Title: A Modern Physical Adsorption Theory Based upon Quantum Mechanics

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One Sentence Summary:

This review demonstrates that It is past time to replace the old Henry's Law physical adsorption theories (such as BET, DRK, etc.) with theories that use later 20th century theoretical chemistry.

Abstract:

The Quantum Mechanical description of physisorption, derived using perturbation theory allows the use of later 20th century theoretical chemistry. The resulting equations for the adsorption isotherm, that is the amount adsorbed versus pressure, and the energy of adsorption are in excellent agreement with the literature for the entire range of the isotherms. This is in contract to Henry's Law type theories (BET, DRK etc.) which agree with selected isotherms over limited ranges. Since the isotherm applies to porous materials, the porosity can be calculated without an external standard. For example, the BET uses only 30% of the data. Other properties such as binary physisorption are relatively easy to calculate. Statistical comparison with older theories, reveal a great advantage over these methods. Further advances require further experimentation and theoretical developments as suggested.

Main Text:

Background:

Physical adsorption or physisorption is the phenomenon whereby molecules bare attracted to a solid surface in an excess in comparison to phase from which the molecules originate. The attraction is what chemist refer to as intermolecular forces: London forces, induced-dipole attractions, dipole-dipole attractions and "hydrogen bonding." Thus, the forces needed for physisorption are not strong enough to bond molecules to one "site" . Site localization is referred to as chemisorption and the forces are chemical bonds, especially covalent. For physisorption from the gas phase, the main measurements used are calorimetric measurements as a function amount adsorbed, and the adsorption isotherm. The isotherm is a measurement of amount of molecules, or moles, adsorbed as a function of the partial pressure of the adsorbing gas at constant temperature. The measurements are normally performed with powders which yield strong experimental signals. For the simple cases, homogeneous and non-porous solids, it has always been the hope that the isotherm could yield the output parameters of surface area and heats of adsorption.

To make inferences and prediction, theories for physical adsorption have been developed since early 20th century. The most prominent of these is the BET theory, named for the authors Brunaur, Emmett and Teller(*1*) ,that has been used to measure the surface area of particles for about 80 years. It is a theory developed before the common use of quantum mechanics in the field of chemistry. BET theory had the advantage that it yielded a quantity believe to be the

surface area. No other theory was believed to yield this value; although both the Harkins-Jura(*2*) method and deBoer-Zwikker(*3*) calculation might have done so with further experimental and theoretical development. The development of the BET theory was undoubtedly a monumental breakthrough. There was no other theory to explain the physical adsorption isotherm. It also had similar characteristics to the Langmuir isotherm, which applies to chemisorption and yielded a high degree of credence.

It is now known that there are multiple problems with the BET method. Some problems were pointed out early by Halsey(*4*) and criticism has continued to this day by many authors including Sing, et. al.(*5*) and others, which includes this author(*6 - 8*). Among the problems are that it is imprecise, inaccurate, contradictory, prone to anomaly and cannot properly measure porosity. It also has the strange tendency to yield an imaginary number for the energy. It definitely does not calculate the energy of adsorption correctly nor is there any indication or theoretical reason that the surface area value is correct. Unfortunately, it is still being used as the IUPAC(*9*) "gold standard" much to the detriment of scientific endeavors.

So what to do about this situation? Today, there are at least two proposals that can properly measure the "monolayer equivalent" adsorption, n_m, which is the most important parameter, and the adsorption energy, E_a. These two proposals include 1) the quantum mechanical perturbation theory, called the χ hypothesis(*6*) that requires no input parameters and yields the outputs n_m and E_a and 2) disjoining pressure hypothesis (DPT) by Churaev, et. al. (*10*) or the excess surface work hypothesis (ESW) by Adolphs(*11*) . (DPT and ESW are the same.) Both χ and ESW make very simple assumptions. The ESW theory is based only on thermodynamic and classical

mechanics and introduces an arbitrary, though reasonable, single input parameter assumption. The ESW can be derived from the χ hypothesis which includes the value of the parameter. This gives credence to both and confirms the assumption made for the one input parameter introduced in ESW.

Objectives: To apply quantum mechanics to physical adsorption.

χ Assumptions:

The χ assumption is reasonable for any theoretical chemist. This assumption is that the wave function of the adsorbate particle may be separable into two 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 of adsorbate molecules directly in contact with the surface and the amount in subsequent "layers." It yields n_m, the monolayer equivalence from the isotherm directly without modeling or standards to compare to the isotherm. 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 "layer" amounts, one obtains an estimate of the amount that fills the pores from each "layer." For actual vertical distance from the surface, one needs to assume an intermolecular potential, such as a Lennard-Jones potential to get the distribution between the "layers."

Notice that the Part 1 involves no input parameters. For a nonporous homogeneous surface, if the resulting equations are fit to the isotherm then there are two output parameters, n_m, and E_a. If porosity exists, Part 2 is used to convert the extra output parameters to radii and volumes.

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

 Figure 1 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 E_q is with a ground state E_a and a perturbation at $(E_q - \varepsilon)$, which will be designate by the letter "α".

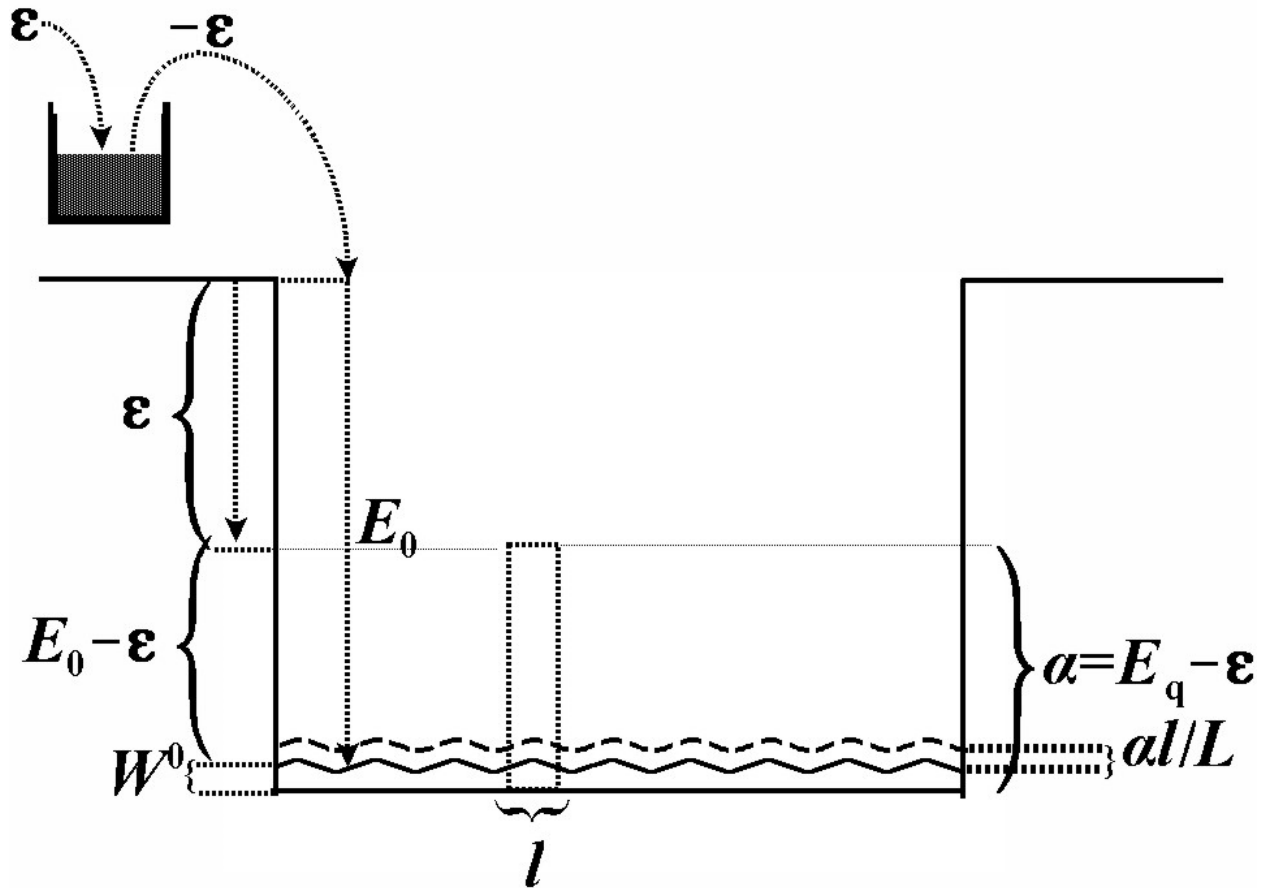*Figure 1* Schematic for QM adsorption potential well with a "tooth" perturbation. ‡

