summations of the heterogeneity strands^x.) To demonstrate the use of this equation a $\Delta\chi$ -plot is shown in **Figure 15** (p.50.)

^w For the **D** function see **Equation (21)**. Bold **n** indicates a function of χ and χ_c used previously.

^x Keep in mind that the $\Delta\chi$ describes the amount of adsorbate but the χ is related to energy. This “contradiction” has implications for hysteresis.

5.3.1 An Example by Guillet-Nicolas, Marcoux, and Kleitz

The following data were measured by Guillet-Nicolas, Marcoux, and Kleitz^{11,y} (GMK), which is backed up with some additional information from Guillet-Nicolas, Wainer, Marcoux, Thommes and Kleitz¹² (GWMTK), on KIT-6, a porous silica heat treated for 24 hr at 373 K.

Figure 15 is the least squared minimized fit to the data.

Both the inverse chi function, χ^{-1} , and the cumulative distribution function, **D**,

^y 9: permission to use data by New J. Chem.

10: The original data has not been altered according to the CC guidelines: Attribution-NonCommercial-NoDerivatives 4.0 International. CC BY-NC-ND 4.0 Deed and is allowed for reuse as data by US copyright laws.

were used to fit the data. Once one has the rough estimates for the parameters, a least squares routine is used to get more accurate results. This was done to compare the two approaches. Both adsorption and desorption were fit by the two methods. In comparing the fits, χ^{-1} vs. **D** there is no indication of which fit is best as is indicated in **Table 11**.

The quantities in **Table 11** are:

n_m = monolayer equivalence early portion,

n_{exp} = monolayer equivalence of last portion,

$\Delta\chi_p$ = the peak of the normal distribution or in **Figure 15** (p.50) the steep increase, and

s_p = the spread parameter in the distribution for **D** and χ^{-1} but

$\Delta\chi = \chi - \chi_c$ so,

χ_c = another parameter used for $n_{a,1}$.

$n_{a,\Sigma}$ = the resultant summation of the adsorbate is the total isotherm.

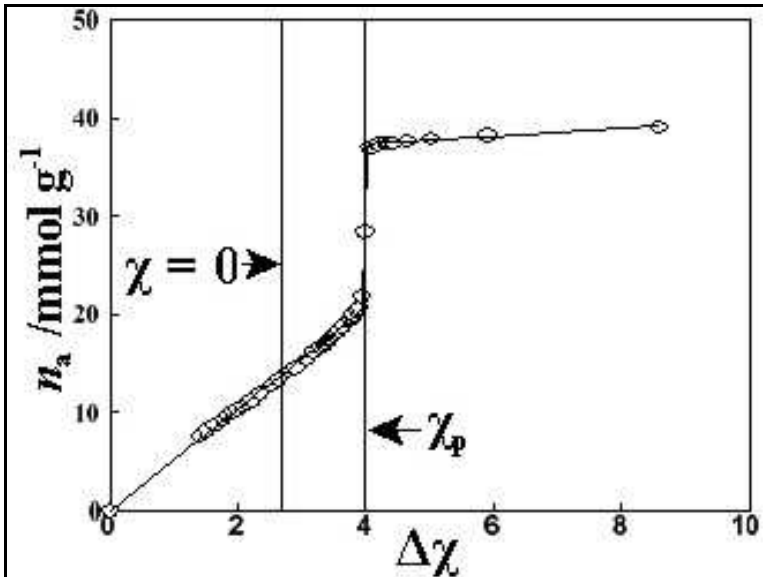


Figure 14 N₂ adsorption on KIT-6 by GMK using the χ^{-1} distribution. Permission to use data by New Journal of Chemistry, obtained through CCC.

Table 11 Parameters and derived values for N₂ adsorption on KIT-6 by GMK using the χ^1 and **D** distribution for adsorption \uparrow and desorption \downarrow branches.

Physical quantity	Adsorption $\chi^1 \uparrow$	Adsorption D \uparrow	Desorption $\chi^1 \downarrow$	Desorption D \downarrow
$n_m / \text{mmol g}^{-1} =$	5.167	5.107	4.983	4.943
$\chi_s =$	-2.6783	-2.7043	-2.7741	-2.8011
$n_{\text{ext}} / \text{mmol g}^{-1} =$	0.403	0.347	0.632	0.715
$\Delta\chi_p =$	3.9823	5.015	3.698	3.995
$n_p / \text{mmol g}^{-1} =$	35.742	35.034	30.977	39.036
$s_p =$	0.0124	0.0294	0.307	0.277
$G =$	1.009	1.009	1.010	0.995
Goodness of fit:				
$s_n / \text{mmol g}^{-1} =$	0.380	0.335	0.359	0.312
$s_{n \text{ FDR}} / \% =$	0.97 %	0.86%	0.98%	0.54%
$r^2 =$	0.998	0.9991	0.9990	0.9995
Derived Physical Quantities:				
$\chi_p =$	1.3037	1.3107	0.9240	0.9774
$n_{n,p} / \text{mmol g}^{-1} =$	4.76	4.76	4.35	4.49
$E_a / \text{kJ mol}^{-1} =$	-9.44	-9.68	-10.39	-13.09
$E_p / \text{J mol}^{-1} =$	-176.1	-174.9	-257.4	-243.7
$A_p^* / \text{m} =$	465.4	465.1	425.0	416.0
$V_p / \text{mL g}^{-1} =$	1.237	1.248	1.073	1.193
$d_p^{**} / \text{nm} =$	10.4	10.7	10.1	11.0
$E_p \downarrow / E_p \uparrow =$	1.46	1.39		
* By IUPAC convention , ** $d_p = 4V_p / A_p$, s_n is the n_a std error.				

All four fits are well within the 1 % FDR. It is too early to draw a

conclusion, but the χ^{-1} was theoretically designed for the mesopore cutoff, but the spread in pore sizes can camouflage the sharp cutoff.

The big uncertainty is that there appears to be some heterogeneity, but without the low pressure data it is difficult to tell. The correction for the P_{vap} is either insignificant or small indicating careful control. The value for cylindrical pore radius, $2V_p/A_p$, yields a diameter of 10 - 11.5 nm. GMK report a diameter of ~8-9 nm. However, perfect cylinders is not the only consideration in this calculation.

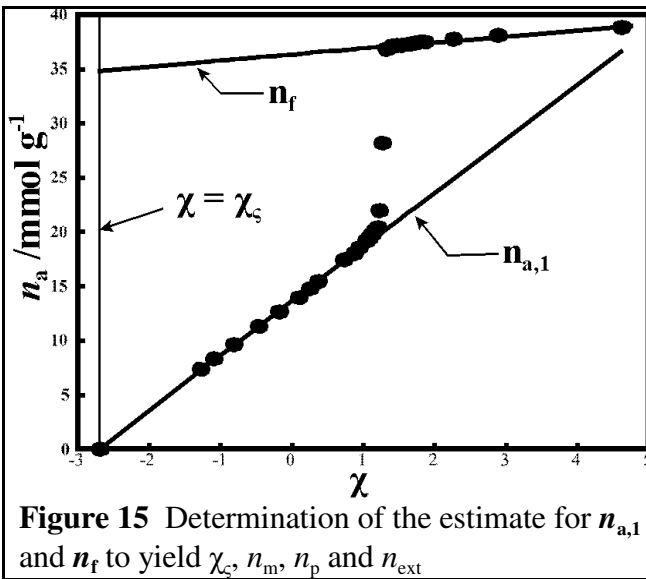
The ratio $E_{p\downarrow}:E_{p\uparrow}$ will be discussed in section 5.4.

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. The following steps are typical for fitting the data. (GMK KIT-6 **Figure 15**) (p.50.)

STEP 1: Obtain the χ -plot (suggestion convert amounts to molar units) by using the χ -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).) Plot the results on the original plot. (Conventional $y = mx + b$ is used here.)



$m = n_m$	b
↘	↘
4.9748	13.6272
0.0485	0.0363
0.9991	0.1201
10507	9
152	0.1299
$-b/m = \chi_s = -2.7392$	
$m = n_{ext}$	$b = n_p$
↘	↘
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 χ_c (< 0 usually.)
See **Figure 17**

STEP 4: Estimate where the “steepest” part of the isotherm. This is the estimate for **D** or χ^{-1} distribution peak, $\Delta\chi_p$. Use the distribution to transition between $n_{a,1}$ and n_f either **Equation (29)** (p 49) or **Equation (30)** (p 49) with s_p temporarily set to a low number ($\sim 1 \times 10^{-10}$)^z. See **Figure 18**. In this case the normal distribution is used.

STEP 5: To illustrate the effect of s_p this is set to 0.1 in place of $\sim 1 \times 10^{-10}$, so the dark line is obtained in **Figure 19**

STEP 6 After running the resulting equation through the least squares routine as the dark line in **Figure 15** (p.50) is obtained.

The desorption branch is performed the same way. All the parameters need to be recalculated using only data from the desorption.

5.4 Possible ways to calculate

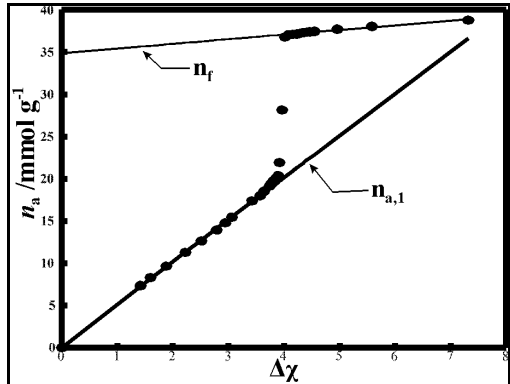


Figure 16 Change the abscissa to $\Delta\chi$.

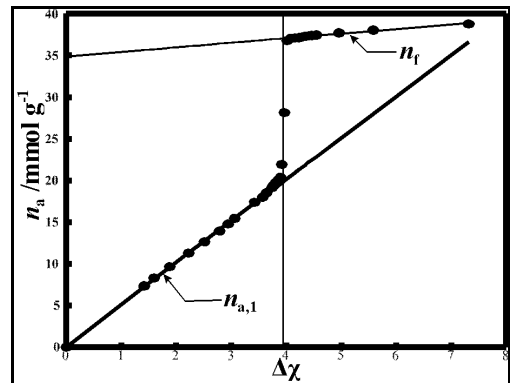


Figure 17 Estimate $\Delta\chi_p$

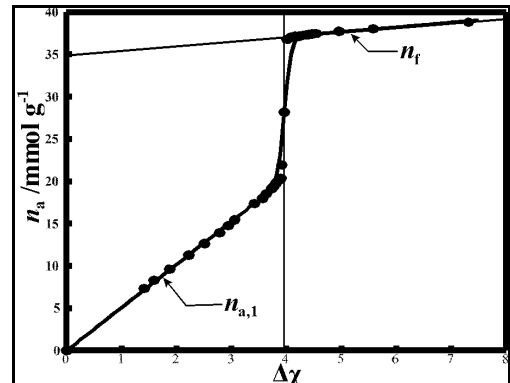


Figure 18 the fit with estimate values

^z Most least squares programs yield an error if σ_p is set to exactly 0.

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 $P = P_{\text{vap}} \times 0.3678\dots$, 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 $-648.5 \text{ J mol}^{-1}$ for N_2 at 78 K (or RT). The “magic point” is an important point in column operations. Basmadjian¹³ 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.^{14,15,16,17}. 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 adsorption energy, $\Delta^{\ddagger}E$, 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. The best choice is to set up a spread sheet.) 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 there is a counter mechanism to QM controlled by the Kelvin (Oswald-Freundlich) or similar equations:

$$-\Delta_a^{\text{lg}} E = RT \ln(X) = \frac{m_\gamma \gamma \bar{V}}{r_c} \quad (31)$$

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, $t + r_c = r_p$ where r_p is the pore radius “measured” in the adsorbate.

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 (See Tarazona et al.^{18,19,aa}) at the pore wall surface. The center-to-center convention yields a smaller number by the value of t for the pore diameter or $1/2t$ 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 (31)**, m_γ is a constant depending upon the geometry of the pore. Ideally, m_γ 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?

^{aa} No longer is this a mysterious potential transmitted in a chain of interactions, such as Polanyi proposed. On this question Brunauer was correct, but even he proposed that some of the adsorbent surface is available for an energy interaction. A strange contradiction. Tarazona simply stated there was a “external potential” that decayed with the half life of a monolayer without any reason for its existence.

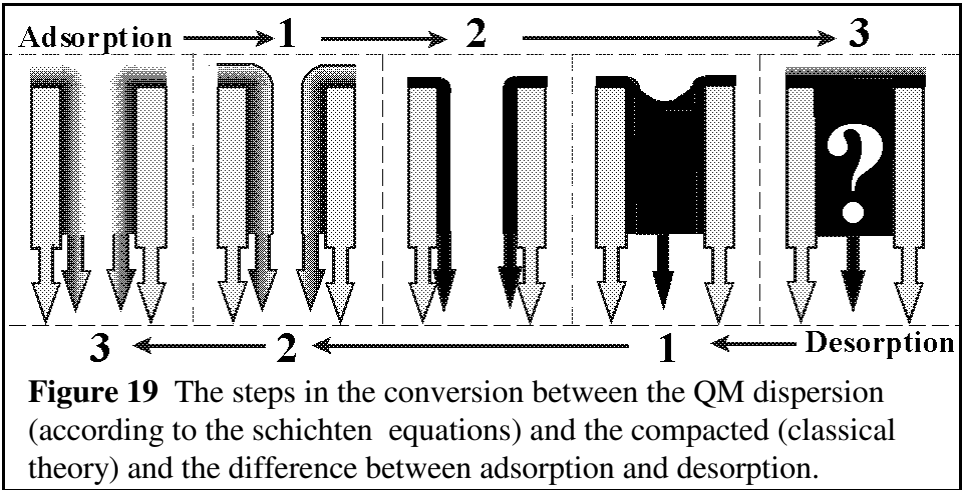
In **Equation (31)**, the symbol $\Delta_a^{\gamma/g}E$ is an attempt at consistency with IUPAC to designate the energy of the formation of the gas-adsorbate interface energy release. The transition from the schichten diffuse situation, where there is no defined interface, to the compaction of all schichten 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 interface compact boundary, γ/g . In this case, the Gibbs' free energy of the transition also includes an entropy term. For calculation of entropy the question, "How to calculate it?" This entropy might be the biggest problem in the following calculations made, because at this time it is being ignored.

