

## A Modern Physical Adsorption Theory Based upon Quantum Mechanics

...or it's time to get rid of the antiquated BET theory and other "Henry's Law" physical adsorption theories based proposals and use late 20<sup>th</sup> century theoretical chemistry.

### Introduction:

The BET theory has been used to measure the surface area of particles for around 80 years. It is a theory developed before the common use of quantum mechanics in the field of chemistry. The advantage the BET theory had was it yielded a value for the surface area. This was believed to be one of the primary objectives of the adsorption experiments. No other theory was believed to yield this value. (Although both the Harkins-Jura<sup>1</sup> method and deBoar-Zwicker<sup>2</sup> calculation might have done so with further theoretical development.)

It is now known that there are multiple problems with the BET method. Some problems were pointed out early by Halsey<sup>3</sup> and has continued to this day by many authors including Sing, et. al.<sup>4</sup> and new ones even by this author<sup>5</sup>. Among the problems are that it is **imprecise, inaccurate, contradictory, prone to anomaly**, incorrectly calculates the energy of adsorption and cannot properly measure porosity. It also has the strange tendency to yield an imaginary number for the energy. Unfortunately, it is still being used as the IUPAC<sup>6</sup> "gold standard" much to the detriment of scientific endeavors.

So what to about this situation? Today, there are at least two theories that can properly measure the "monolayer equivalent" adsorption,  $n_m$ , which is the most important parameter and adsorption energy,  $E_{ad}$ . These two proposals include 1) the quantum mechanical perturbation theory, called the  $\chi$  formation or hypothesis<sup>5</sup>, that requires no additional parameter except the extracted outputs  $n_m$  and adsorption energy and 2) the excess work theory<sup>7</sup> (ESW or DPT.) Both of these make very simple assumptions. The ESW theory is base only an thermodynamic and classical mechanics and introduces a single input arbitrary parameter assumption. The ESW can be derived from the  $\chi$  hypothesis, which gives credence to both and supports the assumption of the one parameter introduced in ESW.

### $\chi$ Assumptions:

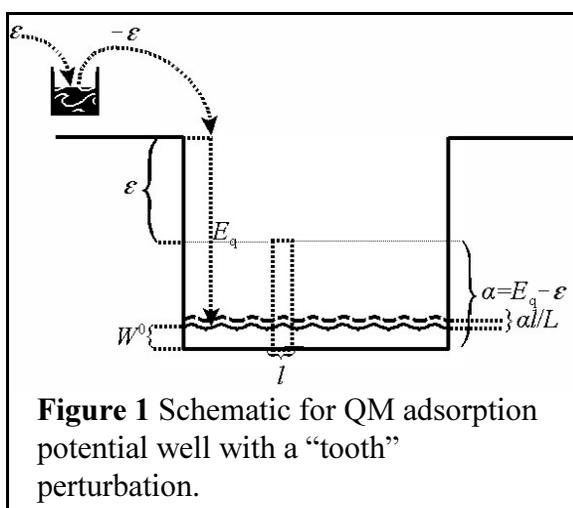
The  $\chi$  assumption is reasonable for any theoretical chemist. This assumption is that the wave function of the adsorbate particle is separable into two parts:

**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  $\chi$  equations are in excellent agreement with those obtained by calorimetry.

**Part 2** is the wave function normal to the surface ( $z$ ). From the "layer" amounts, one obtains an estimate of the amount that fills the pores from each "layer." For actual distance and precise amount, one needs to assume an intermolecular potential, such as a Lennard-Jones potential to get the distribution within 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 there are two output parameters,  $n_m$ , and  $E_{ad}$ . Part 2 is used to calculate the porosity output parameters.

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



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

In **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  $(E_q - \epsilon)$ , which will be designate by the letter " $\alpha$ ".