The theoretical discussion will be as if this were a 2D well, "E" versus "x," to keep the picture simple. (Application to the 3D is difficult but the results are obvious.) The length of the rectangular well is "L" and the length of the molecule is "l." The wave length and energy of the first molecule, W^0, can be easily calculated in the unperturbed well from the Hamitonian, $\hat{H}$

$$\hat{H}^0 \psi_n^0 = W^0 \psi_n^0$$

The superscript 0 indicates the unperturbed wave, ψ^0 and the subscript, n, indicates the various allowed states.

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

Equation 2

and with energy values of:

$$W_n^0 = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

Equation 3

A molecule, of mass m, will now be assumed to be a rectangular perturbation for the next

molecule as illustrated in **Figure 1**. Typically, $l <<< L$ and $\alpha < E_a \therefore \alpha l <<< LE_a$ and this

perturbation is extremely small, Thus, a simple first order perturbation may be used. Beyond this

is the conventional perturbation calculation, for example see Sherwin(*12*), to yield the answer:

$$W_n = W_n^0 + \frac{\alpha}{L}\left(l - \frac{l}{k\pi}\left[\sin\left(\frac{2k\pi x + l}{l}\right) - \sin\left(\frac{2k\pi x - l}{l}\right)\right]\right)$$

Equation 4

for which the **min** and **max** of the sins may be used to yield:

$$W_n = W_n^0 + \frac{\alpha l}{L}\left(1 \pm \frac{1}{k\pi}\right) \cong W_n^0 + \frac{\alpha l}{L}$$

Equation 5

Notice that αl an area is and it does not matter what the functionality of $\alpha(l)$ is. In the case of the

2D surface this is an energy-x,y volume and only the energy-x,y volume matters. Since shape

does not matter and the adsorbed molecules are also waves, and the volume of the wave

probability substitutes for the classical molecular area-energy volume. The term $1/k\pi$ provides

the maximum error that an <u>individual</u> molecule will encounter. This error is small but is also

averaged out with large numbers of adsorbate molecules. Each molecule adsorbed experiences

the same type of energy shift in a cascading fashion. Thus, a sequence is built up with each

successive adsorbate molecule with wave functions and energies are slightly different -

designated here with the primes on the "n"s

$$W_{n,1} = \alpha \quad W_{n',2} = \alpha + \alpha \frac{l}{L} \equiv \alpha \left(1 + \frac{l}{L} \right)$$

Equation 6

$$W_{n'',3} = \alpha \left(1 + \frac{l}{L} \right) + \alpha \left(1 + \frac{l}{L} \right) \frac{l}{L} \equiv \alpha \left(1 + \frac{l}{L} \right)^2 \dots$$

Equation 7

$$W_{n^N,N} = \alpha \left(1 + \frac{l}{L} \right)^N$$

Equation 8

or in 3D: (and for large N, $N + 1 \approx N$,)

$$W_{n^N,N} = \alpha \left(1 + \frac{a}{A_s} \right)^N$$

Equation 9

$$\therefore \quad \Rightarrow E_n = (E_a - \varepsilon) \sum \left(1 - \frac{a}{A_s} \right)^N$$

Equation 10

Noticing that: $\theta = Na/A_a$ then:

$$E_n = (E_a - \varepsilon) \sum_N \left(1 - \frac{a}{A_s} \right)^{\theta A_s / a} \quad .$$

Equation 11

Since A_s/a is very large then:

$$E_n \approx (E_a - \varepsilon) \int\limits_{x=0}^{N} \exp(-\theta)\, dx \quad .$$

<div align="center">Equation 12</div>

(Hint: replace A_s/a with $-n$ and take $\lim n \to \infty$.)

This is inserted into the Grand Canonical Partition Function (*13*) to yield:

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

<div align="center">Equation 13</div>

With the following definitions (with $E_a < 0$ by convention):

$$\frac{n}{n_m} =: \theta, \quad \chi_c =: -\ln\left(\frac{-\bar{E}_a}{RT}\right), \quad \chi =: -\ln\left[-\ln\left(\frac{P}{P_{vap}}\right)\right], \text{ and } \Delta\chi =: \chi - \chi_c$$

<div align="center">Equation 14</div>

This simple equation is the isotherm equation for a simple homogeneous, nonporous surface and may be used as a <u>universal</u> "standard" curve. (The wave functions are given in reference 6, which allows one to calculate the maximum error of this approach.)

A identical equation to **Equation (13)** except for the first definition of **Equation (14)** was derived by Churaev, Starke and Adolphs(*10*) from thermodynamics and fluid mechanics. The first definition of **Equation (14)** was assumed to be correct because of a minimum in excess surface work, or ESW, as a function of coverage. A rationalization, not a proof, is given in reference (*6*) on page 174. However, the quantum mechanical derivation does prove this assumption is correct.

Equation (13) yields the Fuller's(*14*)and Dubinin's(*15*) observation that:

$$\mathbf{q_{la}} = RT\,\mathbf{exp}(-\chi) \equiv -RT\,\mathbf{ln}(P/P_{vap})$$

Equation 15

In this equation $\mathbf{q_{la}}$ is the instantaneous heat of transfer from the liquid state to the adsorbed state. The second term in this expression is the Fuller expression and the last term is the Dubinin "thermodynamic criterion" which was not acceptable in the literature because of the implication that $\Delta \mathbf{S_{la}} = 0$, 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, which is $\theta_1 = 1 - \mathbf{exp(-\Delta\chi)}$. This latter exception is usually a small, possibly unobservable, correction.

Comparison to standard plots. A replacement? :