(Something to consider concerning the energy release upon film formation and the energy provided for the rupture of the film is the kinetics of heat transfer. It might be expected, in a cryogenic cooling system, that the energy release would be faster than the energy adsorption. Would this mean that the desorption branch is much slower than the adsorption branch. Good question for further research. hint, hint.)

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 warrant a collapse to make the *l-g* interface but the schichten amount may be 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_{γ} . If the interface geometry changes from adsorption to desorption, as one would expect from **Equation (31)** (p. 56). 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 20** (p. 58) is a schematic of the steps 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)** (p. 8,) whereas the formation of the *l*-g increases according to **Equation (31)**(p 56.) 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^{bb}. However, the energy of the collapse to densification depending on $m_\gamma=1$ and the “snap back” depending on $m_\gamma=2$ means that the ratio of the energies are 1:2 if $r_p \uparrow$ and $r_p \downarrow$ were the same. Here \uparrow stands for adsorption and \downarrow for desorption. More likely, from **Equation (31)** the relationship becomes:

$$\frac{E_{p,\uparrow} r_{c,\uparrow}}{E_{p,\downarrow} r_{c,\downarrow}} = \frac{m_{\gamma\uparrow}}{m_{\gamma\downarrow}} \quad (32)$$

The E_p s can be measured. This leaves the ratios of either r_c s or m s to be determined. One cannot determine this without some additional information or assumption, for example $m_\gamma = 1$. The virtual thickness can be calculated from the E_p s to calculate the effective^{cc} r_p as an anchor since

^{bb} virtual volume: the volume that the diffuse film would fill if it were to collapse into a dense liquid.

^{cc} The word effective is used here to indicate that even though the r_p is reproducible, one should not give it a macroscopic definition compare to, say, X-ray value. One also needs

it is the same for both adsorption and desorption. These considerations are addressed 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 tension of the adsorptive and the value of χ for the mesopore peak. The data by Guillet-Nicolas, Wainer, Marcoux, Thommes and Kleitz (GWMTK) will be used for illustration. An isotherm was selected, which the adsorptive was N₂ 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:

$$\gamma_{lg,78K} = 8.72 \text{ mN m}^{-1}, \quad \rho_{N_2(l)} = 0.809 \text{ g mL}^{-1}, \quad \bar{V}_{N_2(l)} = 34.63 \text{ mL mol}^{-1}.$$

The nitrogen surface tension at 77K is from the UNIFAC (Dortmund) data base with several authors in agreement. **Equation (31)** (p 56) was used for calculating the radius from energy.

This GMK¹¹ of the adsorption of nitrogen on the SBA-15 silica sample was chosen because it had the worse fit of 1.46 % FDR. Never-the-less, reasonable values for the quantities were obtained comparable to later work by GWMTK¹². The isotherm and the pore size analysis are presented in **Figure 21**. A summary of the output data and derived quantities are presented in **Table 12**. In the NLDFT results by GWMTK had a considerably higher spread, $s \sim 0.8$ nm, for the pores than is recorded here by a factor of about 16 or ~ 0.05 nm. 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 of the first schicht molecules.

to keep in mind the X-ray value is also an effective parameter.

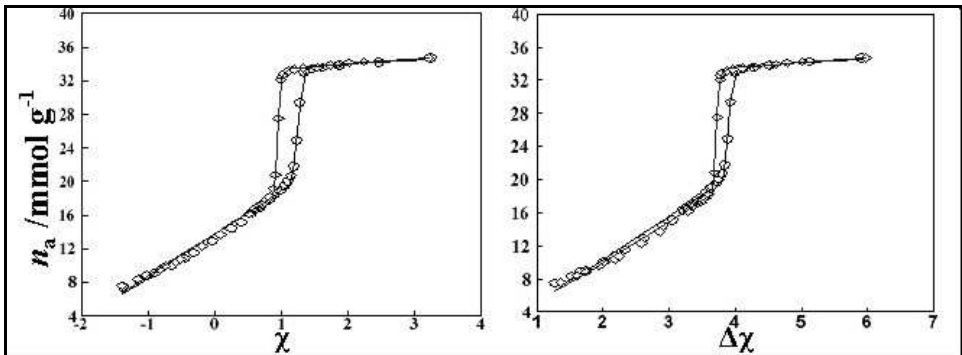


Figure 20 -N₂ adsorption and desorption on SAB-15 by GMK using the χ^{-1} distribution, which shows the effect of χ versus $\Delta\chi$ on the hysteresis. Permission to use data by New Journal of Chemistry, via CCC.

Symbols and definitions for **Table 12**

$\langle X \rangle$ = (when not QM) average of X

\uparrow = for adsorption

\downarrow = for desorption

r = pore radius measured with d from adsorbent edge to opposite edge.

r_c = the “core” radius, measurement from virtual adsorbent, d measured from inner edge to opposite inner edge.

V_{BET} = total pore volume by classical means, BET or Gurvitsch based

A_{BET} = area calculation by BET theory

t = either classical monolayer or schitchen monolayer equiv

t_m = classical molecular layer thickness

χ_p = subscript “_p” means of the peak value

DFT = means from Density Functional Theory

E_p = The differential heat of the peak

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

Table 12 Output parameters and quantities for data by GMK of N2 adsorption on SBA-15 silica sample using the shut-off functions χ^{-1}

QM Values and units			derived from QM (*) or IUPAC convention (I)		
$n_m =$	5.179	mmol g ⁻¹	$A_{tot} =$	505.9	m ² g ⁻¹ (*,I)
$\langle \chi_c \rangle =$	-2.6593		$\langle E_a \uparrow \rangle =$	-9.26	kJ mol ⁻¹ (*)
$n_{ext} =$	0.413	mmol g ⁻¹	$A_{ext} =$	40.4	m ² g ⁻¹ (*,I)
			$A_p \uparrow = A_{tot} - A_{ext} =$	465.4	m ² g ⁻¹ (*,I)
$n_p =$	32.150	mmol g ⁻¹	(<i>antiGervitch</i>) $V_p \uparrow =$	1.113	mL g ⁻¹ (*,I)
			$d_{max} = 4V_p / A \leq$	9.56	nm (*,I)
$\langle \chi_p \rangle =$	1.2187		$t_m =$	0.354	nm (*)
$\langle \Delta \chi_p \rangle =$	3.878	$\langle \chi_p \rangle - \langle \chi_c \rangle$	$t = t_m \langle \Delta \chi_p \uparrow \rangle =$	1.37	nm (*,I)
			$\langle E_p \uparrow \rangle =$	-191.7	J mol ⁻¹ (*)
			$r_c^{(c)}$ from $\langle E_p \uparrow \rangle =$	1.58	nm (*,I)
			$r = r_c + t =$	2.95	nm (*,I)
			$d_p = 2r =$	5.90	nm (*,I)
			$A_{BET}^{(d)} =$	856	m ² g ⁻¹ (I)
			(<i>Gervitch</i>) $V^{(d)} =$	1.20	mL g ⁻¹ (I)
			$d \uparrow^{(d)} = 4 V^{(d)} / A_{BET} \leq$	5.61	nm (I)
			$d \downarrow_{DFT}^{(e)} =$	8.1 (ads)	nm (I)
$\sigma_p =$	0.0540	χ units	$\langle E_p \downarrow \rangle =$	-257.4	J mol ⁻¹ (*)
$s_n =$	0.5379	mmol g ⁻¹	$\langle \Delta \chi_p \downarrow \rangle =$	3.698	(*)
$\sigma_{FDR} =$	1.46 %		$E_p \downarrow : E_p \uparrow =$	1.34	(*)
FDR = "of Full Data Range"					
(b) Measured from admolecules' centers					
(c) Measured across pore admolecules' edges.					
(d) This datum is given by GMK					
(e) Given by GWMTK using NLDFT .					
\uparrow = the pore value for adsorption (default) \downarrow = the pore value for desorption					
$\gamma_{lg^*78K} = 8.9049 \text{ mN m}^{-1}$, $\bar{V}_{N2(l)} = 34.731 \text{ mL mol}^{-1}$. $\Rightarrow 3.02 \times 10^{-7} \text{ J mol}^{-1}$ (NIST)					

The pore diameter calculated from V_p and A_p is greater than or equal to the actual pore size provided assuming the pores are mainly cylindrical. This because there are connecting pores between the cylindrical pores starting at the adsorbent surface. Considering the 3D network, the $4V/A$ could be about double the actual pore size, depending of the wall thicknesses. In this case for the QM measurement on SBA-15 it is 162%.

The BET is often used in conjunction with DFT, so if this is the case, the BET is far from the correct answer. Thus, putting in double the answer for the pore size which is higher than the $4V/A$ value, which is not possible.

In **Figure 21** (p. 60) the calculation of the QM pore distribution used the χ^{-1} distribution. A comparison of the adsorption branch of hysteresis and the desorption branch is shown with the χ plot and the $\Delta\chi$ plots. One can see how they are different and, thus, why the measurement of the E_a is important. This is not unusual, and sometimes the hysteresis actually disappears as noted in the first text book²⁰ as evident by some data by Qiao²¹, et al. The hysteresis loop in MCM samples C10 through C18 closed up and disappeared and the C22 sample the difference was dramatically narrowed. This is given here in **Table 13**. (See table 36 chapter 6 in the reference for complete calculation. Interesting in grafts the C18 is slightly passed the Fuller magic point and C-22 is somewhat past it, and the Basmadjian text book predicts such jumps and the magic point is also at the $\Delta\chi \approx 2.5^{22}$.)^a

Table 13 Hysteresis values for data by Qiao, et al.

MCM name	adsorb r /nm	desorb r /nm
C-10	1.00	1.03
C-12	1.23	1.23
C-14	1.40	1.41
C-16	1.58	1.58
C-18	1.82	1.78
C-22	2.10	1.95

^a Elsevier does not allow quoting of data, which according to their permissions document is a copyright violation. This is inconsistent with US copyright laws since data is not copyright able and fair use also applies.

For the GMK data, In **Table 12** (p. 61) 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. (So, we work with what is available.)

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 $9.77 \times 10^4 \text{ m}^2 \text{ mol}^{-1}$, and the conversion from linear monolayer equivalence is IUPAC classical diameter of $0.354 \text{ nm monolayer}^{-1}$. Opposing sides, however, need to be counted. (The van der Waals $d = 0.31 \text{ nm}$ and the following dimensions apply to solid N_2 : the waste is $d_w = 0.339 \text{ nm}$, and the length is $d_l = 0.434 \text{ nm}$. Thus, classically, this makes a 20% difference due to 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, $-\Delta_l^a \mathbf{H}$, to indicate this^{dd}. If the adsorbent is perfectly smooth, it may be that the transition is above a high θ value (9 monolayer equivalence, $-\Delta \mathbf{E} \sim 1 - 2 \text{ J mol}^{-1}$ compared to $\sim 10 \text{ kJ mol}^{-1}$ 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 12** 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 $m_{\gamma \downarrow} / m_{\gamma \uparrow} \neq 2$, as one expects from ideal cylinders. This is also the case with the GMK data (**Table 11**, p51.) Thus, at this point it does not appear the change in geometry of the interface either is not the explanation for hysteresis or is only partly the cause. Other observations from the data GMK include:

^{dd} It is assumed here that the $\Delta_l^{\text{avg}} \mathbf{S} \neq 0$.

The FDR% is a little high. However the steep portion of the isotherm really throws a lot of scatter into the mix,

1. 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.
2. It is surprising how close the NLDFT and the QM $r_c + t$ are, about 10.1 nm, considering all the uncertainties.

5.5 Conclusion about mesoporosity

So the QM description holds up fairly well for mesoporosity in terms of curve fitting. 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 Basmadjian¹³. There are many cases in the literature where the classical method seems to work, even if the isotherms are misinterpreted.

The data in **Table 11** and **Table 12** are confusing and are probably not interpreted correctly, especially the calculation of pore size. Use of the BET is an obvious problem. However, it seems that the use of the QM for pore area and antiGervitsch rule is fairly reproducible and probably accurate.

The ratio of adsorption versus desorption for this sample seems reasonable, but for some others the ratio is lower than 2, more like 1.4. This explanation is obviously too simple. More work is needed on this. There is a need for better data and more high quality data to test. One explanation is that the K_p is proportional to r . In which case the ratio from Equation (32) (p 58) would be $\sqrt{2}$. Overall this approach seems promising, but there needs to be more research. - Oh, and congratulations, mesoporosity is the hardest section.

6. Heats of adsorption Calculated from the Isotherm

6.1 Some Easy Thermodynamics

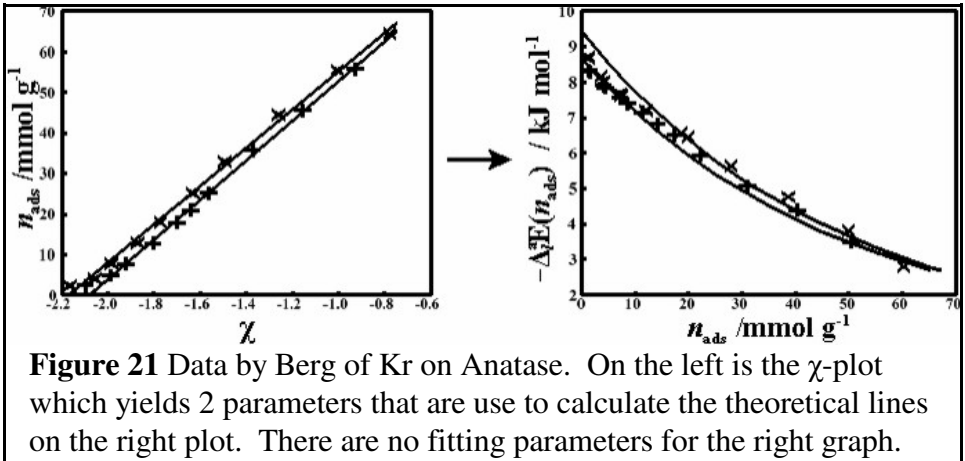
Much of this section will deal with the data by Dr. W. Thomas Berg²³, whose data was simultaneous isotherm measurement and adiabatic calorimetry. The equations used are list above and in Appendix III, QM.

$$\Delta_l^a \bar{E} := \bar{q}_{la} = RT \exp(-\chi) \equiv -RT \ln(P / P_{vap}) \quad (33)$$

which is **Equation (66)** (p. 107) 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)** (p. 8) (or see **Equation (67)** (p.107)):

$$\bar{E}^\ominus(\theta) = -\bar{E}_a e^{-\theta} + \bar{\epsilon} \quad (34)$$

Where the primsoil symbol, \ominus , indicates the thermodynamic standard state. The treatment here assumes no heterogeneity or other complications, so there may be deviations at low pressures.