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 can be easily calculated in the unperturbed well from:

$$\hat{H}^0 \psi_n^0 = W_n^0 \psi_n^0 \Rightarrow \psi_n^0 = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \text{ and energy values of } W_n^0 = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad (1)$$

This molecule will now be assumed to be as illustrated in **Figure 1**. Typically  $l \lll L$  and  $\alpha < E_a$   $\therefore \alpha l \lll LE_a$  and this perturbation is extremely small, Thus, a simple first order perturbation may be used. Beyond this is the conventional perturbation calculation (See [www.genchem.net/QMchi.pdf](http://www.genchem.net/QMchi.pdf) (no link available) or the derivation in a book about the subject.) to yield the answer:

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

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

$$W_n = W_n^0 + \frac{\alpha l}{L} \left( 1 \pm \frac{1}{k\pi} \right) \cong W_n^0 + \frac{\alpha l}{L} \quad (3)$$

Notice that  $\alpha l$  is (with a 2D surface) an energy- $x,y$  volume and it does not matter what the shape of either  $\alpha$  or  $l$  is. It is only the energy- $x,y$  volume that matters. (The the adsorbed molecules that are also waves, and the wave probability matches the assumed classical molecular area-energy volume.) The term  $1/k\pi$  provides the maximum error that an individual molecule will encounter. This error is small but is also averaged out with large numbers of adsorbate molecules. Each molecule adsorbed experiences the same 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

$$W_{n,1} = \alpha \quad W_{n',2} = \alpha + \alpha \frac{l}{L} \equiv \alpha \left( 1 + \frac{l}{L} \right) \quad (4)$$

$$W_{n'',3} = \alpha \left( 1 + \frac{l}{L} \right) + \alpha \left( 1 + \frac{l}{L} \right) \frac{l}{L} \equiv \alpha \left( 1 + \frac{l}{L} \right)^2 \dots \quad (5)$$

$$W_{n^N,N} = \alpha \left( 1 + \frac{l}{L} \right)^N \quad (6)$$

or in 3D:

$$W_{n^N,N} = \alpha \left( 1 + \frac{a}{A_s} \right)^N \quad (7)$$

$$\therefore \Rightarrow E_n = (E_a - \varepsilon) \sum \left( 1 - \frac{a}{A_s} \right)^N \quad (8)$$

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

$$E_n = (E_a - \varepsilon) \sum_N \left( 1 - \frac{a}{A_s} \right)^{\theta A_s/a} \quad (9)$$

Since  $A_s/a$  is very large then:

$$E_n \approx (E_a - \varepsilon) \int_{x=0}^N \exp(-\theta) dx \quad (10)$$

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

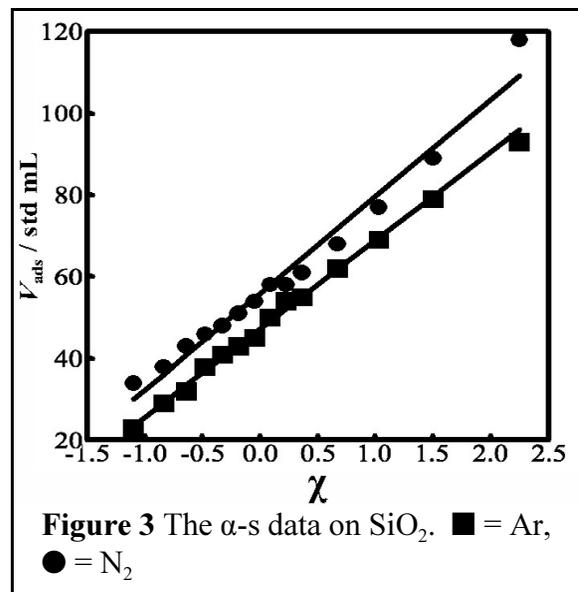
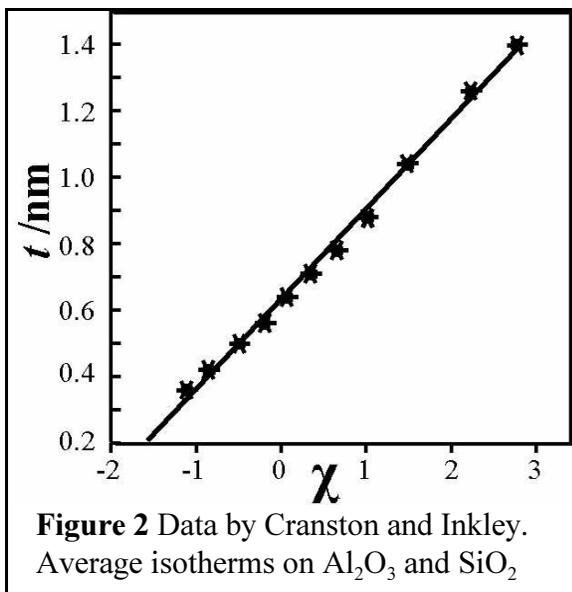
This is inserted into the Grand Canonical Partition function to yield:

$$\theta = \Delta\chi \mathbf{U}(\Delta\chi) \quad (11)$$

With the following definitions:

$$\frac{n}{n_m} =: \theta, \quad \chi_c =: -\ln\left(-\frac{|\bar{E}_a|}{RT}\right), \quad \chi =: -\ln\left[-\ln\left(\frac{P}{P_s}\right)\right], \text{ and } \Delta\chi =: \chi - \chi_c \quad (12)$$

This simple equation is the isotherm equation for a simple homogeneous, nonporous surface and may be used as a universal “standard” curve. (The wave functions are given in ref. 5, which allows one to calculate the maximum error of this approach.)



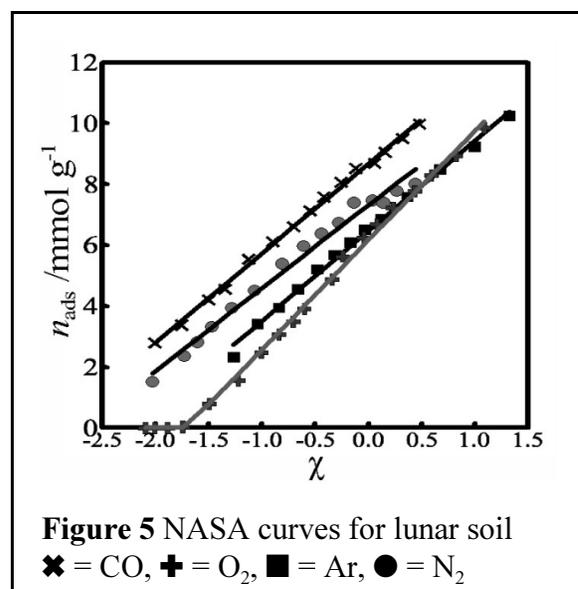
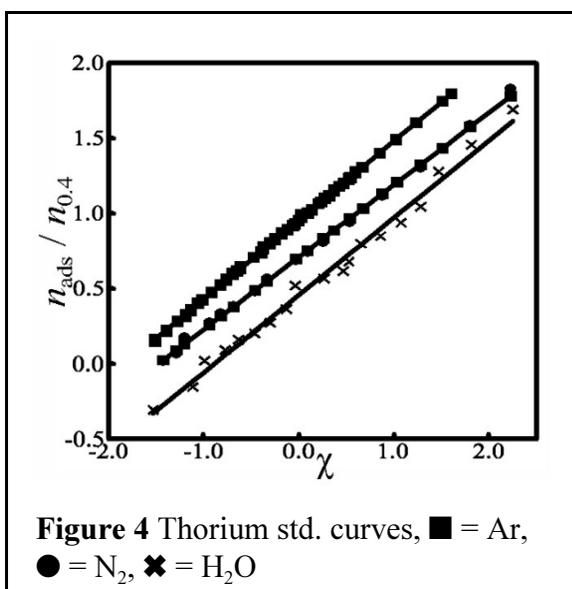
### Use in place of standard plots:

The following graphs of standard plot **data** (not extrapolation or smoothing) is fitted with the  $\chi$ -plot. Ordinate units vary from publication to publication. They are left here in the original form. **Figure 2** is by Cranston and Inkley<sup>8</sup> data; the adsorbent is averages of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> and the adsorbate is N<sub>2</sub>. **Figure 3** is by Sing et. al.<sup>9,10</sup> and is the data for the  $\alpha$ -s of N<sub>2</sub> and Ar on SiO<sub>2</sub>. (See: [www.genchem.net/standards.pdf](http://www.genchem.net/standards.pdf) for more examples.) In **Figure 4** are DOE standard curves for thoria with O<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O are by Gammage, Fuller and Holmes<sup>11</sup>, and in **Figure 5** are