The following graphs of standard plot **data** (not extrapolation or smoothing) are fitted with the χ-plot. Ordinate units vary from publication to publication. They are left here in the original form. **Figure 2** contains data by Berg (*16*). The gas adsorbed is Kr and the solid is anatase. **Figure 3** is by Sing et. al. (*17*,*18*) and is the data for the α-s of N_2 and Ar on SiO_2. (See: www.genchem.net/standards.pdf for more examples.) In **Figure 4** are DOE standard curves for thoria with O_2, N_2 and H_2O are by Gammage, Fuller and Holmes (*19*), and in **Figure 5** are the standard NASA (*20*) curves for lunar soils obtained by Fuller (*21*) and is available in a US government report (*22*).
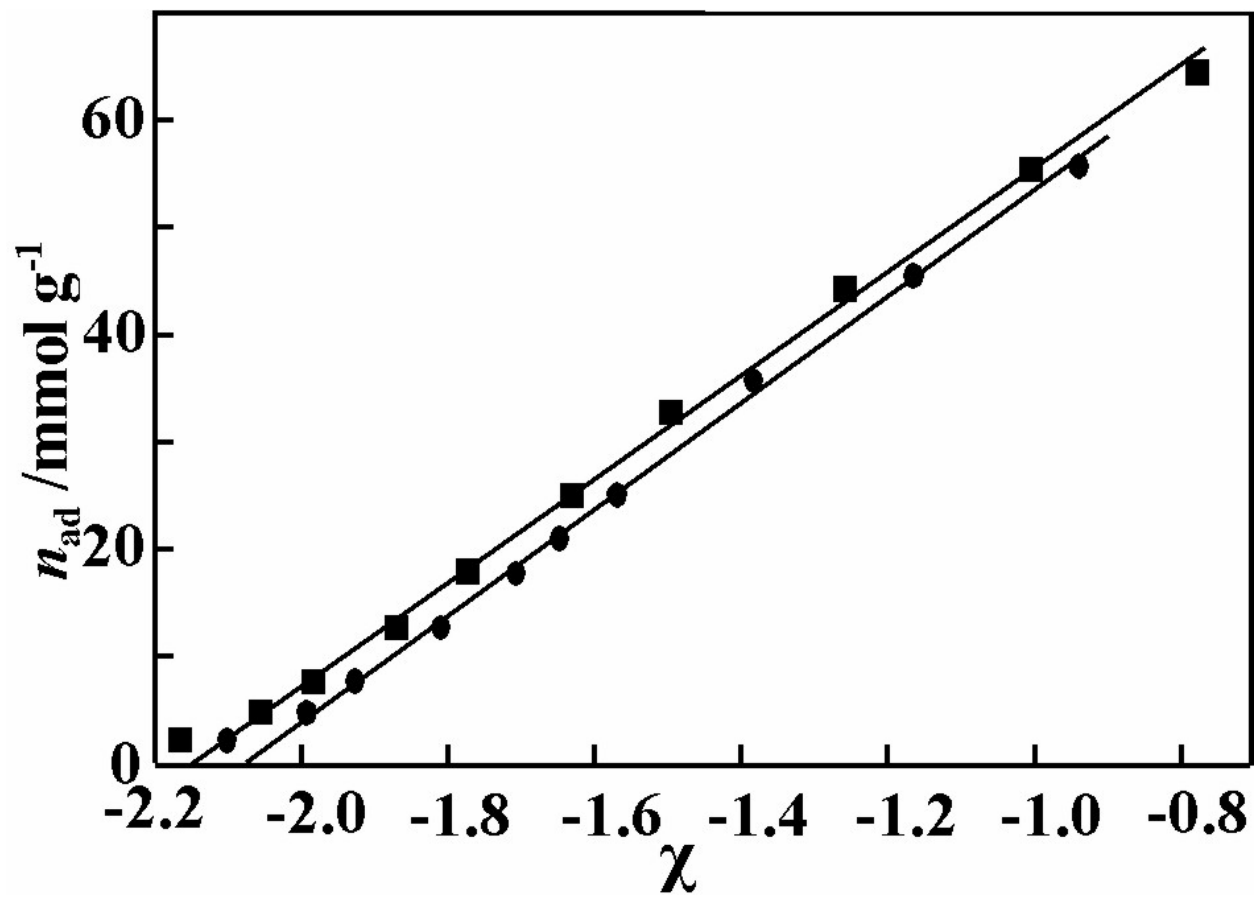
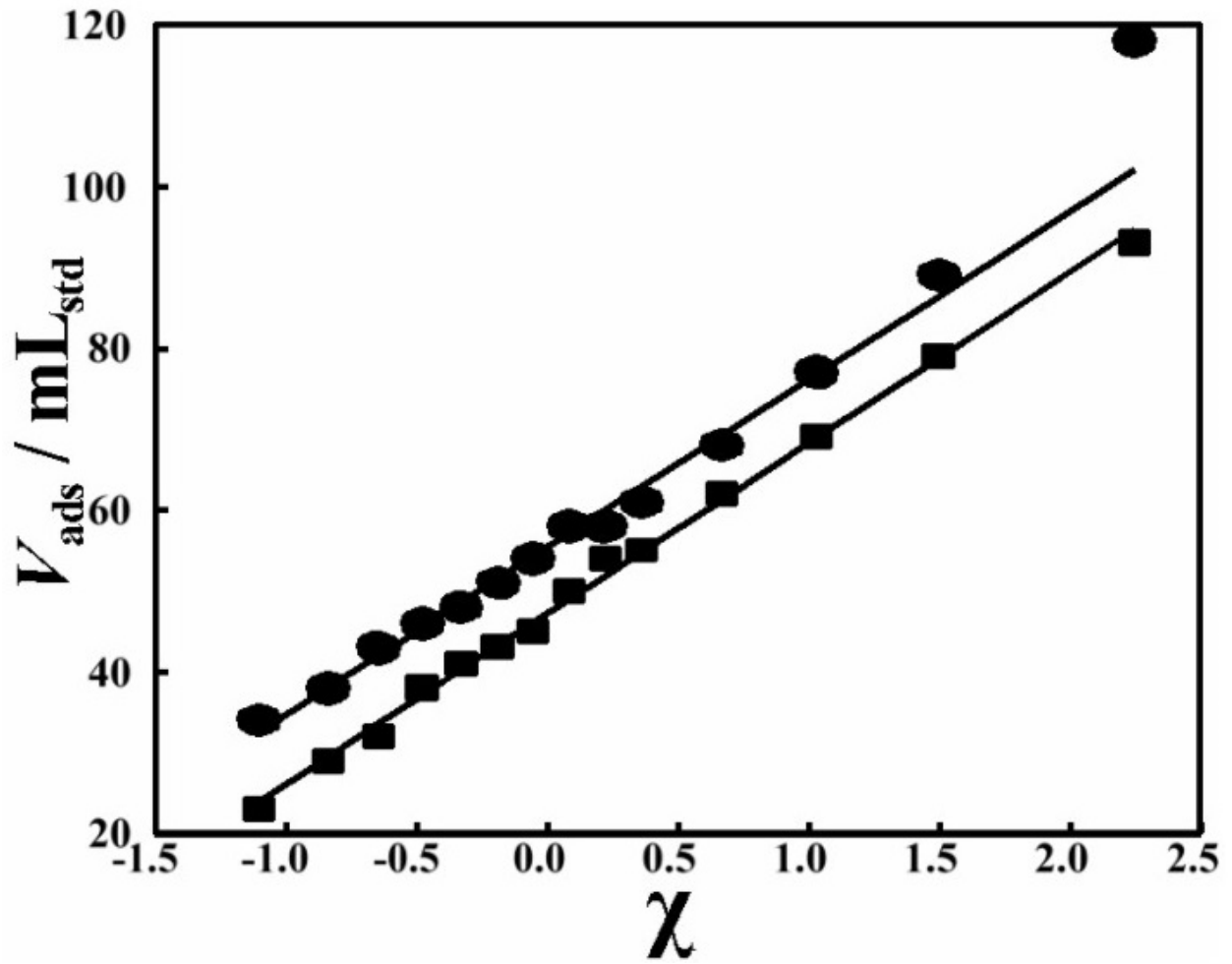*Figure 2* Data by Berg, Kr on anatase at 130 K and 140 K data by Berg(*16*) ‡