6.2 The Berg data²³:

Dr Thomas Berg measured the adsorption of Kr on anatase using calorimetry and isotherms determination on the same sample in the same instrument. His measurements were at 130 K and 140 K. The results of

his experiments are given in the plots of **Figure 22**.

In order to obtain the answers he also had to measure the heat capacities of the adsorbate, which is quite difficult and laborious, as well as the adsorbent. Notice the wording in **Figure 22** that **NO** new parameters are calculated for the graph on the right. In other words this is a **nonparametric calculation** or a pure prediction. This is extremely unusual in the physical adsorption literature.

There have been other attempts measuring the heats of adsorption that are not as convincing due to separate measurements and lack of adsorbate heat capacities. A review of these attempts has been provided in the open literature²⁴. Since the preparation of the surface is critical and the dual measurements are difficult it is understandable why other measurements are inconsistent. In addition, the theoretical background has also not been 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 segment 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 χ -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 one translational mode for the first schicht.

6.3 Conclusions about Heat of Adsorption:

With only two sets of data measuring 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 solves by fitting the integral 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. (Sounds like a thesis project.)

For mesopore adsorption there should be a short burst of heat evolution in the $\sim 5\text{-}400 \text{ J mol}^{-1}$ 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_p .

7. Binary isotherms

There is much room for further research in the area of binary adsorption.. Presented here are some suggestions for analysis. However, the literature seems to lack good data to make tests. The first suggestion is to approach it like the flowing systems analysis. In the flowing systems case 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 analogy seems to be a good guidance.) Thus, the adsorbate with the highest exothermal energy of adsorption at the start of adsorption, should dominate. Put into the QM wording the adsorbate with the highest $|E_a|$ adsorbs first and dominates the energy profile and applies an exponential decay profile from the surface for the second adsorbate.

The logic is as follows:

- The adsorbate with the greatest exothermic 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 and, thus, also changing the threshold pressure for the second. This effect one should be able to calculate if one knew how the E_a shifts. it should be similar to the effect of contamination by 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 densification influencing the Δ^*E decay.
- This continues until the effect of the surface becomes relatively negligible and the bulk interaction energies dominate.

The predominance of the higher energy adsorbate is the basis of the proposed “Henry’s Law” for binary adsorption¹³. 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:

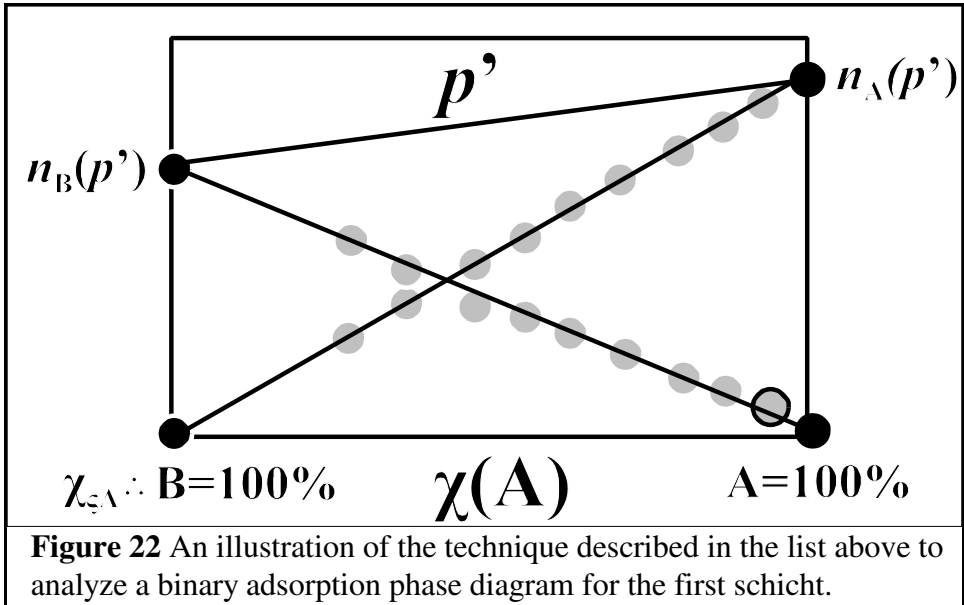
Logic above would indicate that the onset of adsorption and its continuation is governed by the more exothermic of the two adsorbates. In The following list is a procedure to take advantage of this for binary mixtures where the E_a s are different enough. This procedure would apply to a given total pressure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

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

1. Do the χ -plot for both adsorbates.
2. The adsorbate with the lowest χ_c (highest $|E_a|$) adsorbate “A,” labeled with “ $\chi_c(A)$.” The other data set as “B.”
3. Create a graph with the abscissa as the χ (i.e. the highest $|E_a|$) for A (i.e. χ_A).
4. Determine what total pressure you wish to have the phase diagram for. (call this p' .)
5. Determine the value of n_a from both isotherms of the adsorbates at pressure p' . Designated these $n_A(p')$ and $n_B(p')$
6. Draw straight lines for A from $(\chi_{c,A}, 0)$ (B = 100% corner) to $(\chi_A(p'), n_A(p'))$
7. and for B from $(\chi_A \text{ (on A!}^{ec}), 0)$ (A = 100% corner) to $(\chi_A(p' \text{ (on A!}^a)), n_B(p'))$

This appears a bit confusing, so a diagram in **Figure 23** illustrates this.

^{ec} The “!” is placed here to emphasize that one uses only the χ_A values for A.



Faux data points are placed on the lines created. (If 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 get an estimate of the data points without doing the whole isotherm. 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 χ_B as the abscissa.)

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

7.2 Isobaric by Danner and Wenzl²⁵

The data by Danner and Wenzl were used for some tests. They analyzed adsorption of CO, N₂ and O₂ on 5A and 10X zeolite at 144.3 K. The P_{vap}^S were calculated from data by Clayton and Giaque²⁶ for CO₂ and Streng²⁷ for O₂, which has some uncertainty. For N₂ the Dortmund data base, mentioned previously, was used. **Table 14** provides the starting parameters for the

physisorption binary phase diagrams obtained from the individual

Table 14 Relevant properties of the DW data to construct binary physisorption phase diagrams at 1 bar and 144.2 K.

$P_{\text{vap}}(\text{O}_2) = 29.96 \text{ bar}$	$P_{\text{vap}}(\text{N}_2) = 55.28 \text{ bar}$	$P_{\text{vap}}(\text{CO}) = 45.97 \text{ bar}$
On 5A zeolite:		
$\chi_c(\text{O}_2) = -2.1939$	$\chi_c(\text{N}_2) = -2.5415$	$\chi_c(\text{CO}) \leq -3.0554$
On 10X zeolite:		
$\chi_c(\text{O}_2) = -1.9215$	$\chi_c(\text{N}_2) = -2.3370$	$\chi_c(\text{CO}) = -3.4720$

isotherms.

There are, however, some uncertainties about the extrapolated χ_c , 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 χ_c s, a log-law might be useful. Therefore, both the χ -plot and the log-law were used and a judgement as to which is clearer in the determination was made, which appeared to be the log-law in this case.

The graphs in **Figure 24** 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:

The individual isotherms are presented in the graphs at the top In **Figure 24**. The maximum and minimum are each determined and are the 2 points each for straight lines in the raw binary graph to the bottom left. Thus forming two prediction lines. In this case, the data from the binary is available and is plotted in the same graph along with the linear regression of the data. This is presented to show the degree on consistency between the predicted 2-point lines and the actual data.

(This data was undoubtedly below mesopore considerations and there was

no indication of observed mesoporosity. Indeed, the isotherms up to one bar is for only about one monolayer equiv. In individual isotherms the straight lines are determined by a linear regression to the data. As crude as this seems, one only needs to know which is the isotherm with the most negative χ_c and an approximate value for the χ_c for the most energetic isotherm.)

Up to this point then the procedure determines:

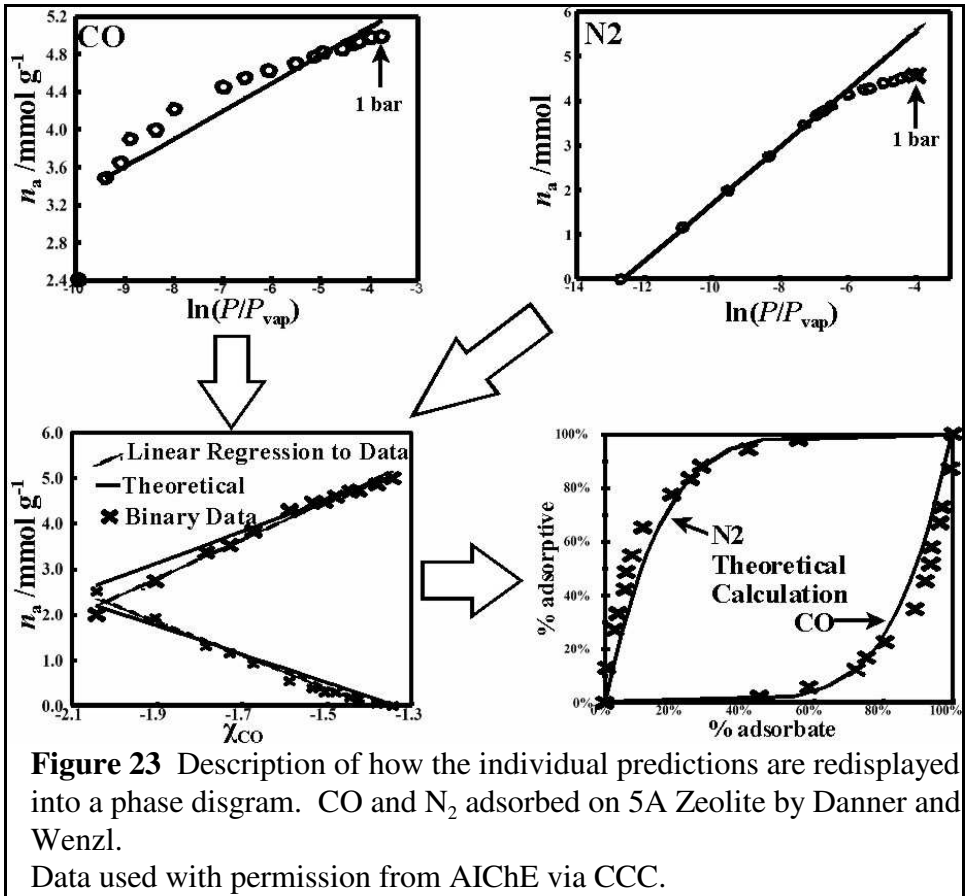
- 1 Which individual isotherm has the most negative χ_c .
- 2 For this most negative χ_c use $n_a = 0$
- 3 Using this same isotherm determine the value of n_a at the selected pressure for the other end of the line.

These two points are used to create the high line on the combined graph. For the low line do the following:

- 4 Use the n_a designate pressure at χ_c (χ_c is still of the high isotherm) for the value at χ_c .
- 5 Use 0 at $P = 0$.

These two points are the endpoints for the low χ_c isotherm.

To obtain the traditional binary diagram, select values of χ for pairs of data and convert to percentage by dividing one and then the other value in the pair by the sum of the two values.



In **Figure 24** the four steps are shown for the method to measure the isotherms for N₂ and CO. Using the maximum and minimum points (black lines) one extracts the values, pressures and amount and plot them on the binary diagram lower right.

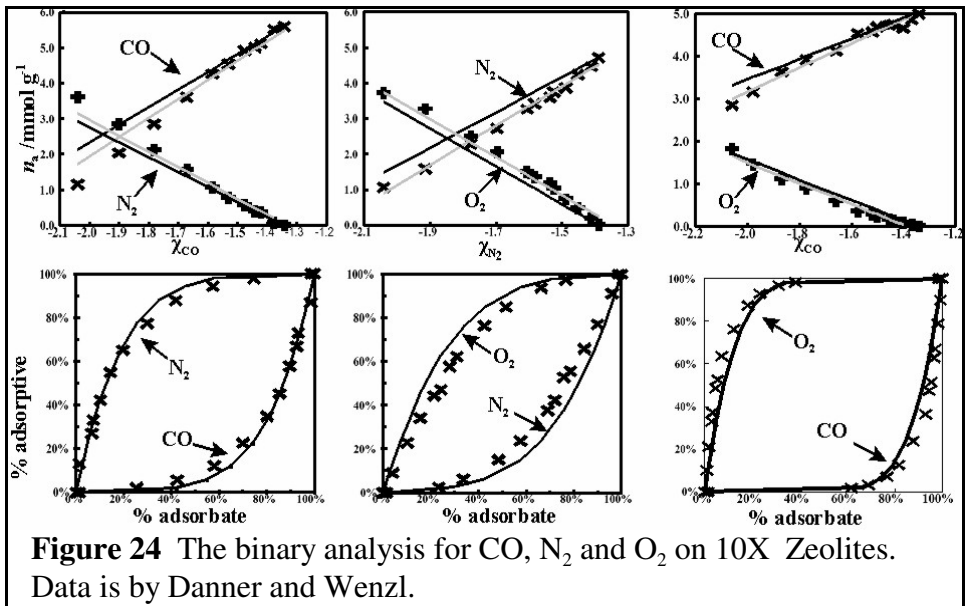
If one has the full isotherms plotted for the lower left, one can get a more accurate binary diagram by using a regression analysis for this figure. The regression analysis is present in the combined χ -plots (lower left) as grey lines. However, this may not be available, so the final high and low points must suffice, that is, the 4-point method, is used as described.