**Table 1 -  $\chi$  theory analysis of parameters of some useful standard curves.**

adsorbent and adsorbate	$n_m$ in original units	$\chi_c$	$E_a$ /kJ mol <sup>-1</sup>	$R$	Ref.
Avg Ar and N <sub>2</sub>	2.7 nm thick	-1.6	3.2		5
SiO <sub>2</sub> Ar (alpha-s)	21.0 std mL g <sup>-1</sup>	-2.335	6.01	0.997	6, 7
SiO <sub>2</sub> N <sub>2</sub> (alpha-s)	20.8 std mL g <sup>-1</sup>	-2.666	9.33	0.993	6, 7
ThO <sub>2</sub> Ar	2.81 /0.4 unit	-1.816	3.99	0.9997	8
ThO <sub>2</sub> N <sub>2</sub>	2.60 /0.4 unit	-1.993	4.76	0.998	8
ThO <sub>2</sub> H <sub>2</sub> O	2.45 /0.4 unit	-1.855	4.14	0.989	8
Lunar soil / Ar	2.98 mmol g <sup>-1</sup>	-2.186	5.76	0.995	9, 10, 11
Lunar soil / CO	2.93 mmol g <sup>-1</sup>	-2.951	12.4	0.997	9, 10, 11

the standard NASA<sup>12</sup> curves for lunar soils was obtained by Fuller<sup>13</sup> and is available in a US government report<sup>14</sup>. Each of these curves yield the monolayer equivalent,  $n_m$ , or something similar, and the value for  $\chi_c$  which in turn yields the value for  $E_a$ . These are tabulated in **Table 1**. There are many standard curves available in the literature. This has been required for each adsorbent-adsorbate pair for comparison between isotherms. However, it is highly unlikely that the non-porous and porous adsorbent are chemically identical. 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 with using $\chi$ :

There are at least three ways to use  $\chi$  hypothesis to determine porosity without a separate standard curve. Again, there is **no guarantee** that the porous material has the **same  $E_a$  or  $n_m$**  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.

There have been attempts to do without a standard in NLDFT. 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  $\chi$  calculation, but statistically it is stable in this range. (Why? - It allows for the phase transition or “threshold”  $P_c$ .)

### If microporosity is indicated:

The **first method** is the most approximate. Generally, the microporous isotherm in a  $\chi$  plot starts linear. Soon it has a negative curvature and ends up linear. The first linear portion is analyzed as a simple  $\chi$ -plot yielding the entire surface area and  $E_a$ . Using a plot with  $\Delta\chi$  as the abscissa the 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  $\chi$ . According to the  $\chi$  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  $\chi$  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  $\chi$  (a good fitting and easily differentiable function needs 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. The equation for this is:

$$n_{ads} = n_m \mathbf{Z}(\chi, \langle \chi_c \rangle, \sigma_c) - n_p \mathbf{Z}(\chi, \langle \chi_p \rangle, \sigma_p) \quad (13)$$

where:

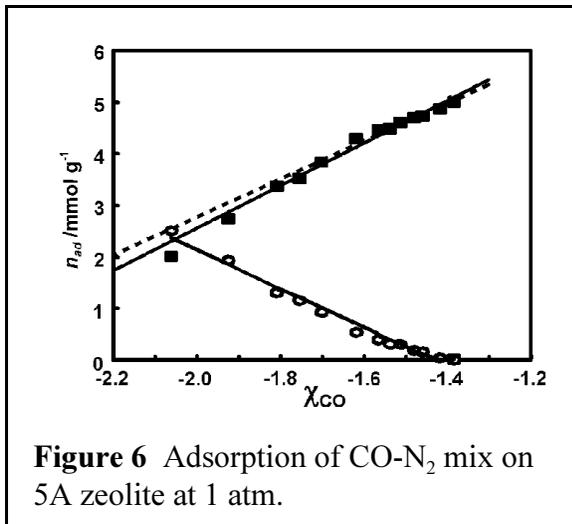
$$\mathbf{Z}(x, y, s) = \frac{s}{\sqrt{2\pi}} \exp\left(-\frac{(x-y)^2}{2s^2}\right) + \frac{x-y}{2} \left(1 + \mathbf{erf}\left(\frac{x-y}{s\sqrt{2}}\right)\right) \quad (14)$$