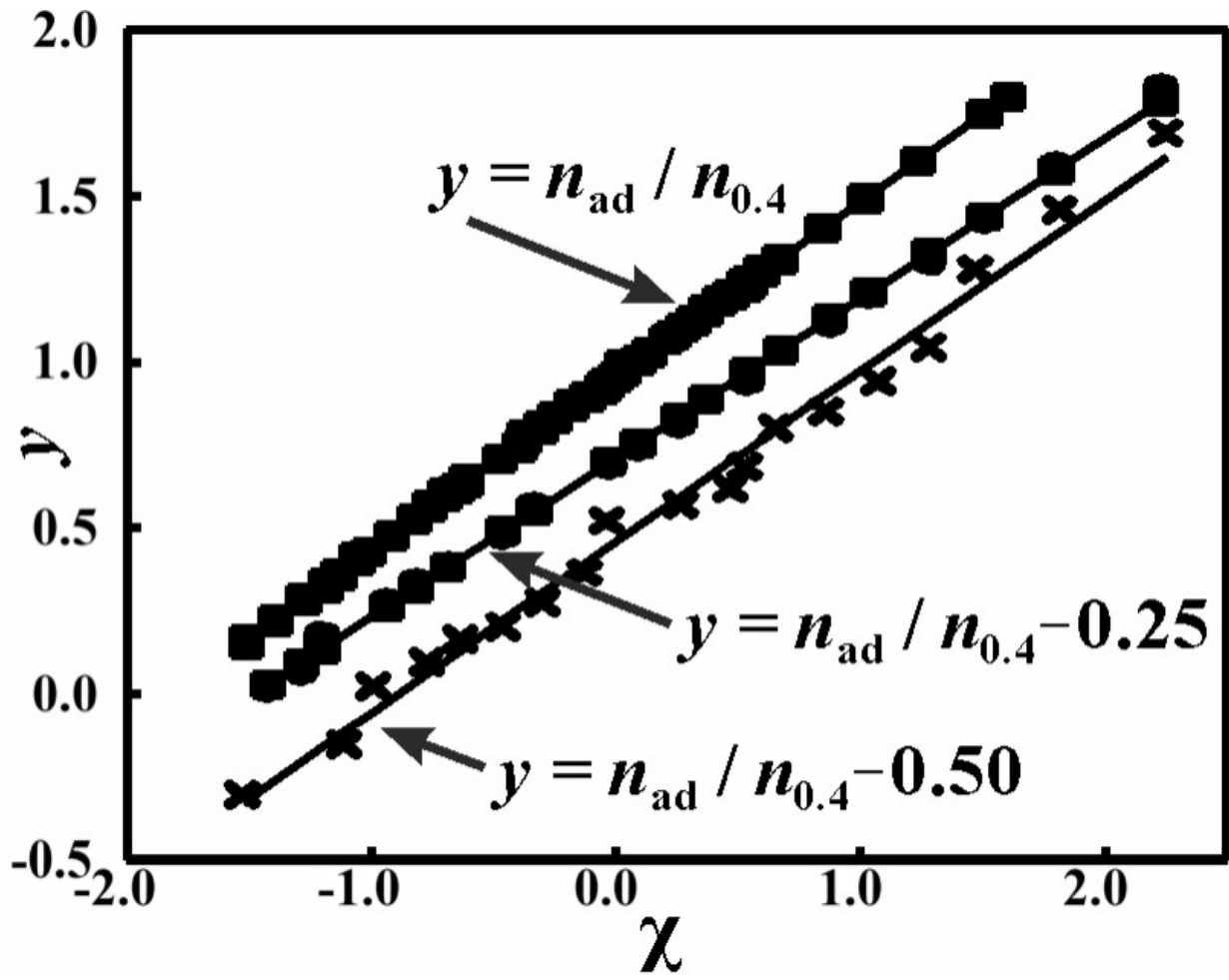*Figure 3* The α-s data on SiO_2. ■ = Ar, ● = N_2 by Sing, et. al. (*17,18*)[†]

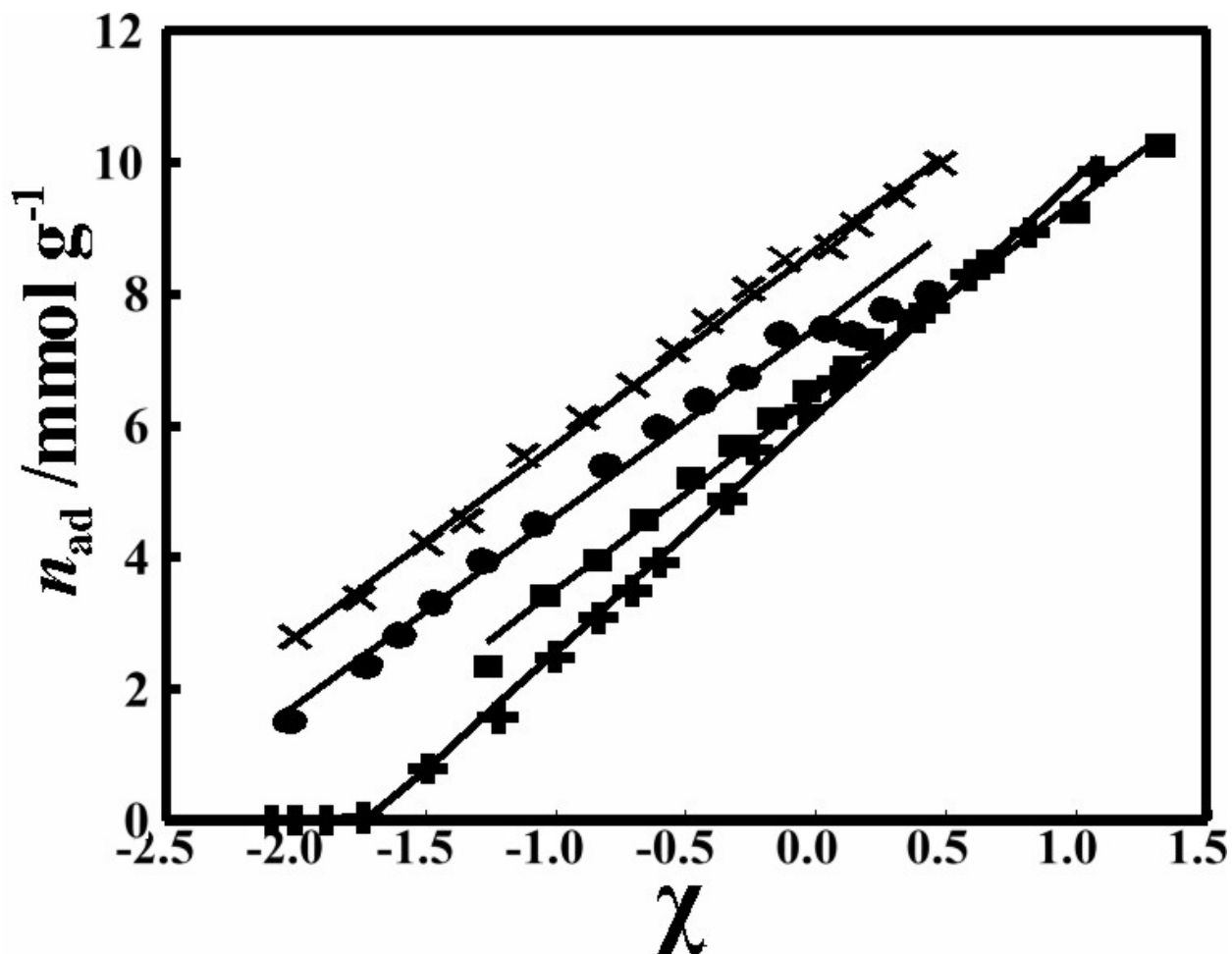*Figure 4* Thorium std. curves, ■ = Ar, ● = N_2, ✖ = H_2O Gammage, Fuller and Holmes(*19*) [†]

Figure 5 NASA std. curves for lunar soil ✖ = CO, ✚ = O$_2$, ■ = Ar, ● = N$_2$ from the Standard NASA curves (*20 -22*) [†]

Each of these curves yield the monolayer equivalent, $n_{m,}$, and the value for χ_c, corresponding to a phase transition pressure threshold, which in turn yields the value for E_a. These are tabulated in **Table 1**. (The uncertainty in Berg n_m is due to uncertainty in sample mass. The sample mass was stated about 10 g. From the data here, it was back-calculated and it seems the two samples have slightly different weights. The n_{ads} is for the total sample so the lines are not parallel.)

There are many standard curves available in the literature, since this has been required for each adsorbent-adsorbate (solid-gas) pair for comparison between isotherms. However, it is highly

<u>unlikely</u> that the non-porous and porous adsorbents are chemically identical, especially on the

surface.