Notice that in **Figure 24** the χ -plot values for the 4-point binary diagrams are normally a little imprecise when combined to the binary. There is, however, considerable data scatter, especially for the O₂ isotherm. 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. It is interesting that the binary plots seem to have higher precision than the original isotherms.

In normal practice, for example, screening studies, the full data set for the binaries would not be used, if this technique proves correct. Here one can see what the accuracy and precision would be expected.

A big caveat is that this is perform in a reange slightly past a monolayer. No testing has be made so far for data reaching past this amount.

7.3 The whole data set from Danner and Wenzl



Modern Hypothesis for Physical Adsorption

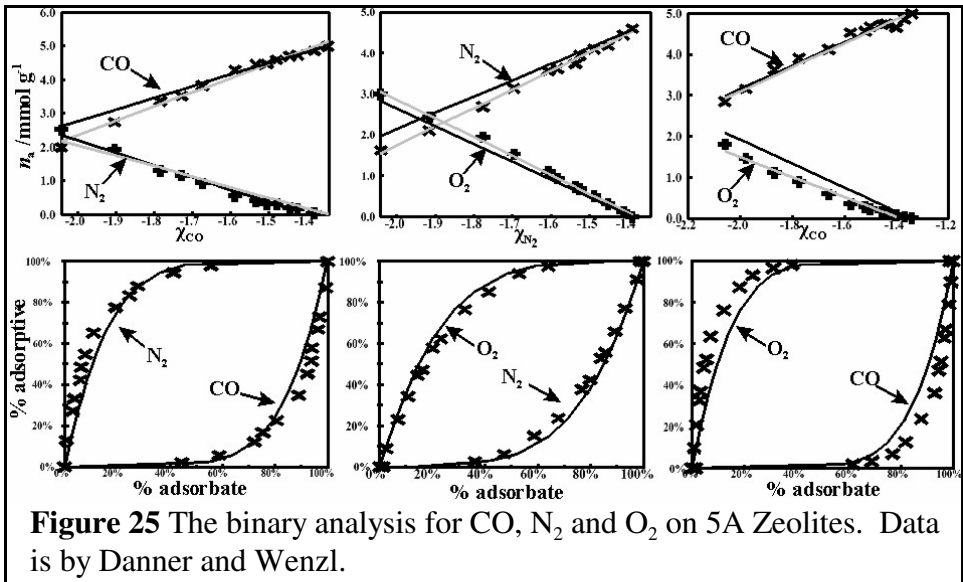


Figure 25 The binary analysis for CO, N₂ and O₂ on 5A Zeolites. Data is by Danner and Wenzl.

Using the entire data set from Danner and Wenzl, one can see how precise the present state of the art is. In **Figure 25** (p 74) and **Figure 26** (p 75) are all six of the binary calculations for the diagrams. Most of the predictions were fairly good.

P. S. Can you now figure out why the detailed data at low χ_A are not needed so long as the approximation to χ_S is reasonably close?

7.4 Conclusion for Binary Adsorption:

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 be addressed schicht by schicht. This seems like several thesis projects. Furthermore, the precision is not very good for the fitted (grey) lines. Why this is the case, is not obvious.

8 Conclusion for the Book:

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 concepts made here that need revision,
- many new uses, subtleness and quicker ways of approaching the solutions,
- or perhaps a genuine disproof of all or part of this presentation, but get a list of illogical arguments before you do.^{ff}

I wish you all the best and good luck. Get inspired.

-JBC

^{ff} See: <https://www.vanderbilt.edu/writing/resources/handouts/illogical-arguments/>
I don't accept Ad Hominem well, so if you don't want me to inform you supervisor of your behavior, do not use it.

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.

Adsorbent: The solid material upon which the gas adsorbs.

Adsorptive: The gas phase of the component that is adsorbing

Anti-Gurvitsch Rule: The pore volume is the extrapolation of the n_{ext} to the ordinate axis of the $\Delta\chi$ -plot.

Calorimeter: An instrument used to measure heat transport to or from the surroundings to the isothermal system or for an adiabatic system measure the temperature change of the system.

Core radius: The radius of the empty volume that is formed after the QM - classical collapse, r_c

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

Gravimetric: Measurements made using a mass balance.

Gurvitsch Rule: The pore volume is the extrapolation of n_a to $P = P_{\text{vap}}$

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

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Isotherm: The output of an isothermal experiment.^{§§}

Isothermic: (or isothermal) Measurements made at constant system 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 mass. The total mass is usually measured before loading the sample onto 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.

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

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

^{§§} Def: Isotherm is literally “at constant temperature.” Since this data was taken at constant temperature. For physisorption, graphs of this type have the abscissa is a function of P only and the ordinate is a function of n_a only. Only n_a , P are allowed statistical computing, all other functions are mathematically disallowed. However, if one variable standard error is required the other axis can be any function of P .

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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 is characterize by the areal density compared to n_m .

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

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, except for heat exchange for the isothermal system.

System: (Thermodynamics) a delineated place in physical space defined to be consistent with logical and specified boundaries, in the physisorption case it is adsorbent plus adsorbate.

Thickness: (symbol t) same as potential thickness.

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.)

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

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

\mathbf{D} = The Normal Cumulative distribution function

E = (QM) The total energy of a particle (adsorbate molecule)

E_a = The preexponential in the heat of adsorption function

\bar{E}_a = The preexponential 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} .

$\hat{\mathbf{H}}$ = The Hamiltonian operator

R = The gas constant - units $\text{J mol}^{-1} \text{K}^{-1}$ or $\text{kJ mol}^{-1} \text{K}^{-1}$

m_γ = the geometry constant in the Kelvin (Oswald-Freundlich) equation.

n_a = specific^{hh} amount adsorbate - usually in mmol g^{-1} or $\mu\text{mole g}^{-1}$

n_j = specific amount of adsorbate in the j^{th} schicht.

n_m = specific amount adsorbate in a monolayer equivalence, units "

\mathbf{N} = The normal Distribution Function

P = pressure usually in units of bar

P_{vap} = Vapor pressure of adsorptive at the temperature of the adsorbent

P_ζ = The threshold pressure

q_{la} = the differential heat of adsorption referenced to the liquid state at the

^{hh} For physisorption, the “specific” amount is amount of adsorbate divided by the mass of the (thermodynamic) system = approximately the mass of adsorbent.

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

s_n = The Standard error of n_a

$s_{n,FDR}$ = The Standard error of n_a compared to the Full Data Range.

t = Either classical monolayer or virtual monolayer thickness

V_{BET} = total pore volume by classical means, BET or Gurvitsch based

X = “relative pressure” = P/P_{vap}

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

A1.2.2 Greek:

δ = an extremely small increment

ε = Heat of vaporization of the adsorptive at the temperature of the adsorbent

$\Delta\chi = \chi - \chi_c$

$\Delta_l^a E$ = The internal energy function change from the liquid state to the adsorbed state at the temperature of the adsorbent

$\Delta_a^{y/lg} E$ = the energy at which the Kelvin (or other) equation and the $\Delta\chi$ energy match.

$\Delta_l^g H(N_2)$ = Enthalpy of vaporization of N_2

$\Delta_l^a S$ = The entropy change in the system going from a liquid to adsorbate.

$\Delta\chi = \chi - \chi_c$

ε = energy of vaporization,

$\bar{\varepsilon}$ = molar heat of vaporization

θ = The coverage, n_a/n_m

$\theta_N = n_N/n_m$ the amount in the N^{th} schicht compared to 1 monolayer equiv,

σ = standard deviation or spread of a normal distribution.

$\chi = -\ln(-\ln\{P/P_{vap}\})$ a vaiable

$\chi_c = -\ln(-\ln\{P_c/P_{vap}\})$ an output parameter

ψ = (QM) the wave function

ψ^* = (QM) the complex conjugate of the wave function ψ

A1.2.3 Other:

$\langle X \rangle$ = (when not QM) average of X

$\langle X|Y \rangle$ = vector multiplication

↑ = for adsorption

↓ = for desorption

A1.2.4 Subscripts

m = “monolayer equiv”

n = n^{th} schicht

ς = a threshold quantity (Greek low case terminal sigma)

ς_X = a threshold quantity for the X adsorptive

A1.2.5 Superscripts:

\ominus (primsoll) = designates the thermodynamic standard state as superscript.

$\overline{\quad}$ (overline) = designates the quantity is molar (IUPAC alternative)

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

BET = Brunauer, Emmitt, Teller

DW = Danner and Wenzl

ESW = Excess Surface Work

FDR = (percent of) Full Data Range

GCPF = Grand canonical Partition Function.

HF = Hellmann-Feynman

HV = High Vacuum (1.3×10^{-3} to 1.3×10^{-6} Pa or 1×10^{-5} to 1×10^{-8} Torr)

IUPAC = International Union of Pure and Applied Chemistry

JKO = Jaroniec, Krug and Olivier

KIT-6 = Silica used by GWMKT

MKR-RBP = Madani, Kwong, Rodríguez-Reinoso, Biggs, Pendleton

NASA = National Aeronautics and Space Administration

ND = Nguyen and Do

NLDFT = Non-Local Density Functional Theory

NLLS = Non-Linear Least Squares

ORNL = Oak Ridge National Laboratory

QM = Quantum Mechanics

QM = Quantum Mechanics

SBA-15 = Silica used by GWMKT

SSLR = Silvestre-Albero, Silvestre-Albero, Llewellyn, and
Rodríguez-Reinoso

UHV= Ultrahigh Vacuum (1.3×10^{-7} to 1.3×10^{-9} Pa or 1×10^{-9} to 1×10^{-11}
Torr)

UNIFAC = Dortmund physical data tables. (Universal Functional Group
Activity Coefficient)

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 but must have a companion law “Raoult’s Law” that is coupled by thermodynamics. Thus, the phrase “Henry’s Law” is not appropriate for physical adsorption. It is a false analogyⁱⁱ. 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, where it is now conspicuously missing.

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 are in direct proportionality and P goes to 0 if and only if n_a goes to 0.

$$P/n_a = C \text{ and } \lim_{n_a \rightarrow 0} (P) = 0 \quad (35)$$

Another way of saying this is the isotherm theory must pass or extrapolates to (0,0) linearly by **Equation 35**. However, it seems that any theory that extrapolates to (0,0) is acceptable, such as the Freundlich isotherm. So, to get away from the misnomer and the thermodynamic error the symbolism

ⁱⁱ I don’t accept this argument well either.

(0,0) will now replace the words “Henry’s Law.”

The list of (0,0) isotherm theories is quite long, Most prominent are the BET and Langmuir theories^{jj}. However there are many more including modification of these two. These modifications include 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 comparison to a new theory, which yields the same output parameters or fewer, the (0,0) theory is statistically much worse. The word “much” is meant to mean that by any statistical measure or test the old theory turns out to be obviously worse and not just worse by statistical tests, such as the “F” test , etc. This is assuming that nearly 100% of the data is used and not just 15-30% as common with BET.
2. The theory predicts something that experimentally is not true. In this case the (0,0) law is predicts a phenomenon incorrectly.
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.

A2.3 #1 Statistics with Standard Curves:

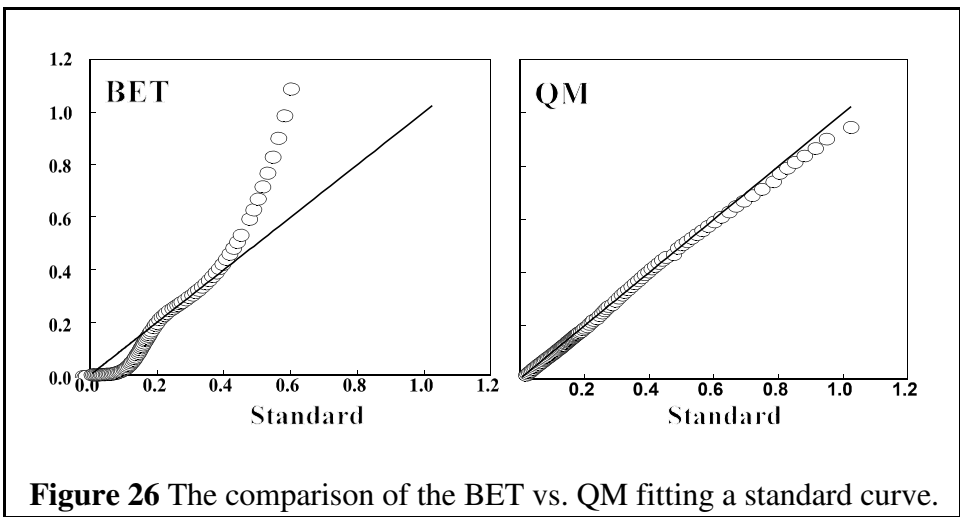
Standard Curves for physical adsorption have been used since 1928. The idea is to find a pure, nonporous adsorbent and carefully measure the isotherm. This will be used as a “standard” against which other isotherms will be compared. It seemed obvious that any material of the same chemical composition would behave very close to identical in the isotherm. Therefore, if a sample is identical chemically but the size of the

^{jj} Notice that I have presented neither the BET nor the Langmuir equation. All previous references to my two books were used to present them in spite of my warning not to. **shame** on those authors and editors. This grounds for editorial withdrawal.

particles are different, then a ratio be the sample to standard is the ratios of there surface area. There are some serious glitches in this idea but it is not important here for what is presented^{kk}.