Here  $\sigma_c$  is the standard deviation in  $E_a$  and  $\sigma_p$  the standard deviation in pore radius. These are not independent but follow the variance addition rule:  $\sigma_2^2 = \sigma_c^2 + \sigma_p^2$ .

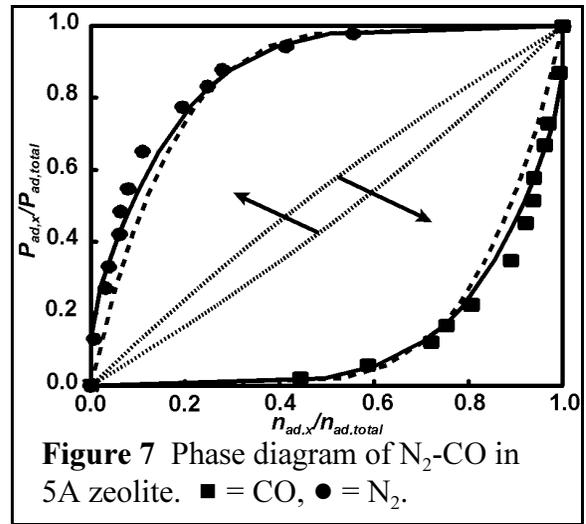
The **third method** uses the  $\chi$  hypothesis  $N$  layer. Similar to the NLDFT models are created assuming a certain number of layers, fractional even, and a distribution for the layers based on a Lennard-Jones potential. In the ground state this distribution can be approximated as a harmonic oscillator. The amount adsorbed is the integral of these “layers” with their distributions catenated through the layers and truncated either with a step function for slits or and linear decay for pores. Since the  $N$  layer calculation has not been provided here, it makes no sense to present more about this method.

### 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  $\chi_c$  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 is given in **Figure 6** and **Figure 7**. In **Figure 6** a  $\chi$  plot the abscissa used is the  $\chi$  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.



**Figure 6** Adsorption of CO-N<sub>2</sub> mix on 5A zeolite at 1 atm.



**Figure 7** Phase diagram of N<sub>2</sub>-CO in 5A zeolite. ■ = CO, ● = N<sub>2</sub>.

From **Figure 6** the phase diagram in **Figure 7** can be constructed. In both figures, the solid lines used the mixed adsorbate  $\chi$  plot whereas the dashed line used the data from the single adsorbate 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.

### Statistical comparison to previous claim 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<sup>4</sup> 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 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 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 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  $\chi$  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.<sup>15</sup> for silica ( $\alpha$ -s), and data by Fuller<sup>16</sup>, et. al., for thoria.

<b>Table 2</b> Statistics comparing the BET, DP and $\chi$ formulations						
	Adsorption on silica ( $\alpha$ -s)			Adsorption on thoria.		
N <sub>2</sub> adsorption:	$\chi$	BET <sup>1</sup>	DRK <sup>1</sup>	$\chi$	BET <sup>1</sup>	DRK <sup>1</sup>
range:	full	.05→.35	.05→.60	full	.05→.36	.02→.08
sigma on data -full:	0.16	1.05	1.12	0.0053	2.09	0.163
sigma on data -range:	0.023	0.0032	0.057	0.0056	0.028	0.153
R <sup>2</sup> full <sup>1</sup> :	0.9969	0.757	0.894	0.9983	0.9987	0.50
R <sup>2</sup> selected range <sup>3</sup> :	0.9969	0.994	0.932	0.9983	0.9980	0.85
Ar ad:						
range:	full	.05→.35	.05→.60	full	.05→.35	.05→.60
sigma on data -full:	0.050	0.29	0.63	0.0024	0.82	0.192
sigma on data -range:	0.045	0.0063	0.065	0.0026	0.027	0.103
R <sup>2</sup> full <sup>1</sup> :	0.9952	0.810	0.842	0.9994	0.998	0.38
R <sup>2</sup> selected range <sup>2</sup>	0.9952	0.994	0.958	0.9994	0.885	0.967
<sup>1</sup> fit for BET the x-axis is transformed. DRK both axes are transformed						
<sup>2</sup> Full range is complete data set 0.05→0.90+.						
<sup>3</sup> Selected ranges: BET = 0.5 - 0.35, DK = "linear portion", $\chi$ = BET range						