Table 1 - χ theory analysis of parameters of some useful standard curves.					
adsorbent and adsorbate	n_m in original units	χ_c	E_a /kJ mol^{-1} *	R	Ref.
Anatase / Kr	~4.4 mmol g^{-1}	-2.173	9.32 (140 K)	0.997	*16*
Anatase / Kr	~4.3 mmol g^{-1}	-2.103	9.33 (130 K)	0.996	*16*
SiO$_2$ Ar (alpha-s)	21.0 std mL g^{-1}	-2.335	6.01	0.997	*17,18*
SiO$_2$ N$_2$ (alpha-s)	20.8 std mL g^{-1}	-2.666	9.33	0.993	*17,18*
ThO$_2$ Ar	2.81 /0.4 unit	-1.816	3.99	0.9997	*19*
ThO$_2$ N$_2$	2.60 /0.4 unit	-1.993	4.76	0.998	*19*
ThO$_2$ H$_2$O	2.45 /0.4 unit	-1.855	4.14	0.989	*19*
Lunar soil / Ar	2.98 mmol g^{-1}	-2.186	5.76	0.995	*20 - 22*
Lunar soil / CO	2.93 mmol g^{-1}	-2.951	12.4	0.997	*20 - 22*
Lunar soil / O$_2$	3.59 mmol g^{-1}	-1.718	3.61	0.997	*20 - 22*
Lunar soil / N$_2$	2.71 mmol g^{-1}	-2.688	9.53	0.984	*20 - 22*
* does not include ΔH_{vap} (ε) This must be added to compare to calorimetric measurements. Also for some data the correction for loss of one degree of translation ($\frac{1}{2}RT$) is significant.					

The data by Berg is particularly important since both the isotherm and the calorimetric data were

taken on the same samples simultaneous. The calculated heat of adsorption for the calorimetric

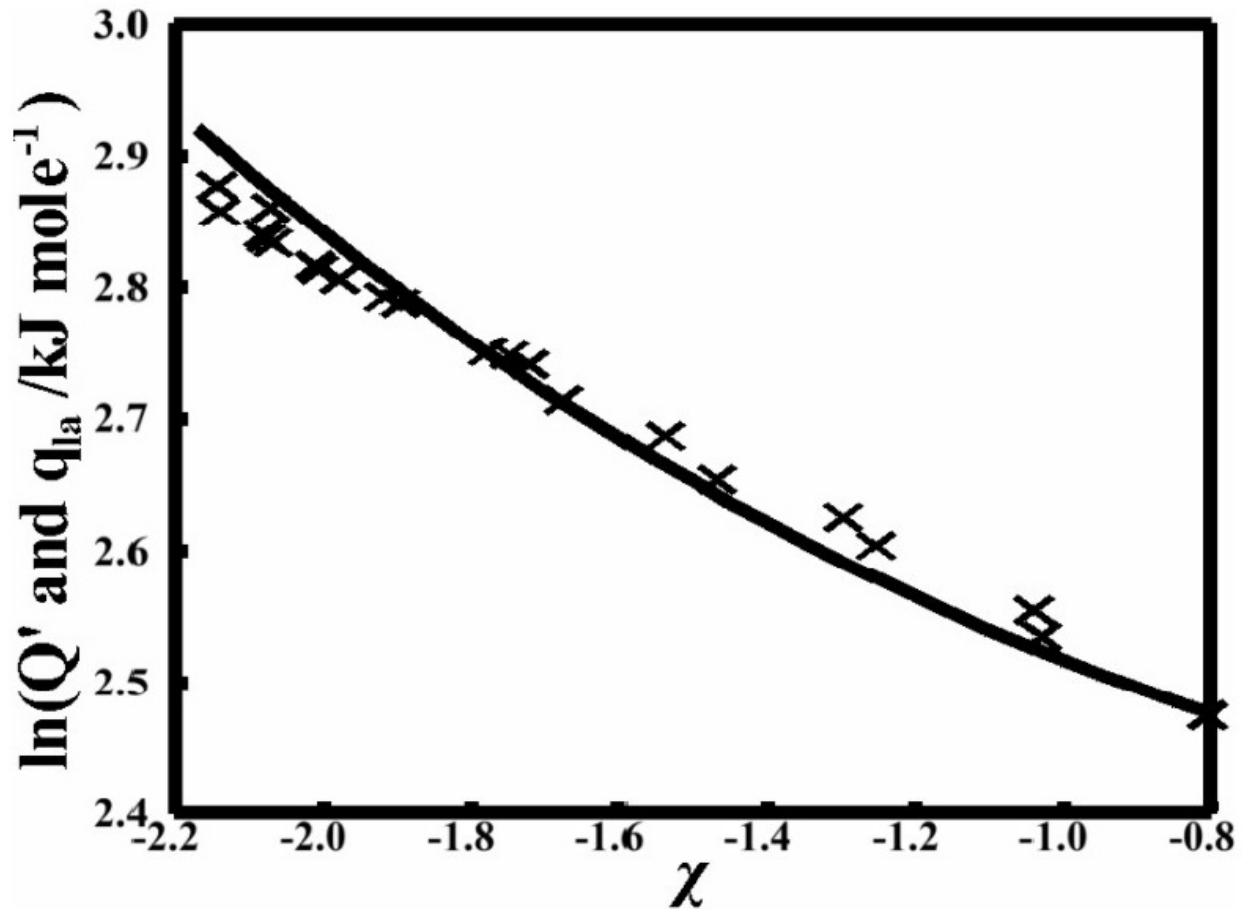data was made using only the isotherm data to yield an excellent fit.

Figure 6 Heat of adsorption comparing **Q'** from calorimetry with the calculation from the χ-plot. ● are experimental and curved line the calculation. Data by Berg(*16*)

This agreement of the calculated heats of adsorption to the data using only the output parameters of the isotherm is illustrated in **Figure 6.** This included the small correction for loss of one degree of freedom in the first "layer." There is a slight difference between the **Q'** (data), the piecewise integral heat, and the $\mathbf{q_{la}}$ (calculation,) the instantaneous heat of adsorption. Except for $n_{ads} \sim 0$ where this error is amplified, the agreement is very good.

These arguments seem to lend support for the χ/ESW hypothesis but the big question is, "What experimental data support the conclusion that the n_{ads} is an indication of the surface area?" This

question was pursued for the BET theory with little success. The BET seemed to yield a surface area 2 - 3 times that of actual area. This was often attributed to submicroscopic roughness, and such pursuits were generally discounted and the efforts abandoned. An example is the data by Hobson(*23*) of nitrogen adsorption on pyrex®. This data could be discounted after the introduction or the requirement of not using the BET below 0.05 P/P_{vap}. (This, of course, virtually eliminates any observation of a threshold pressure.)