What is presented is the comparison of theoretically calculated fits of the isotherm against the standards. 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 Olivier⁵ (KJO) seems to be well done with the temperature control problem solved. See **Figure 27**

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 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



^{kk} Except to give some you some guidance what to look for. All previous isotherms have the error of using chemical bonding and chemical equilibrium to describe physisorption. Implying that the adsorbed state is a different component than the adsorptive. Thus, increasing, theoretically the number of components and miscounting the number of phases and not counting the surface itself in the thermodynamics.

the statistics. In **Figure 27** are two graphs. On the left is the calculation of the BET in comparison to the KJO standard. On the right is the QM calculation described in this book^{ll} in comparison to the KJO standard. Both of these are the 2 parameter fits. The BET cannot be expanded past 2 parameters to logically account for features such as heterogeneity and P_{vap} correction, whereas the QM can be.

The very large deviation of the BET after 0.3678...^{mmm} 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...ⁿⁿ the line does a fair job of fitting, but not as well as the QM. However using the conventional BET “transform” on the ordinate yields a better fit. This, however, is mathematical illegality since over a certain range it effectively plots the abscissa against itself^{oo}. Furthermore, that statistics is invalid.

Another problem in the practice of calculating the fit to the BET is the standard deviation is usually that obtained with the ordinate transformation. This is incorrect, one needs to compare the original data, that is to the fit obtained for n_a versus P . In other words, plot the experimental data as n_a versus P/P_{vap} , NOT y calculated from the transform versus P/P_{vap} . This latter use of statistics is simply WRONG and is mathematical trickery!

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

^{ll} See the discussion about the JKO fitting in the text when hysteresis and pressure correction is added to the fit is amazing.

^{mmm} The Fuller magic point.

ⁿⁿ This is refer to today as the Rouquerol criterion, Y, used for $0.1 - 0.5 < X < Y$. Past Y the function is no long approximate by a straight line.

^{oo} There does not seem to be a classification for the type of function. At any rate if there is, it is incorrect here.

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 been preformed in the past to determine this and that answer has always been high by a factor of 2 to 3 if in the Rouquerol range when above $X = 0.2$. However, below $X = 0.1$, the answers are always low by a factor of $\frac{1}{2}$ to $\frac{1}{3}$. With respect to this latter result, simply looking at the graphs reveals why.

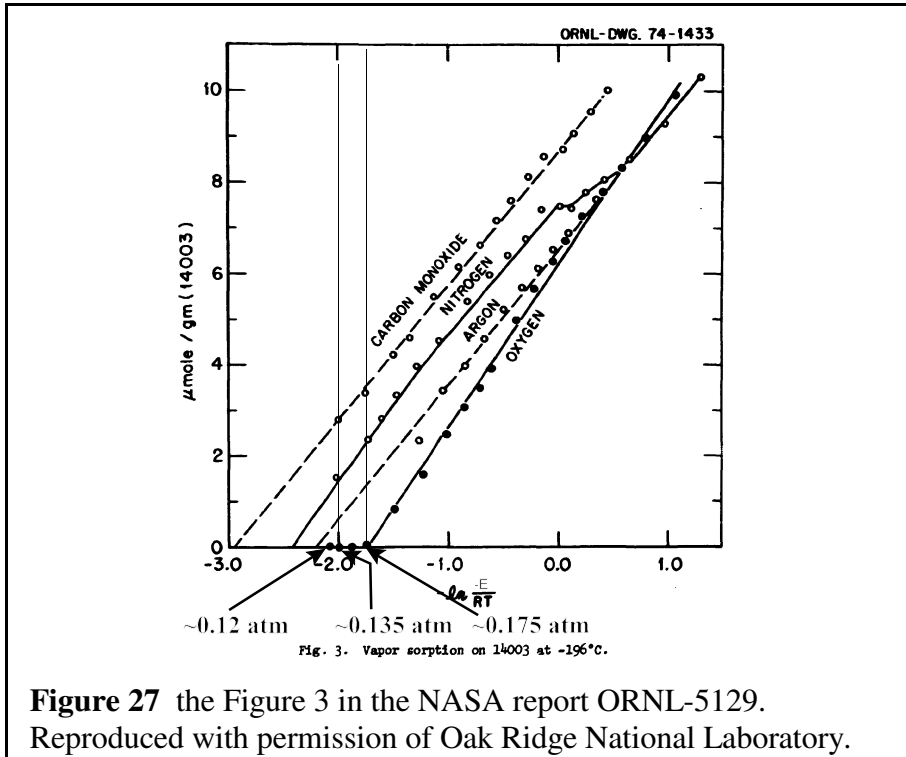
A2.4 #2 the [0.0] fallacy:

Obviously to see the problem at (0,0) one needs to go to $n_a = 0$. (Langmuir in his famous paper⁷ reported a positive offset in n_a for $P = 0$. This is clearly impossible and must have been experimental or extrapolation error. Also, only one of his data sets seems to yield a fair fit for the entire isotherm, but not by modern standards. Several data sets that had 6 to 8 points, but they were clustered in two tight bunches wide apart, so they were effectively two points. It is not hard to get a straight-line fit, regardless of the transform, used if one has only two data points.

A2.5 The Light Bulb Comes on - Fuller, Agron & NASA:

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 instance is the data by Fuller and Agron²⁸ of common gases on lunar soil from the Apollo moon shot. The graphs shown in **Figure 28** (p.88) 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.

The arrows and pressure values in **Figure 28** are added for clarity. This points out that the reading were below to the normal isotherm readings of $1.0 \mu\text{mol g}^{-1}$. 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



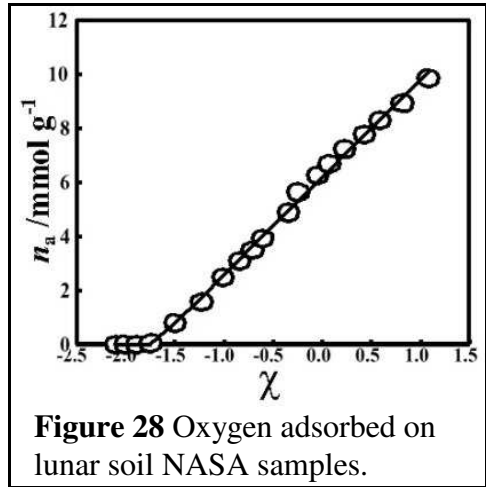
for the experiment, something unusual happened. Every step on every aspects of Appolo was overseen by at least two people with check sheets, so to be sure procedure is followed. Thus, the the pressure range was fixed “too low” and the data ran below the threshold value to yield a quandary.

In Fuller’s Lab^{PP} many contradictions were discovered 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

^{PP} 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, porosimetry, etc.

was later realized that this is what one would expect from the admolecules that 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.

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. However, before bring in some work from outside Oak Ridge, more information about what was found is presented here.



A2.6 More about NASA Lunar Soil by Fuller, et al.

In **Figure 29** 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⁽²⁹⁾. It is probably the best out-gassed sample ever measured. After all, it had been out-gassed in super-ultrahigh vacuum with cosmic out-gassing bombardment for about 3×10^9 years and brought to earth in a special UHV box.

Notice that there are 4 data points are 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 researchers probably might not have done this. (...and these government bureaucrats are useless?)

A2.7 More data by Fuller and by Thompson.

The next example has a very important point. The threshold pressure is high enough that even with the crudest instruments can detect it. This is Teflon® as the adsorbent, which should have a very low energy of adsorption, and argon with an argon bath. It is presented in **Figure 30**. This is by Thompson⁽³⁰⁾ who also found a threshold pressure for hydrogen cleaned Al₂O₃. The H₂ cleaning was to remove unknown contaminants on the surface. Furthermore, he also found that diamond that had the graphic carbon removed from the surface by the hydrogen cleaning had a clear indication of a threshold pressure. See reference 2 for more graphics.

There are several more examples in reference (2), some of which are not obvious but are also disprove the (0,0) isotherm 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 that point to $(n_{\text{ads}}, P/P_{\text{vap}}) = 0$. Due to the linearity of "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.) Any abscissa transform for this, but the straight line must be calculated from the untransformed abscissa, i.e. using n_a versus P .

Thomson demonstrated the importance of special treatment to get the baseline isotherm. Thus, samples that do not have vigorous surface cleaning may have heterogeneity due to contamination, and the threshold pressure is difficult to see and measure⁹⁹.

There are others not associated with ORNL. These are reported in

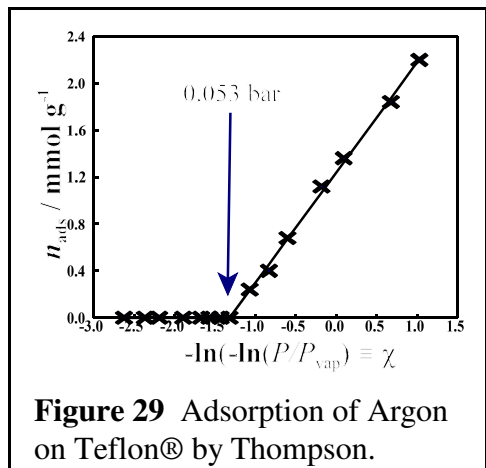


Figure 29 Adsorption of Argon on Teflon® by Thompson.

⁹⁹ This data was presented at a DOE conference on Surface Chemistry and Physics and available from DOE.

a book^{2,rr}. Furthermore, three of the above publications in this report evidenced the threshold pressure. These are:

A2.8 The data by SSLR again

Presented in **Figure 12** (p. 40) is one and in **Table 9** (p. 41) are the calculations made using the data by Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso⁸ (SSLR). This is Nitrogen adsorption on activated carbon LMA223. There are more features about this isotherm that deserves discussion, but the important feature in this discussion is the line leading down in pressure and reaching zero adsorption at a finite pressure. Yes, the pressure is small, $1.94 \times 10^{-7} P/P_{\text{vap}}$, but it is still real. Listed here are the examples in the data by (SSLR.):

- a. N_2 on at 77.4 K on activated carbon LMA233 with $X_c = 1.9 \times 10^{-7}$
- b. N_2 at 77.4 K on activated carbon DD52 with $X_c = 5.5 \times 10^{-7}$
- c. N_2 at 77.4 K on silica SBA-15 with $X_c = 1.2 \times 10^{-5}$. This last one has two data points that are clearly $n_a = 0$

A2.9 Data by Nguyen and Do again:

The data by Nguyen and Do⁶ (ND) in **Figure 35** (p. 113) and **Appendix VI** appears very obvious. The χ plot is obviously headed to $n_a = 0$, since in order for heterogeneity to create a quick a very sharp positive curvature a very unrealistic value of s would be required.

A2.10 Data by MKR-RBP again:

Madani, Kwong, Rodríguez-Reinoso, Biggs, Pendleton (MKR-RBP) in **Figure 13** (p. 43) where the $\Delta\chi$ -plots are shown with the value of -2.6591 for the offset for χ_c .

The evidence of the threshold pressure seems to actually widely visible in

^{rr} See especially the hydrogen cleaned carbon and alumina. The Teflon® experiment is also easy to do and also needs some cleaning routine.

Modern Hypothesis for Physical Adsorption

the literature, but totally overlooked. (That is, ignored in plain sight.)

3 Appendix III Derivation of the QM equations

A3.1 Assumptions:

The most common objection presented by most chemists, engineers, and some physicists is that the adsorbate molecules are “too big and massive” to behave according to quantum mechanics. The argument goes so, “molecules are too big to behave like a wave.” This is, of course, bogus. This argument is also widely disputed by the physics literature with critical experiments^{ss}. Firstly, why would QM for high mass molecules not apply? Physics dictates, today, that all matter is controlled by QM. Secondly, this argument has been proven false by several Young’s experiments^{31,32}. These molecules include He molecules, I₂ molecules (molar mass 254), C₆₀ “bucky balls”^{33,34} (molar mass 720) and superposition with a series of molecules over 1×10^4 amu. Indeed, quantum interference has been observed with several fluorinated thiol chains with masses above 10,000 amu³⁵. If this had not been true it would have “disproved the linearity of QM, something at this time would be a big shock to physics.”³⁵ Thus, the wave nature of adsorbate molecules is expected and is made the first assumption of the derivation and the modern QM concepts are accepted with superposition, entanglement and delocalization. These are firm and well-based assumptions, no known exceptions! The QM physisorption depends upon these latter phenomena as well as perturbation theory.

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

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

^{ss} Critical Experiment Def: an experiment that can potentially disprove a theory. Closely related is

Experiment Crisis: Def: an experiment that disproves all other theories for a particular phenomenon.

of adsorbate molecules directly in contact with the surface and the amount in subsequent schichten^{tt}. 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 χ equations are in excellent agreement with those obtained by calorimetry.

Part 2 is the wave function normal to the surface (z). From the schichten amounts, one obtains an estimate of the amount that fills the pores from each schicht. 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 normal direction distribution between the schichten.

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. This requires a convention about size, which for the lack of a better choice, is the IUPAC convention.

A3.2 Thermodynamic conventions - The system vs surroundings and standard/reference problem.

Firstly, the definition of system and surroundings. In the case of physical adsorption the thermodynamic system is the adsorbent plus adsorbate. The surroundings of importance is the adsorptive with the ability to measure the P/P_{vap} . In both the volumetric and gravimetric case there is need to be sure the separation is clear and correct for interfering surrounding effects. For example, the volumetric is corrected for sample changing the volume and the gravimetric corrects for the buoyancy.

There are three conventions about what comparison pressure is used.

^{tt} See the explanation for schichten in the beginning chapter in section 1.2.

1. At the start of the derivation, a “particle in the box” well is constructed and the bottom of the well is $E_0 = 0$. Strictly speaking the first energy level, W_0 , is the lowest level but the difference between E_0 and W_0 is very small compared to the overall energy. Therefore, it is assumed $E_0 \approx W_0$.
2. The reference then is shifted to the thermodynamic standard of 1 bar,
3. and then to the reference used for the isotherm of the vapor pressure of the adsorbate at the temperature of the adsorbent, P_{vap} .

A3.3 The wave function parallel to the surface (x,y).