In this table are the analyses using, in addition to the BET and  $\chi$  fit, the Dubinin-Radushkevich-Kaganer<sup>17</sup>. This equation is:

$$\ln\left(\frac{V}{V_0}\right) = A \ln^2\left(\frac{P_{\text{vap}}}{P}\right) \quad (16)$$

It has been assumed that this formulation for flat surfaces yields the surface area, but there is not a very substantial theoretical bases for this. It does, however, usually fit the data quite well over a broader range than the BET.

Neither the BET nor the DRK model come close to the performance of the  $\chi$  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 5.) This is especially true for the entire isotherm, but is usually true for the limited ranges.

### 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. No other method 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 observation is sufficient to disprove the BET and all other Henry law compatible formulations. For example, see herein O<sub>2</sub> in **Figure 5** and other examples in reference 5.

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 finally 5) revision of the IUPAC recommendations.

### References:

1. W. D. Harkins and G. J. Jura, J. Am. Chem. Soc., 66 (1944) 919.
2. J. H. deBoer, C. Zwikker, Z. Phys. Chem., B3 (1929) 407.
3. G. Halsey, J. Chem. Phys. 16 (1948) 931.
4. Rouquerol, F., Rouquerol, J., Sing, K. S. W., Llewellyn, P., and Maurin, G., *Adsorption by Powders and Porous Solids, Principles, Methodology and Applications, 2 edition*, Elsevier/Academic Press, Oxford, UK, (2014) ISBN 9788-0-08-097035-6
5. J. B. Condon, *Surface Area and Porosity Determinations by Physisorption - Measurement, Classical Theoris and Quantum Theory, 2<sup>nd</sup> Edition*, Elsevier, Amsterdam, Netherlands and Oxford, UK (2019) ISBN 978-0-12-818-2.
6. IUPAC Technical Report, Pure Appl. Chem. 2015; 87(9-10): 1051–1069.
7. N.V. Churaev, G. Starke, J. Adolphs, J. Colloid Interface Sci. 221 (2000) 246.
8. R. W. Cranston, F.A. Inkley, Adv. Catal. 9 (1957) 143.
9. M. R. Bhambhani, P. A. Cutting, K. S. W. Sing and D. H. Turk, J. Coll. Interface Sci., **38**, 109 (1972).
10. D. H. Everett, G. D. Parfitt, K. S. W. Sing, R. Wilson, J. Appl. Biochem. Technol. 24 (1974) 199.
11. R. B. Gammage, E. L. Fuller, Jr., H. F. Holmes, J. Colloid Interface Sci. 34 (1970) 428.
12. R. B. Gammage, H. F. Holmes, E. L. Fuller, Jr., D. R. Glasson, J. Colloid Interface Sci. 47 (1974) 350
13. E. L. Fuller, Jr., J. Colloid Interface Sci. 55 (1976) 358.
14. E. L. Fuller, Jr., P. A. Agron, “The reactions of Atmospheric vapors with Lunar Soil” U. S. Government Report ORNL-5129 (UC-34b) March 1976.
15. D. A. Payne, K. S. W. Sing, D. H. Turk, J. Colloid Interface Sci. 43 (1973) 287.
16. R. B. Gammage, E. L. Fuller, Jr., H. F. Holmes, J. Colloid Interface Sci. **34** (1970) 428.
17. M. G. Kaganer, Zhur. Fiz. Khim. 33(1959) 2202.