In **Figure 7** is the UHV data by Hobson using a χ representation. The sample surface used was either a 30 cm^2 area or 60 cm^2 run. Both type of runs yielded data that when divided by the respective areas were the same.
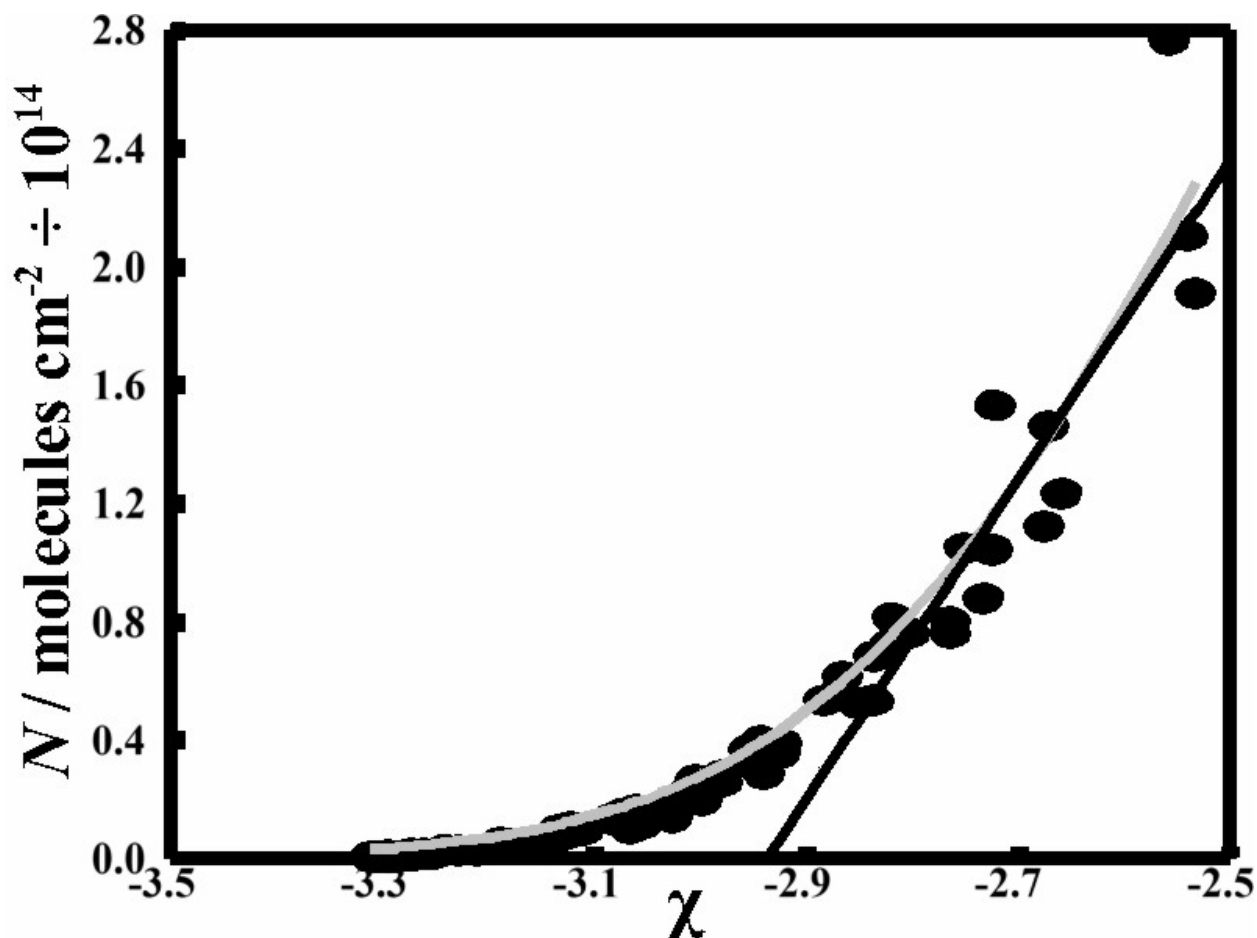
Figure 7 Data by Hobson on a χ plot ● data points, black line linear fit, grey line is a fit for a normal distribution in E_a. Data by Hobson (*22*)

This data, in units of molecules cm^{-2}, indicates that the surface was heterogeneous, that is, it has patches with slightly different E_as. Here a normal distribution of energies with respect to χ is used. To obtain n_m one can fit the curve when it becomes "linear" as is shown with the dark line fit, or use the equation for fitting with an energy distribution which is shown by the grey curved line.

The answer obtained for n_m (or rather N_m) from the straight line was 5.4×10^{14} cm^{-2} with a 2σ of 1.3×10^{14} cm^{-2}. The heterogeneous fit yielded $N_m = 6.0 \times 10^{14}$ cm^{-2}. Both of these numbers are close to the IUPAC standard value of 6.4×10^{14} cm^{-2} within the scatter of the data. The scatter would seem to make a conclusion difficult, but at least it is not 2 to 3 times too high as the BET would have predicted.

The next two topics "porosity measurements" and "binary adsorption" will be summarized. These are very long and detailed and there is more than one approach for each of them

Porosity Measurement using χ:

There are at least three ways to use χ hypothesis to determine porosity <u>without a separate standard curve</u>. Again, there is **<u>no guarantee</u>** that the porous material has the **same E_a** as the surface of the non-porous standard. This is a very large problem for the normal method of using standard curves. The assumption is that the adsorption energy of the porous material is the same as a "chemically identical" non-porous material. **This is extremely unlikely** and probably impossible. However, using the χ determination, the initial surface area and energy are mostly determined by the pores. Thus, the pore can be analyzed as one would using a standard or by some other equation derived from the original χ equation.

There have been attempts to do without a standard in Non-Local Density Functional Theory (NLDFT) (*24,25*). However, unstable oscillation for the low-pressure range (high vacuum)

where the n_m can be determined is the result. Determination of this n_m is critical for calculating

NLDFT. It is also critical for χ calculation, but for χ determination in this range is statistically

stable. (Why? - It allows for the phase transition or "threshold" P_c.)

If microporosity is indicated:

The **first method** is the most approximate. Often, the microporous isotherm in a χ plot starts

linear. Sometimes, it the has a negative curvature and quickly ends up linear. In either case, this

first linear portion is analyzed as a simple χ-plot yielding the entire surface area and E_a. Using a

plot with $\Delta\chi$ as the abscissa a final linear portion is likewise analyzed and the ordinate

intersection yields moles adsorbate needed to fill the pores. The intersection of the first line and

second line yields the $\Delta\chi_p$ (a $\Delta\Delta\chi$), an indication of the radius of the pores. Thus, for slit pores:

$d_p = 4\Delta\chi_p r$ where r is the radius of the adsorbate molecule. This method assumes no distribution

in either pore size or E_a.

The **second method** assumes that both the E_a and the pore radius have a distribution that is

normal in χ. According to the χ hypothesis a positive curvature at low pressures, $\Delta\chi < 2$, is an

indication of a distribution in E_a. A negative curvature in an intermediate range, $\Delta\chi \sim 2$ - 4, this

is indicative of microporosity. (A special case occurs if n_{ads} is linear with **ln**(P), which shows up

in the χ plot consistently as a negative curvature. This indicates that there is ultramicroporosity

which is restricted to a monolayer only.) Unfortunately the E_a distribution and the micropore

distribution can overlap. In this case one fits the isotherm to an arbitrary function of χ. Any good fitting and easily differentiable function may to be used. The first derivative yields the instantaneous n_m of the unsaturated surface and the second derivative yields the distributions E_a positive and n_p, moles in the pores, as negative. If these overlap, then further modeling is required. Assuming normal distributions the equation for this is:

$$n_{ads} = n_m \, \mathbf{Z}\left(\chi, \langle \chi_c \rangle, \sigma_c\right) - n_p \, \mathbf{Z}\left(\chi, \langle \chi_p \rangle, \sigma_2\right)$$

Equation 16

where:

$$\mathbf{Z}(x, y, s) = \frac{s}{\sqrt{2\pi}} \exp\left(\frac{-(x-y)^2}{2s^2}\right) + \frac{x-y}{2}\left(1 + \mathbf{erf}\left(\frac{x-y}{s\sqrt{2}}\right)\right)$$

Equation 17

Here σ_c is the standard deviation in E_a and σ_p the standard deviation in pore radius. These are not independent but follow the variance addition rule:

$$\sigma_2^2 = \sigma_c^2 + \sigma_p^2$$

Equation 18

The **third method** uses the χ hypothesis N "layer." ("Layer" is in quotes because in χ the 2nd, 3rd, etc. are being partly filled before the 1st "layer" is full. Indeed, at least in principal the 1st layer is never completely full.) Similar to the NLDFT, models are created assuming a certain number of "layers," fractional even, and a distribution for the "layers" based on a Lennard-Jones potential. In the ground state Lennard-Jones potential may be approximated as a harmonic oscillator. Using the Gausian-like distribution of the ground state, the amount adsorbed is the integral of these "layers" with their distributions catenated through the "layers." This series is truncated either with a step function for slits or and linear decay for cylindrical pores. Since the

N layer calculation has not been provided here, it makes no sense to present more about this method.