The system is an open system, therefore, the grand canonical partition function is used to obtain the thermodynamics and other properties.

Figure 31 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 assumed that $W^0(0) = 0$ (not necessary.) and a first perturbation, which is designated by the letters “ $\alpha a/A$ ” since $E_0 \approx 0$.

The simplest QM calculation starts with the Hellmann-Feynman theorem to yield the monolayer equivalence, n_m , and the internal energy function change $\Delta_i^a E(n_a)$. The assumption above allows dealing only with the wave function parallel to the surface. Superposition and indistinguishability implies “non-locality.” This means that as the adsorbate molecules accumulate, they contribute to the overall surface potential. Each new adsorbate molecule modifies the surface with its potential as seen in **Figure 31** through **Figure 34**. This is a simple particle-in-a-box with a tooth^{uu} instead of a supplementary hole. In the classical (the Fuller ASW) picture, the teeth begin to overlap each other randomly.

^{uu} Even the concept of a tooth and the perfect vertical straight sided well is classical. The potential is spread out over the aliquant as a wave and thus the integral of the wave over the aliquant yields the 3D potential, (x,y,E) .

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 energy of 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 cover the whole surface aliquant as indicated by experiments that support the QM characteristics of large molecules.

The cross-sectional area of the admolecule, a , compared to the surface aliquots, A , which is $a \ll A$ or typically $< 1:10^6$, thus the Hellmann-Feynman Theorem is applicable for the perturbation. (...and also for first approximation for perturbation theory.) Thus, the first adsorbed molecule provide a very small perturbation on the surface as in **Figure 31**

$$\langle \psi^* | \{E + \delta E\} | \psi \rangle = \langle \psi^* | \hat{\mathbf{H}} + \delta \mathbf{H} | \psi \rangle \quad (36)$$

and:

$$E + \delta E = \frac{\langle \psi^* | \hat{\mathbf{H}} + \delta \mathbf{H} | \psi \rangle}{\langle \psi^* | | \psi \rangle} = \hat{\mathbf{H}} + \frac{\langle \psi^* | \delta \mathbf{H} | \psi \rangle}{\langle \psi^* | | \psi \rangle} \quad (37)$$

Looking at **Equation (37)**, $\delta \mathbf{H} = \delta E$, and since $E = \mathbf{H}$ and the total universe for this derivation is restricted to A , thus:.

$$E_1 := E_0 + \delta E = E_0 + \beta a / A \quad (38)$$

Since $E_0 \approx W_0 = 0$ then **Figure 31**:

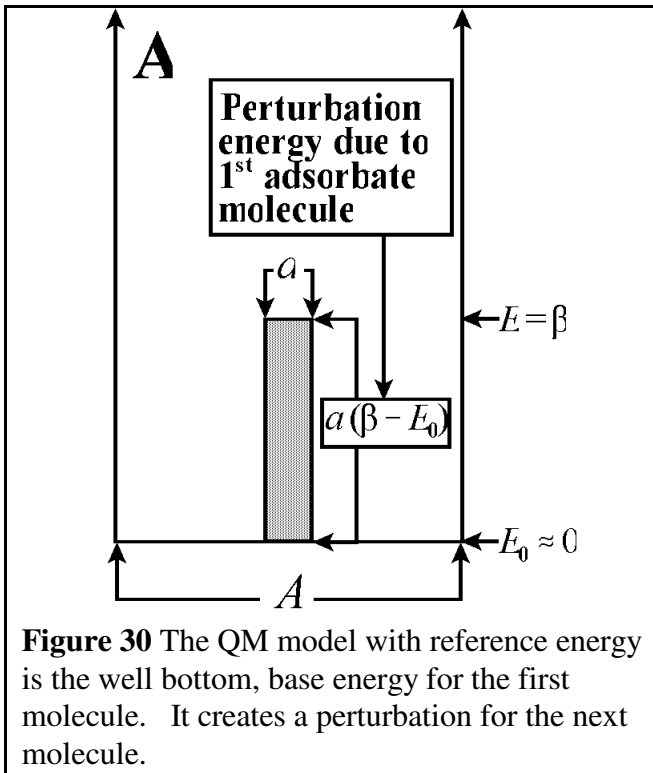
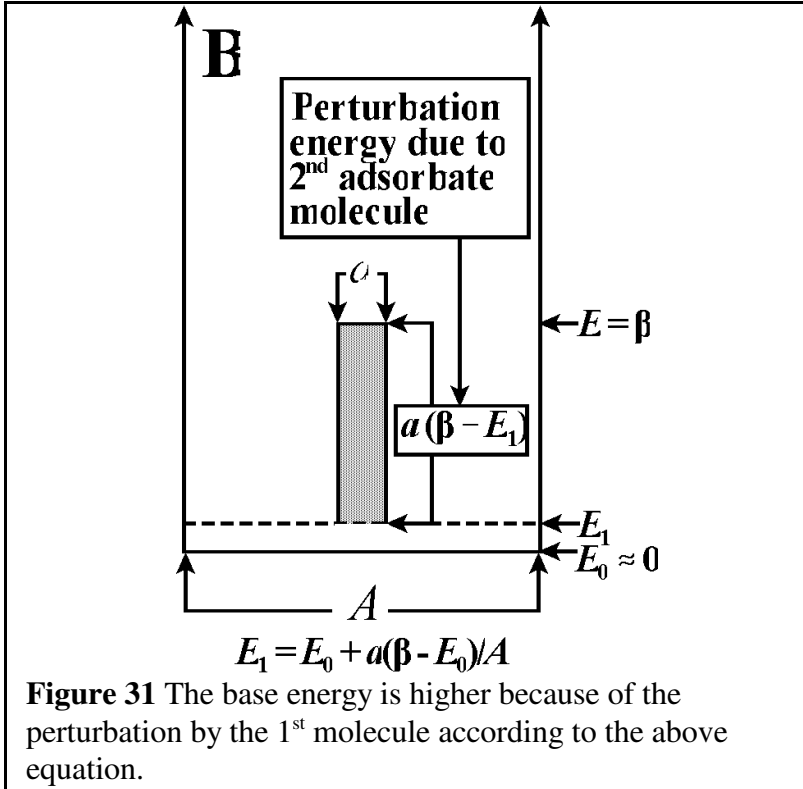


Figure 30 The QM model with reference energy is the well bottom, base energy for the first molecule. It creates a perturbation for the next molecule.

So that:

$$E_1 = \beta a/A \quad (39)$$



For E_2 (The 2nd molecule **Figure 32**) is:

$$E_2 = E_1 + a(\beta - E_1)/A = (a/A)\beta + (a/A)\beta - (a/A)^2 \beta \quad (40)$$

...and recognizing “completing the squares” by pulling out a β yields:

$$E_2 = \beta - \beta(1 - a/A)^2 \quad (41)$$

Repeating this for the 3rd molecule, one obtains:

$$E_3 = \beta - \beta(1 - a/A)^3 \quad (42)$$

By induction one obtains for a large $N \approx N+1$:

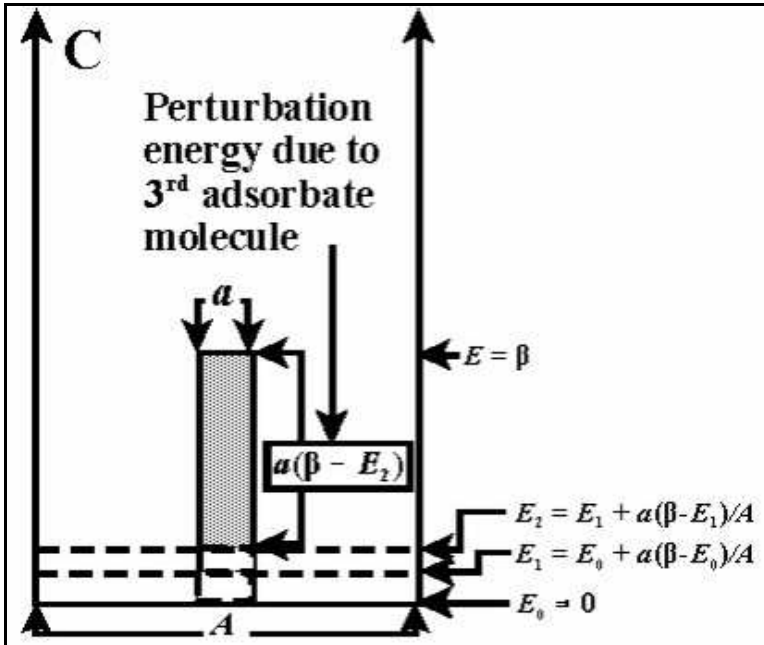


Figure 32 Continuing the adsorption to the 3rd molecule.

$$E_N = \beta - \beta(1 - \alpha/A)^N \quad (43)$$

Furthermore, A/a is very large and the number of adsorbate molecules, N , is also very large. By definition $\theta = Na/A$ which means $N = \theta A/a$. Making the substitution of $x = A/a^{\vee\vee}$

^{v\vee} 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. Another handy number to remember is $e^{-1} = 0.3678....$ This is the relative pressure value for the inflection point or Fuller magic point of $\chi = 0 \text{ Jmol}^{-1}$.

$$E_N = \lim_{x \rightarrow \text{large}} \beta - \beta \left\{ (1 + 1/x)^x \right\}^{-\theta} \quad (44)$$

By the definition of the **exp** function then:

$$E_N = \beta - \beta \mathbf{exp}(-\theta) \quad (45)$$

This can be substituted into the Grand Canonical Partition Function (GCPT) since the normal physisorption experiment is a thermodynamic open system. (For simplicity, the count has been shifted down.) Noticing that: $\theta = na/A_a$ and usually the number of adsorbate molecules are at least in the range of nanomoles or $O(1 \times 10^{14})$ molecules g^{-1} , then the summation may, with an extremely insignificant error, be written as an integral.

Noticing that A/a is extremely large and the number of adsorbate molecules, N , is also extremely large, and by definition $\theta = Na/A$ which means $N = \theta A/a$, thus by the definition of the **exp** function the approximation of the summation being the integral (again $N \approx N + 1$):

$$\sum_{m=1}^N E_m = N\beta - \beta \int_{\tau=0}^N \mathbf{exp}(-\theta) d\tau \quad (46)$$

The question of the open “uncovered^{ww}” surface now becomes important for any particular N . **Equation (45)** states that the N^{th} molecule does not release the energy β but less than that by $\beta \mathbf{exp}(-\theta)$. This is the amount of energy “missing,” or alternatively it is the “empty” amount:

$$\theta_{MT} = \mathbf{exp}(-\theta) \quad (47)$$

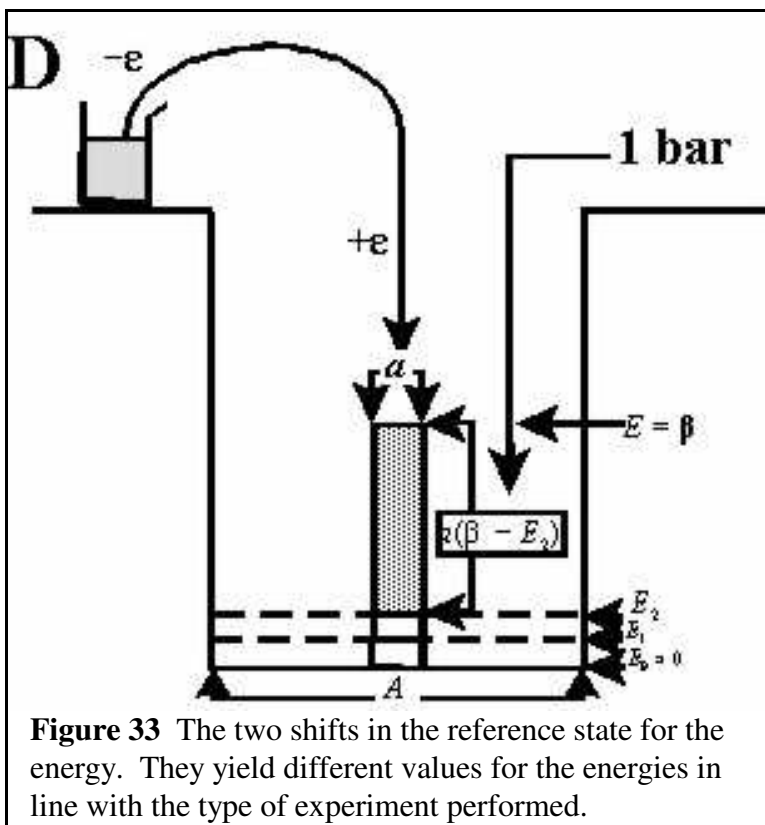
or up to the N^{th} molecule:

$$\theta_{MT}^N = \sum_{m=1}^N E \theta_m = \beta \int_{\tau=0}^N \mathbf{exp}(-\theta) d\tau \quad (48)$$

This will become clearer and why it is important with the introduction of schichten.

^{ww} “Empty” here is defined by the relative areal density of the 1. schicht by $\theta_{MT} = 1 - \theta_1$.

The term E_0 compared to W_0 at the bottom of the box is still relatively quite small so the shifting the standard state from W_0 to the thermodynamic standard state with reference to 1 bar E^\ominus is not problematic. With this shift one can plot energy of adsorption versus amount adsorbed, n_a . A second shift to the state referenced to the vapor pressure of the adsorptive at the temperature of the adsorbent is made. This yields the dependence of n_a on the independent variable called the “relative pressure,” P/P_{vap} . (Sometimes the “relative pressure” variable is



given the symbol “X” following the Brunauer convention.)

These shifts for the reference are shown in **Figure 34**. Notice that initially the energy changes were positive, that is, endothermic. After the change in reference state, the energies are negative, that is exothermic which is in

alinement with experiments.

1. With the right indicating arrow the standard thermodynamic convention reference applies to 1 bar pressure.
 - a. This is the convention used for calorimetry and
2. On the left with the indicating arrow indicates the reference against the vapor pressure of the adsorptive at the temperature of the adsorbent,
 - a. which is the normal reference using relative pressure in the conventional isotherm representation.

This is far as the QM can take this derivation. A relationship now is need between the surroundings, for which the adsorptive is the component of importance, and the thermodynamic system, the adsorbate and adsorbent. This requires the **The Grand Canonical Partition Function** or the GCPF.

A3.4 The Grand Canonical Partition Function (GCPF):

The classical GCPF is used here. By including the canonical partitian function in the GCPF, the shift to the vapor pressure for the relevant comparison state is implied as indicated in **Figure 34**.

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

$$\Xi = \sum_N (\lambda Z)^N \exp \left[- \left(E_a \int_0^N \exp(-\theta) dx - N\varepsilon + \frac{1}{2} N_1 kT \pm N f(T) \right) / kT \right] \quad (49)$$

The following are the meaning of the terms:

- term 1: λZ this is the canonical partition function for the adsorbent = $\ln(\tilde{p})$, \tilde{p} = fugacity but will be replaced here with SIO pressure (not necessary.)
- term 2: with the integral is equation ?
- term 3: $N\varepsilon$ - the interaction between adsorbate particles - assumed to be the same as in the liquid state, since it is now obvious adsorbate and adsorptive are the same component.
- term 4: $\frac{1}{2} N_1 kT$ - the loss in translation mode to 2D instead of 3D. This

needs to be restricted to the molecular density in the first schicht. This is very small and might not be observed, but it needs modification to be restricted to the first schicht by the calculation of θ_1 - an advanced topic.

item 5: $Nf(T)$: changes in internal adsorbate modes such as rotation and vibration. This is mostly also for the first schicht.

Items 4 and 5 are ignored here. They are for advance topic consideration if at all. A further consideration for calculating the surface area is the orientation of the adsorbate molecules, if they are not symmetrical.

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

$$0 = \frac{\partial \ln(\Xi_{\text{max term}})}{\partial N} = \ln(\tilde{p}) + -\left\{ E_a \exp(-\theta) - \varepsilon + \frac{1}{2}(1 - \theta_1)kT \pm f(T) \right\} / kT \quad (50)$$

Ignoring term 4 and 5 (ignoring is not necessary,) and converting to molar amounts then and moving the pressure term to the left:

$$-\ln(\tilde{p}) = -\frac{\bar{E}_a}{RT} e^{-\theta} + \frac{\bar{\varepsilon}}{RT} \quad (51)$$

Using P in place of \tilde{p} , since the experiments are normally performed at $P = 1$ bar or less. (Again is not necessary, \tilde{p} could continue.):

$$-\ln(P) = -\frac{\bar{E}_a}{RT} e^{-\theta} + \frac{\bar{\varepsilon}}{RT} \quad (52)$$

Taking the limit $\theta \rightarrow \infty$ one obtains:

$$-\ln(P_{\text{vap}}) = -\frac{\bar{\varepsilon}}{RT} \quad (53)$$

So, **equation (51)** becomes:

$$\ln\left(\frac{P}{P_{\text{vap}}}\right) = \frac{\bar{E}_a}{RT} \exp(-\theta) \quad (54)$$

The point that disturbs most researchers is that as $\theta \rightarrow 0$, while P approaches a finite value, P_c . 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^{xx}. This phase change occurs when:

$$\ln\left(\frac{P_{\zeta}}{P_{\text{vap}}}\right) = -\frac{\bar{E}_a}{RT} \quad \text{or} \quad P_{\zeta} = P_{\text{vap}} \exp\left(-\frac{\bar{E}_a}{RT}\right) \quad (55)$$

with P_{ζ} being referred to as the “threshold pressure.”^{yy}

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

$$\chi = -\ln\left\{-\ln\left(\frac{P}{P_{\text{vap}}}\right)\right\} \Rightarrow \chi_{\zeta} = -\ln\left\{-\ln\left(\frac{P_{\zeta}}{P_{\text{vap}}}\right)\right\} \quad (56)$$

with a definition of:

$$\Delta\chi = \chi - \chi_{\zeta} \quad (57)$$

For the simple case one can indicate:

$$\frac{n_a}{n_m} := \theta = \Delta\chi \quad \Delta\chi \geq 0 \quad (58)$$

The subscripts “a” and “m” indicate “adsorbate” and “monlayer equivalence” respectively. Obviously $\Delta\chi$ cannot be less than 0. This is a simple straight-forward equation with a simple straight line with the abscissa as χ or $\Delta\chi$ and n_a for the ordinate. It does not fulfill the definition of segmented line as some have claimed, it is simply discontinued at $n_a = 0$, with no obviously no function for $n_a < 0$.

^{xx} I have tried to call this a “preliquid” or a “subliquid” to the ire of reviewers. It’s obviously part of the liquid phase with a different gradient of density.

^{yy} The definition of P_{ζ} .

A3.5 The Schichten Equations

Equation (47) (p.100) 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 schicht. is:

$$\theta_1 := \frac{n_1}{n_m} = 1 - \exp(-\Delta\chi) \quad (59)$$

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

$$n_1 = n_m + \frac{n_m RT}{\bar{E}_a} \ln \left(\frac{P}{P_{\text{vap}}} \right) \quad (60)$$

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 $P = P_{\text{vap}}$. It will therefore not follow a straight line χ -plot from the start of adsorption, but rather a logarithmic curve - i.e. the log plot. If there is a 2nd schicht, or a partial 2nd schicht the χ -plot will start out linear up to the distance where the 2nd schicht is inhibited further. (This is assuming that the external surface area is insignificant.)

Lemma 1: n_1 always approaches n_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."

Other Lemmas could be created for the 3. 4. etc. schichten.

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

$$\theta_2 = 1 - \exp(-\Delta\chi + \theta_1) \quad (61)$$

$$\theta_3 = 1 - \exp(-\Delta\chi + \theta_1 + \theta_2) \quad (62)$$

⋮

$$\theta_{n+1} = 1 - \exp\left(-\Delta\chi + \sum_{m=1}^n \theta_m\right) \quad (63)$$

↓

$$\therefore \theta = \sum_{n=1}^{\infty} \theta_n = \sum_{m=1}^{\infty} 1 - \exp\left(-\Delta\chi + \sum_{m=1}^n \theta_m\right) \quad (64)$$

The last equation can be proven correct for non-porous adsorbents. The easiest was to demonstrate this, to ones satisfaction, is digitally. Mathematical proof is difficult. This series of equation may be obtained by assuming any molecule in schicht “*n*” sees and average energy for schichts <“*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. Have fun.

A3.6 Relationship to ESW (Excess Surface Work)

Historically, an identical equation which include equations (55) (p.104) through (58) (p. 104) was derived by Churaev, Starke and Adolphs^{14,15,16,17}, although written differently. The first definition was assumed to be correct because of a minimum in the disjoining pressure. The minimum is assumed to be at one monolayer equivalence. This monolayer thickness is the same a the slope of the isotherm at the Fuller magic point. This analyses is called excess surface work, or ESW. The assumption that the half life of the DP curve is the monolayer equivance is supported by the quantum mechanical derivation.

The ESW equations can be arrive at by calculating to total molar energy:

$$\Delta_l^a \mathbf{U}_T(n_a) = -n_a \Delta_l^a \mathbf{E}(n_a) \quad (65)$$

This equation relates back to the slope of the untransformed isotherm to obtain the monolayer coverage at the Fuller magic point. This is also the equation that Dr. James Olivier presented at a conference in Naxos, Italy, but decided not to publish.

This method is explained more thoroughly in reference 2 (pp 16-17.) This, however, is limited to isotherms in which the porosity does not interfere³⁶.

A3.7 The Fuller formulation and the Dubinin's Thermodynamic Criterion

Equation (51) (p. 103) yields Fuller's⁽³⁷⁾ and Dubinin's⁽³⁸⁾ observation that:

$$\Delta_l^a \bar{E} := \bar{q}_{la} = RT \exp(-\chi) \equiv -RT \ln(P / P_{\text{vap}}) \quad (66)$$

This equation expresses the internal energy function change, $\Delta_l^a \bar{E}$, for the change from the liquid at the temperature of the adsorbent to the adsorbate state. In this equation \bar{q}_{la} is the instantaneous heat of transfer^{zz} or the "differential" heat. The second term in this expression is the Fuller expression and the last term is the Dubinin "thermodynamic criterion,"^{aaa} which was not acceptable in the literature because of the implication that $\Delta_l^a S = 0$, that is, the entropy from liquid state is 0. This criterion is correct according to χ hypothesis, with the exception of the loss of one degree of translational freedom ($\frac{1}{2}RT$) 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 Berg²³ seems to show this. For calorimetry, the normal thermodynamic internal energy function is use, \bar{E}^\ominus , with the standard state as 1 bar pressure.

$$\bar{E}^\ominus(\theta) = -\bar{E}_a e^{-\theta} + \bar{\epsilon} \quad (67)$$

A3.8 Is this evidence of entanglement?

The admolecules, once adsorbed, are indistinguishable. Thus, all the molecules will respond according to the Equation (66). In other words, they are entangled. This is consistent with a recent publication by Wu, Fassioli, Huse and Scholes³⁹ 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

^{zz} Traditional but not present day IUPAC

^{aaa} Einstein rejected this criterion very strongly. Thus, discouraging anyone to follow Dubinin's lead. That is what uninformed authority does to progress.

lines, both for surfaces and for pores.

A4 Appendix IV a short history of QM for 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, but generally unknown until today because of journal rejections. However, the history of the physical adsorption is a hundred year history of a few powerful people fighting to retain their positions at the head of science. These include Brunauer, Einstein, Teller and Emmett. On the other side were London, Polanyi, DeBoer, Zwiiker and Fuller. Dr. Jürgen Adolphs, who is the inheritor of the "Russian branch" of inquiry, and myself mentored by Fuller, may succeed to present a more reasonable and scientific approach to the field.

This book is based upon my experience to the events - the development of knowledge and discoveries regarding physical adsorption. I worked as a collaborator with Dr. E. L. Fuller, Jr.†, whose group ran perhaps thousands of isotherms^{bbb} or more isotherms, which were used for production quality control. It was Fuller who noticed that the BET not

^{bbb} In this respect, JBC engineered and constructed, in 1969, 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 by 3cm diameter to avoid problems with the temperature gradient zone, the temperature detector was a gas-liquid thermometer close to the sample, baffles were used and placed 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 over the range of 10^{-6} bar to 10 bar. An (LSI) computer was used to record pressure, temperature, weight gain and other diagnostics, which was unusual at that time. Importantly, earth quake detectors were available and the 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 microbalances that weighed 10g that were also capable of pressure up to 25 bar. Sapphire windows were used to pass light beams to the balance position detector. Each balance had the sensitively of $1:10^9$ (1 ppb). The balances were not originally built for physisorption but for another program, but the 1 mg balance was transferred to the analytical group, for which Fuller was a senior scientist and Dr. Ken Thompson took over the microbalance responsibility.

only did not work, but yielded the wrong answers for the surfaces area. These answers seemed to have no correlation to anything.

Dr. Fuller noticed and determined that the Polyani theory did fit a majority of the time, even though the theoretical basis was uncertain and the surface area parameter was not thought to be 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, which was a side line to my main assignment, it created weird results, I consulted Dr. Fuller about it. I also consulted with Dr. John Kirkpatrick, a world famous mathematician. Dr. Kirkpatrick discovered an 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 one reviewer was, "This is ridiculous." I agree with the statement but not the target. Unfortunately, there did not seem to be an answer to my problem to publish, so it was not published. Since then I have received many rejections for proposed publications based always on non-scientific^{ccc} and other illogical reasons. I was apparently blocked and did not publish for many years until later Elsevier contacted me for my first book.

Fuller, on the other hand had a method that had many advantages. Although essentially empirical, it was consistent, reproducible, applied to the entire isotherm, the anomalies were nonexistent and the thermodynamics was more reasonable. It just seemed that it must have a solid theoretical explanation behind it, but what was it?

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 energy of adsorption have an

^{ccc} Usually with conflict with the literature or the editor's own publications, opinions and shocking mathematic illiteracy.

exponential decay based on amount. I had some previous experience with quantum mechanics (QM) and it immediately occurred to me that perturbation theory should work instead of classical chemical^{ddd} 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 given the name “Auto-Shielding Physisorption,” (ASP) a classical analogy.

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_m 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 be 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. There are potential disproveability paths for the QM derivation and it would be interesting if these paths are taken.

End of story - almost, or will it continue?

^{ddd} 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: 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 winner of the Kendall Award. His thesis disproved the multiplet theory of benzene chemisorption, requiring other explanations for reaction pathways.

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 but solved the problem anyway, so he was retained as a consultant for several fields of physical chemistry. He is the inventor of the modern hydrogen in/on metals analyzer. This analyzer 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. (Those were the good-old days when requests were made with post-cards. Today, copyright laws makes it difficult for authors to share their information. A science unfriendly move by the publishers.) 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 problem. 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. He receive an award from DOD and DOE.
- ◆ He is 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 Physiker at the Institut der Festkörper Forschung (IFF, Institute for Solid State Research) in the Forschung Zentrum Jülich.

Dr. Condon has over 100 open literature publications 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. (You didn't know there are classified patents?)

A6 Appendix VI 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, without heterogeneity and P_{vap} corrections. Only when one gets the basics correct can one discern the more subtle features such as heterogeneity and P_{vap} corrections.

So it is with the Nguyen and Do data. In (67) 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 added the pressure correction. The heterogeneity test yielded no significant heterogeneity. Notice there are slight differences in the common parameters and for the standard deviation of the fit in T.

Statistically, the ratios of the s_n s are almost indistinguishable, and indeed an extra digit is present that normally would not be shown. Both fit qualify as valid under the $\sigma_{\text{FDR}} < 1\%$. Inspecting the **Figure 35** compared to **Figure 4** it seems intuitive that the Pressure correction should be selected, but again this is not an unbiased decision. However, there does not seem to be any other explanation for the deviation at the high

pressures.