If ultramicroporousity is indicated:

According to the derived equations, if only one monolayer is physically able to adsorb, then the log-law, that is, n_{ad} versus the **ln**(P/P_{vap}), should be linear. This is the result when $N = 1$ maximum. From this plot one can obtain E_a and n_m for the pores. After the pores are filled one then obtains these parameters for the outer surface if it is significant enough.

A quick note about binary adsorption:

There a couple ways to handle binary adsorption. One is a complete reformulation of the Grand Canonical Partition function. Another is if the χ_c for one adsorbate is considerably less than the other, in which case the *N* layer formulation works well. This latter method is particularly applicable for screening adsorbent-adsorbate pairs for separation processes. In preparation, the isotherms for the pure adsorbates are measure and the binary calculations are bases on these isotherms. An example by Danner and Wenzl (*26*) (DW) is given in **Figure 9** and **Figure 10**. In **Figure 9,** a χ plot, the abscissa used is the χ value for the higher energy adsorbate. This is analogous to the "Heavy Henry's" constant used for the carrier flow systems. The points are the full 12 isotherm measurements.

From **Figure 8** the phase diagram in **Figure 9** can be constructed. In both figures, the solid lines used the mixed adsorbate χ plot whereas the dashed line used the <u>data from the single adsorbate</u>

isotherms only. **The advantage:** The calculation shown required 2 isotherms (and really only starting and ending points but one usually doesn't stop there) versus 12 that were performed.
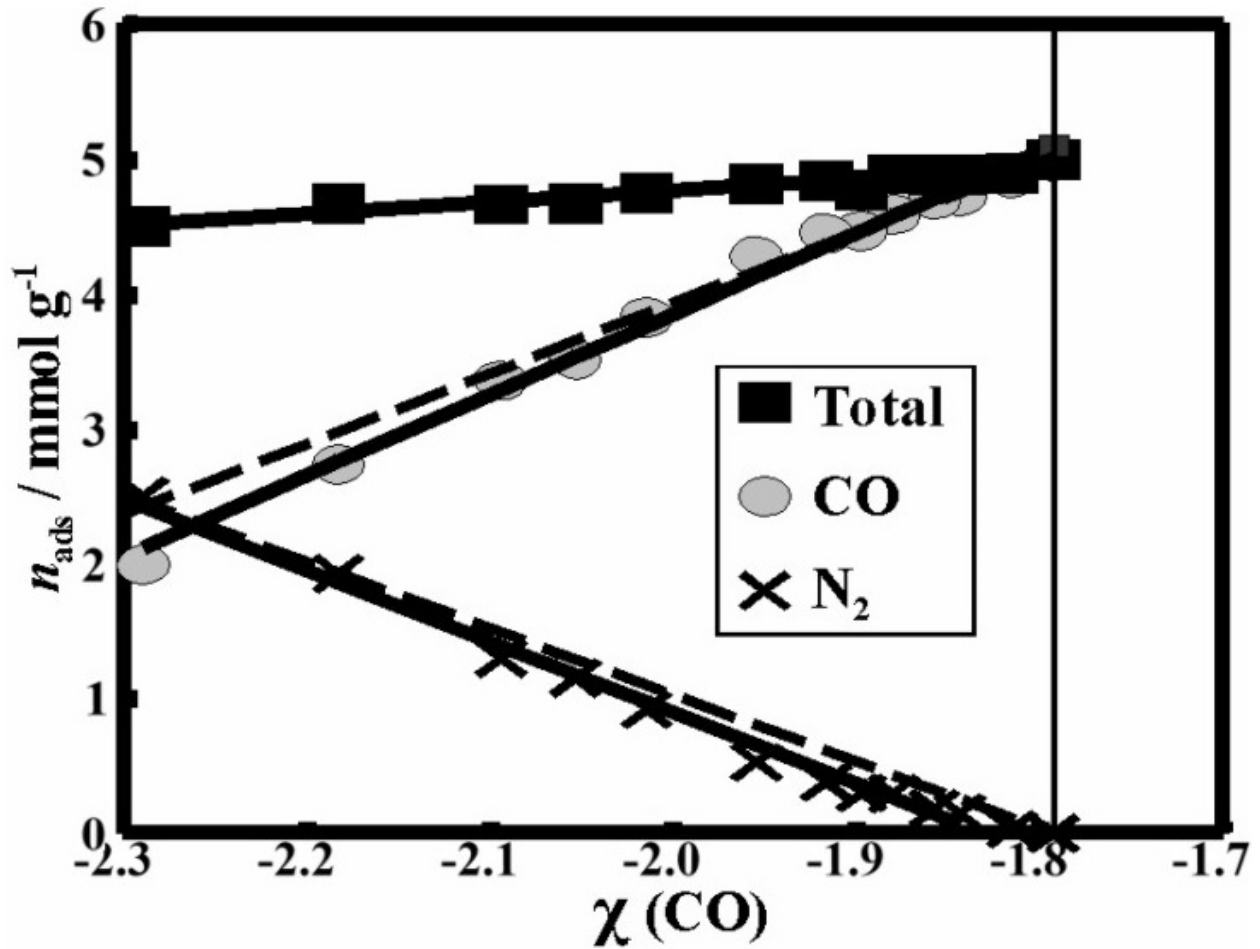

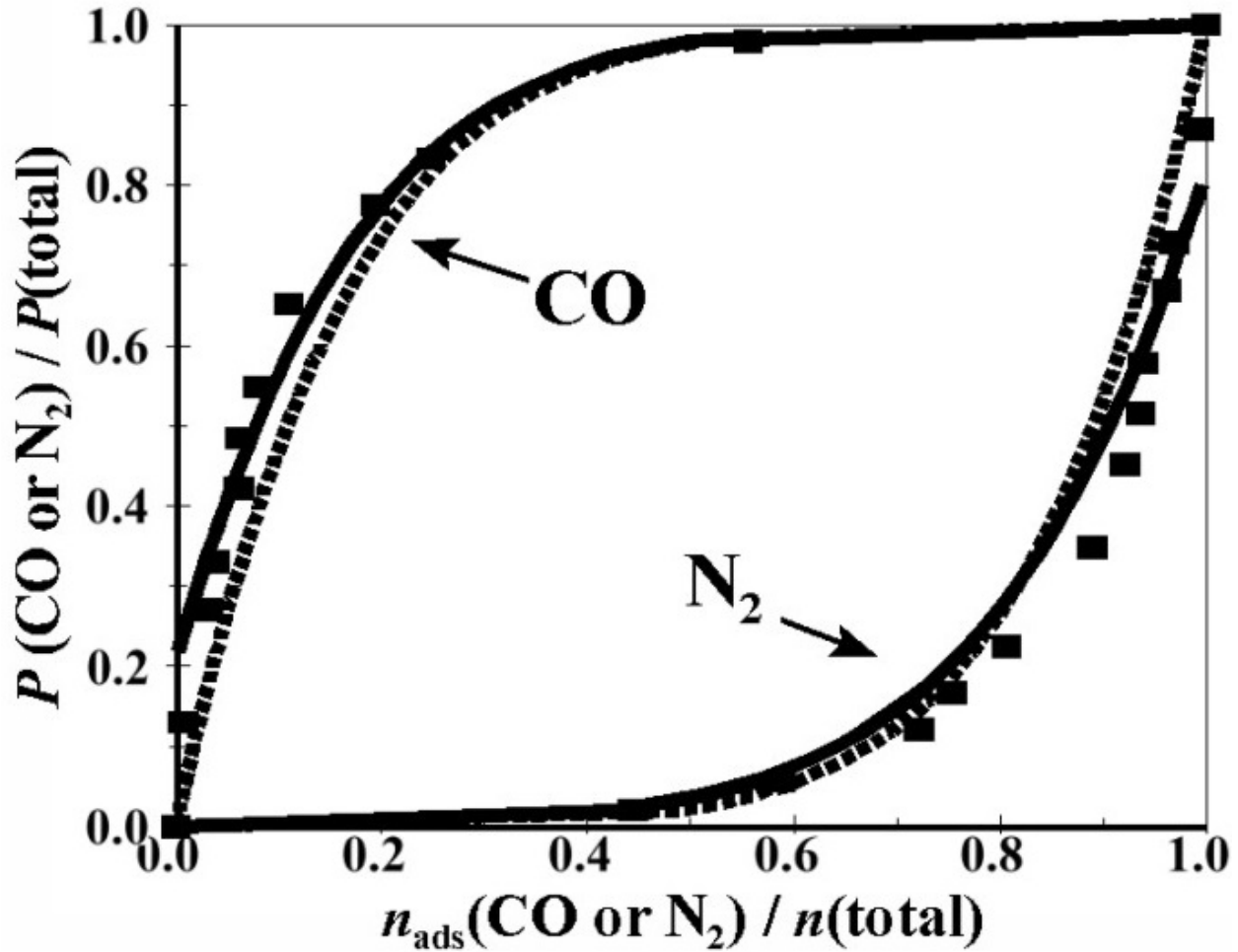*Figure 8* Adsorption of CO-N$_2$ mix on 5A zeolite at 1 atm. Data by Danner and Wenzel(*26*) [‡]

Figure 9 Phase diagram of N_2-CO in 5A zeolite. ■ = CO, ● = N_2. Data by Danner and Wenzel(*26*) [‡]

Statistical comparison to previous claims of describing the isotherm:

One of the questions that most investigators ask is does this description yield the surface area.

This has been attempted with the BET equation several times with little success but as Sing[4] has

pointed out there is the question as to what the meaning is of "surface area." Such a calculation

from the cross-sectional area of a molecule to surface area might indeed be meaningless.

The disagreement between BET surface area and other physical methods of measurements has usually been attributed to surface roughness, usually given as a factor of 2.5 to 3. Here, however, this question is avoided by simply saying that the important quantity is not surface area but rather n_m. This avoids performing two conversions and allows one to correlate cross-sectional areas of adsorbate molecules directly. This avoids many of the questions that Sing has brought forth.

So, if one were to wish to make a comparison between the calculation methods cannot be compare, as of today, between the answer for the "surface area." The way they can be compared is how good the statistical analysis works in fitting the isotherm. This is best done with the standards that have been characterized already. In **Table 2** is a comparison between the theories and χ that claim to yield the value for n_m. The comparison here is made for the standard curve data, not the fitted curve, for the data by Sing, et. al.(27) for silica (α-s), and data by Fuller, et. al.(15), for thoria.

Some explanation about is in order. Firstly, all the units for amount adsorbed were converted to mmol g^{-1}. This allows direct comparisons of the standard deviation of the different transformed data. In other words, the BETs and DRKs were transformed for the linear fit and the *x,y* answers were converted back to yield the mmol g^{-1} predicted from the theories. The χ did not have to be converted since for the data fit was directly to the amount adsorbed untransformed.

The pressure is assumed to not be a problem as a contributor of statistical scatter since it is easily measured to much greater degree of relative precision than the amount adsorbed. This is normally the case and is also according to the authors.

Table 2 Statistics comparing the BET, DP and χ formulations						
	Adsorption on silica (α-s)			Adsorption on thoria.		
N_2 adsorption:	χ	BET[*]	DRK[*]	χ	BET[*]	DRK[*]
Range:	full	.05→.35	0+→.35	full	.05→.36	0 + →.21
σ /mmol g^{-1} for all	0.061	4.5	1.8	0.0053	0.29	0.18
σ /mmol g^{-1} for range	(0.028)	2.3	1.0	(0.0028)	0.0038	0.0051
R^2 for all	0.993	0.971	0.627	0.9983	0.806	0.931
R^2 for defined range:	(0.995)	0.951	0.939	(0.995)	0.9981	0.984
	Adsorption on silica (α-s)[**]			Adsorption on thoria.		
Ar adsorption:	χ	BET[*]	DRK[*]	χ	BET[*]	DRK[*]
Range:	full	.05→.35	0+→.35	full	.05→.35	0+
σ /mmol g^{-1} for all	0.050	3.9	1.5	0.0024	0.45	0.046
σ /mmol g^{-1} for range	(0.045)	1.7	0.078	(0.0026)	0.0031	0.0021
R^2 for all data:	0.997	0.890	0.828	0.9994	0.885	0.908
R^2 for defined range:	(0.987)	0.994	0.962	(0.9980)	0.9979	0.9973
[*] For the fit for BET the x-axis is transformed. DRK both axes are transformed.						
Numbers in () in χ column are for the defined BET range for comparison.						
[**] There is an obvious disconnect at ~ 0.40 and the highest point fails the M-test thus deleted						
Units for adsorbate and therefore sigma are mmol g^{-1}						

In addition to the BET and χ fit, the Dubinin-Radushkevich-Kaganer(*28,29*) (DRK) is presented. This equation is, among the various forms in the literature:

$$\ln\left(\frac{n_{ad}}{n_m}\right) = A\ln^2\left(\frac{P_{vap}}{P}\right)$$

Figure 10

Its normal use is for porous material, but since this equation did a fairly good job of fitting the data on nonporous materials, Kaganer assumed that this formulation also yields the surface area. It is included here because of this claim, but there is not a very substantial theoretical bases for

this. Normally, however, it does fit the data quite well over a broader range than the BET. The above examples, which are standards, apparently do not yield this result.

The BET and DRK analyses for the fit were performed on the transformed data. It is from the transformed data that the R^2 was obtained. Since n_{ad} is transformed in both cases one could question the meaning for the R^2 numbers. R^2, however, is an indication of goodness of fit of the equation to the data and is unit-less.   The standard deviations (sigma) values are a better comparison. The is because it is a direct comparison between the experimental n_{ad} and the predicted values.

It is not surprising that both the BET and DRK perform over the restricted range of P/P_{vap} quite well, since that is the reason these restrictions were introduced. But even there, the σ value indicate superior χ fits, even within their best performing range. However, with respect to the BET, this must be one of the few places in science that, by routine, ignores 70% of the available data range.

Neither the BET nor the DRK model come close to the performance of the χ equations in fitting the data. This has been generally true for all of the standard curve data analyzed to date. See chapter 3 of reference (*6*). This is especially true for the entire isotherm, but is also usually true for the limited ranges.

In Conclusion:

The quantum mechanical interpretation seems to be the most powerful method of interpreting the phenomenon of physical adsorption. It is also the simplest and quickest to analyze. The mathematics is relatively easy and no tables of Kernels or curves are needed for analysis. The computations do not require a large computer or complicated programs. No other method to date is capable of accurately predicting the variety of observations, which, by the way, includes the **observed** phase transition, referred to as the "threshold" pressure. This phenomenon, observed multiple times by several investigators, is sufficient to disprove the BET and all other Henry law compatible formulations and calculation. For example, see herein O_2 in and other examples in reference (*6*).

What is now needed seems to be: 1) work on binary carrier gas flow systems, 2) more work on binary phase diagram, both experimental and theoretical, 3) reconciliation with NLDFT, 4) more attempts to observe the threshold pressure which requires UHV systems, 4) more testing and comparison studies and 5) revision of the IUPAC recommendations.

6) Finally, there is one more recommendation. Early in the investigations of physical adsorption, there were attempts to measure the surface area independent of the BET. These would then be compared to the BET answer. Hobson's attempts was one, but at least he published his data. Others published the BET results and comparison without data. Many attempts were not published at all and were considered failures. This included some attempts performed in the laboratory in which this author worked. It might be useful to attempt this again by using thin foils or well characterized microcrystals and compare the answers to the χ/ESW formulation.

References and Notes:

Notes regarding permitted use of material:

‡ These figures are reprinted from reference (*6*) with the permission of Elsevier Publishing.

† These figures were reworked from the information from the data given in reference (*6*).

All the data used in this report is also available from the literature. See, however, the comments in reference (*6*) about the uses of the oldest data where temperature control was not considered as well as today.

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