Table 15 the parameters yielded by the 2 and the 3 parameter fit for ND

Quantity	linear regression	with $G \times P/P_{vap}$	units
$n_m =$	0.5536	0.5536	mmol g ⁻¹
$\ln(P/P_{vap})$	-14.9619	-15.0418	
$P/P_{vap} =$	3178×10^{-7}	2.934×10^{-7}	
$\chi_\zeta =$	-2.7055	-2.7108	
$E_a =$	-22.49	-22.54	kJ mol ⁻¹
$G =$		0.923	
$s_n =$	0.0238	0.0236	mmol g ⁻¹
$\sigma_{FDR} =$	0.280%	0.272%	

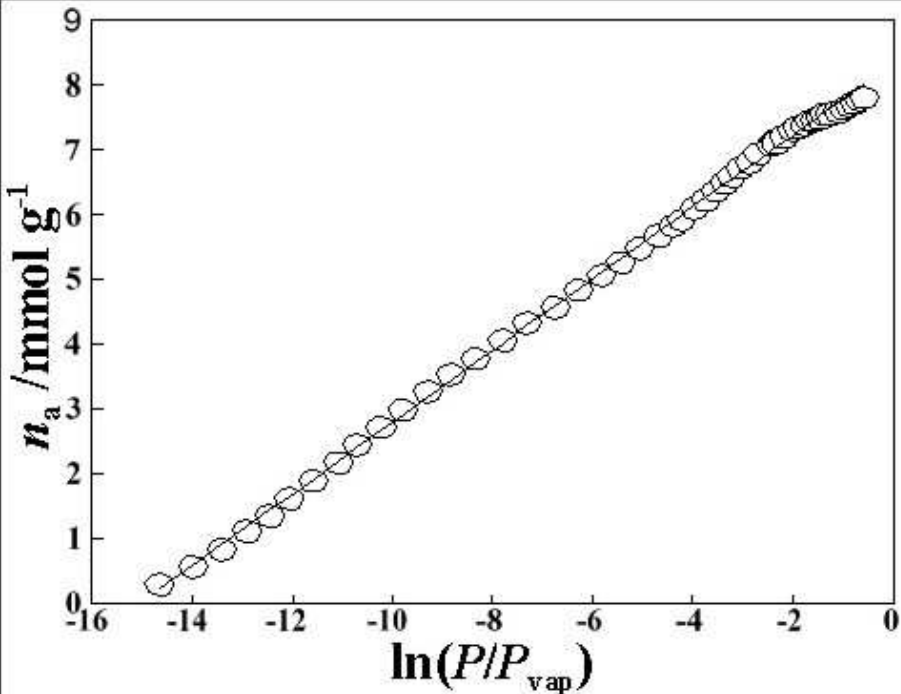


Figure 34 The fit to the ND data including the log-law, mainly, followed by the linear fit for external adsorption. However in this case there is a pressure correction. Compare this to **Figure 4** (p. 14.)

A7 Appendix VII Some data tables

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

These tables present the calculation for the output parameters that the QM calculation generates. The instructions for Elsevier publication indicate that the data is copyrighted. This is not valid according to U.S. copyright law, which does not allow data to be copyright protected. However, it may not be invalid in other countries. Therefore, the original data is not shown here and the original authors did not supply the original data to make these QM calculations. You may not reverse engineer this table in countries where the copyright to obtain the approximate values used does not permit such action. See the original paper or buy the data from Elsevier if you have a need for it.

Table 16 A7.1 KIT-6 data Sample K(100)48_N

$-\exp(-E_i^a/RT)$	χ	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

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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

$$s_n = 0.1575$$

$$s_n_{\text{FDR}} = 0.43\%$$

$$\text{Transition zone} = 1.229 - 1.327$$

$$\chi_\zeta = -2.685$$

Table 17 A7.2 SBA-15 Sample S(140)24_N:

χ -plot adsorption results

$-\exp(-E_i^a/RT)$	$-G^*\exp(-E_i^a/RT)$	χ	mmol g ⁻¹	fit	residuals
0.0133	0.0133	-1.4637	4.0140	3.4816	0.5324
0.0216	0.0216	-1.3445	4.3228	3.9730	0.3498
0.0332	0.0332	-1.2254	4.7087	4.4644	0.2444
0.0448	0.0448	-1.1332	5.1719	4.8449	0.3270
0.0614	0.0614	-1.0262	5.3263	5.2861	0.0402
0.0730	0.0730	-0.9621	5.6350	5.5506	0.0844
0.0846	0.0846	-0.9040	5.8666	5.7901	0.0765
0.0929	0.0929	-0.8654	6.0982	5.9494	0.1488
0.1061	0.1062	-0.8076	6.4070	6.1880	0.2190
0.2040	0.2041	-0.4633	7.3333	7.6085	-0.2752
0.2554	0.2555	-0.3108	7.9508	8.2375	-0.2867
0.3085	0.3086	-0.1618	8.3368	8.8519	-0.5151
0.3582	0.3584	-0.0258	8.7999	9.4130	-0.6131
0.4544	0.4546	0.2379	9.8806	10.5007	-0.6201
0.5539	0.5542	0.5271	11.1929	11.6941	-0.5012
0.5755	0.5757	0.5940	11.5016	11.9700	-0.4683

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0.5954	0.5956	0.6576	11.8104	12.2322	-0.4217
0.6186	0.6189	0.7343	12.1964	12.5485	-0.3521
0.6352	0.6355	0.7910	12.5051	12.7825	-0.2774
0.6534	0.6537	0.8555	12.8139	13.0485	-0.2346
0.6700	0.6703	0.9162	13.1227	13.2992	-0.1765
0.6849	0.6852	0.9729	13.3543	13.5330	-0.1787
0.6998	0.7002	1.0316	13.5858	13.7751	-0.1893
0.7131	0.7134	1.0857	13.8174	13.9985	-0.1810
0.7297	0.7300	1.1562	14.3578	14.2893	0.0685
0.7430	0.7433	1.2152	14.8209	14.5326	0.2883
0.7595	0.7599	1.2926	15.4385	14.8525	0.5860
0.7811	0.7815	1.4001	16.5191	15.4052	1.1139
0.7910	0.7914	1.4528	17.5226	16.1658	1.3568
0.8010	0.8014	1.5077	18.9121	18.4216	0.4905
0.8093	0.8097	1.5554	21.8454	22.4013	-0.5559
0.8192	0.8196	1.6150	28.3296	29.2405	-0.9110
0.8275	0.8279	1.6669	35.6628	34.3881	1.2747
0.8375	0.8379	1.7323	37.7470	37.6301	0.1169
0.8474	0.8478	1.8014	37.9786	38.4752	-0.4966
0.8574	0.8578	1.8748	38.2874	38.6327	-0.3453
0.8707	0.8711	1.9803	38.5961	38.7470	-0.1508
0.8856	0.8860	2.1116	38.8277	38.8854	-0.0577
0.8955	0.8960	2.2085	39.0593	38.9875	0.0718
0.9071	0.9076	2.3332	39.2909	39.1190	0.1719
0.9519	0.9524	3.0200	40.2172	39.8428	0.3743
0.9950	0.9955	5.4020	42.2242	42.3534	-0.1292

$$s_n = 0.534$$

$$s_{n \text{ FDR}} = 1.27\%$$

$$\text{Transition zone } 1.229\text{-}1.327 \quad \chi_c = -2.3076$$

A7.3 Ar adsorption on Si-1000 by Krug and Jaroniec⁴⁰ (KJ.) The analysis

Table 18 A7.3 Ar adsorption on Si-1000 by Krug and Jaroniec as a standard curve in. Here are the output parameters for the 4-parameter fit.

		Value	Units
$-\ln\{-\langle E_a \rangle RT\} = \mu$	$\langle \chi_c \rangle =$	-1.9506	
monolayer equiv.	$n_m =$	0.1699	mmol g ⁻¹
normal peak	$s =$	0.5041	mmol g ⁻¹
$G \times P_M = P_R$,	$G =$	1.019	
n_a std. error	$s_n =$	0.00097	mmol g ⁻¹
s_n /full data range	$s_{n \text{ FDR}} =$	0.192%	
	$r^2 =$	99996	
	$E_c =$	4.50	kJ mol ⁻¹

is presented in **Table 18**. The fit is presented in **Figure 36**. As seen by the figures and statistics, this is a very good fit.

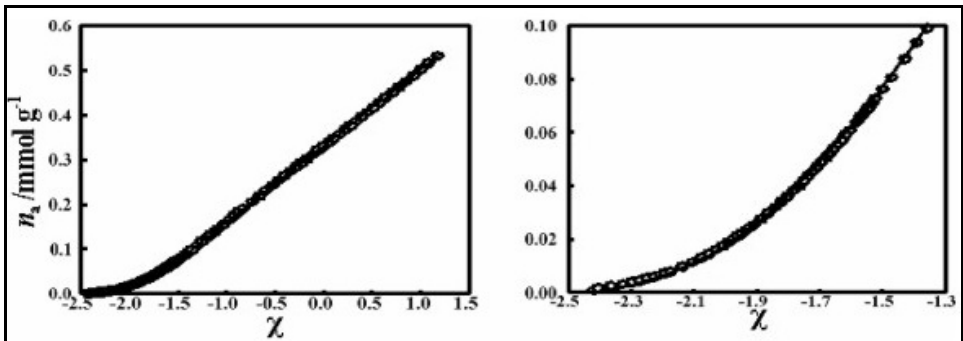


Figure 35 χ -plots for Ar on Si-2000 by KJ.

See other parameters in section A8.1

A8 Appendix VIII IUPAC-QM convention conversions and calculating geometries

A8.1 Example of Sample: S(140)24_N₂ see **Table 19**.

Table 19 Geometries of porous silica by using QM-physisorption of N₂ on sample S(140)24 N₂ to obtain geometries using the IUPAC conventions to convert to dimensions.

quantity	adsorption	desorption	unit
$n_m =$	4.125	3.967	mmol g ⁻¹
$\chi_s =$	-2.3076	-2.372	
$n_{ext} =$	1.054	1.572	mmol g ⁻¹
$n_p =$	34.2	31.9	mmol g ⁻¹
$\Delta\chi_p =$	3.905	3.660	
$\sigma_p =$	7.64E-02	6.58E-02	mmol g ⁻¹
$G =$	1.00048	1.01160	
$s_n =$	0.53429	0.36602	
$\sigma_{FDR} =$	1.27%	0.87%	
$A_{total}^* =$	403.0	387.6	m ² g ⁻¹
$A_{ext}^* =$	103.0	153.6	m ² g ⁻¹
$A_p^* =$	300.1	234.0	m ² g ⁻¹
$\langle E_a \rangle =$	-6.52	-6.95	kJ mol ⁻¹
$s_p =$	1.5978	1.2875	
$\langle E_p \rangle =$	-131.21	-178.95	J mol ⁻¹
$\langle E_p \rangle$ ratio =	1.36		
$V_p =$	767	714	mL g ⁻¹
$d_1 = 4V_p/A_p^* =$	10.2	12.2	nm
$d^{\dagger} =$	10.1		nm
$A_{BET}^* =$	580		m ² g ⁻¹
$V_{BET}^* =$	1420		m ² g ⁻¹

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$d_{\text{BET}}^* =$	9.79		nm
$t_m^* =$	0.709	0.709	nm
$t^* =$	2.77	2.59	nm
$m =$	1	2	
$r_c^* =$	2.30	3.37	nm
$r^* = r_c^* + t^* =$	5.07	5.97	nm
$d_2 = 2r^* =$	10.14	11.94	nm
† = the NLDFT value found by GWMTK			
* using IUPAC convention for conversion of units.			
d_1 anti-Gurvitsch rule & IUPAC conversion to area from QM			
d_2 uses the QM calculations and IUPAC convention			

A9 Appendix IX How Science is Supposed to Work

I taught General Chemistry, and 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.

A9.1 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 disprovable
 - are always tentative
- The official deference between the words for explanations are.
 - Laws - laws are able to describe the observations without the necessity of an 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.

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- 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.

A9.2 Scientific Protocols:

My observation over 57 years of scientific research, is that these protocols are very often not followed. Why they are not is due to various reasons such as:

- protecting funding, which is probably the biggest,
- incompetence,
- protecting ones own “theory,” basically pride and fear.

I have also observed that some of the violations of scientific integrity have costed millions and even billions of dollars.

The protocols include:

- Respecting other researchers moral rights and referencing them where appropriate.
- Letting other researchers have access to your data. A protocol that Elsevier violates in their copyright assignment document.
- Refraining from logical fallacies to counter arguments:
 - especially Ad hominem but others commonly seen:
 - Appeal to Authority (and Everyone Knows)
 - False Analogy
 - Red Herring
 - Straw Man
 - Distorted Mathematics, i.e. trickery, Ex. the BET transform. This is not mentioned in most lists.

There are others but these seem to keep popping up frequently. For a list of illogics see:

<https://www.vanderbilt.edu/writing/resources/handouts/illogical-arguments/>

Acknowledgments:

Firstly, I wish to thank those who supplied me with the original digital data including Prof. Mandani and Prof. Pendleton, and Calzafarri and Prof. Brühwiler, and Dr. Kenneth Thompson. Having the original data has been a great help

I wish to thank Dr. Jürgen Adolphs for his continued help and encouragement in recent years. I look forward to his future publication on ESW and other advances in physisorption. He is on the leading edge.

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 thermodynamics that support the QM hypothesis. I miss him also.

I also acknowledge the work of Dr. John Kirkpatrick, whose mathematical 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!"

Finally, to the 100 year chain of frustrated investigators including London, Polanyi, deBoer, Zwikker, Fuller and possibly many others I don't know about because they could not get past the reviewers - you had it right! (I think.)

Corrections: Send your comment and correction to:

Physisorption@genchem.net - They are welcome. Thank you.

References: (Note, I have not included all the relevant reference, only those useful for the subject matter or required by moral rights. The complete list runs into the thousands. See reference 2 for longer lists.) DeBoer, who is historically speaking extremely important, alone would run into hundreds, and he is not even referenced here.

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