**2.2)**

**2.2) The Langmuir and BET theories**

One could define a class of theories for physical adsorption as “Henry’s Law” theories. That is, they predict the following:

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| Equation 1 The statement of “Henry's Law” |

The symbolism here is:

*P =* the adsorptive pressure

*n*ads = moles of adsorbate

*n*m = the maximum moles of adsorbate that can be in direct contact with the adsorbent surface

The symbol *θ* is often used for the ratio *n*ads/*n*m and is called the “coverage."

Thus, the “Henry’s Law” isotherm, theoretically, pass thru (*n*ads, *P*) = (0,0). This class of theoretical isotherms is large, but the most well are described by the BET and Langmuir theories. Looking at the BET:

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| *Equation 2 the BET equation* |

Where:

*C* = The “BET *C”* constant which is arbitrary for each isotherm. It is interpreted as equilibrium constant. Notice that if *P* = 0 then *n*ads = 0 because the denominator on the right side is finite. (Theoretically, *C* > 0 or the associated energy is an imaginary number or undefined.)

The Langmuir theory equation is the BET equation without the term (1 - *X + CX*).

In principle, to be a “Henry’s Law” isotherm, *X* and *θ* need to be raised to the same power. There are other theories[[1]](#footnote-1) where the powers differ. An example is Freundlich isotherm equation. However, these isotherm equations also predict that (*n*ads,*P*) = (0,0).

Above it was stated that there are ways to prove a hypothesis invalid:

* That the hypothesis predicts something that by observation is incorrect. A single observation of the contradiction is logically enough for a disproof, but except for mathematics, is not convincing for those in the discipline.
* That the hypothesis does not do as good a job fitting the data as another, simpler (Ockham’s razor) and more reliable hypothesis.

The second one is usually arrived at with statistics, but it should be overwhelming and convincing statistics and should not be a more complex hypothesis in terms of exceptions and required parameters.

**Observational Disproof of “Henry’s Law” for physical adsorption.**

The first thing to realize is that analogy is not a logical argument. It might be a good learning tool but it should not be used to prove. Thus, it is important to realize that Henry’s law does not apply to physical adsorption, it is formulated for solution chemistry with a companion law – Raoult's law. For a single adsorbate, considerations for Raoult’s law in physisorption is impossible[[2]](#endnote-1).

To disprove this concept a few examples will be presented and reference to others given. The first example is a very important publication for reasons other than “Henry’s law” disproof.

*Example 1)* *Data by Silvestre-Alberto, Silvestre-Alberto, Llewellyn and Rodríguez-Reinoso:*

The data of N2 adsorbed on porous carbon by Silvestre-Albero, Silvestre-Albero, Llewellyn, and Rodríguez-Reinoso[[3]](#endnote-2) (AALR) evidences the threshold pressure at 2 x 10-7 bar. The adsorbent was microporous activate carbon (LMA233.) In *Figure 1* is a graph of data obtain for the referred to AALR paper.

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| Figure 1 Data by AALR on microporous carbon illustrating 1) effect of dead space gas and 2) clearly shows the threshold pressure. This uses the log-law, one of the important law associated with the modern hypotheses.  |

They also observed a threshold pressure for the adsorption of N2 adsorbed on ordered mesoporous silica SBA-15 at ~2 x 10-6 bar and on activated carbon DD52 at ~6.5 x 10-6 bar.

Although the purpose of this paper was to warn researcher how to handle “dead space” gas out-gassing, as a side issue it clearly shows the threshold pressure in the high vacuum range.

The graph by AALR shows the isotherm as a log-law. This law is predicted from the modern hypothesis model for adsorption that is physically restricted to one monolayer. (See derivations below.) Notice that the data points are not ending at (*n*ads,X) = (0,0), but end at (0,~2×10-7).

Example 2) The Nguyen and Du Data.

The threshold pressure can be seen from the data by Nguyen and Do[[4]](#endnote-3), of argon adsorbed on microporous carbon. This is shown in *Figure 2* or directly in their figure four.

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| Figure 2 Date by Nguyen and Do of nitrogen adsorbed on microporous carbon. The grey line in the log-law fit (1st layer) the black line in the Δχ plot is the external area line. The vertical line in the log-law plot is approximately where the external line fit |

The grey line in the log-law fit (1st layer) the black line in the Δχ plot is the external area line. The vertical line in the log-law plot is approximately where the external line fit

From the data one can obtain the total monolayer coverage for the pores and external area, *n*m, the volume of the pores, *n*pore, the parameter *E*a, the energy of the first adsorbate molecule (from χς a threshold parameter,) and the external monolayer equivalence, *n*m,ext:

*n*m = 8.25 ± 0.019 (0.24 % full range) mmol g-1

χς = -2.7118 → *E*a = -9.76 kJ mol-1

*n*pore = 6.91 ± .028 (0.34 % full range) mmol g-1

*n*m,ext = 0.26 ± .0077 (0.094 % full range) mmol g-1

By the self-imposed of criteria of σ < 1 % full range used for QM fits, these values of 0.24 % are relatively precise. All these values were obtained using the modern hypotheses.

Although some additional information can be extracted from these plots, the important points is that they obviously intersect the abscissa making *n* > 0 at some low but finite pressure. This is the concept of “threshold pressure” and is given the symbol *P*ς. This concept is critical for the modern hypotheses and critical in disproving all the “Henry’s Law” isotherms, which is why it has been so controversial and an excuse to reject these hypotheses.

There is more to be said about this and additional disproofs after the derivations of the hypotheses.

**Conclusion:**

In the above it should be clear that a localized isotherm theory, of which there are many, must follow “Henry’s law.” They all depend upon a site-adsorbate “complex” which leads to a multiplicative expression at low pressures. If any isotherm demonstrates that the condition started above, that is *P* → 0 if and only if θ →0, is not true, then this disproves all “Henry’s” law type physisorption isotherms. They are proven indisputably false without major revisions.

1. The word “theory” is used much to loosely in the adsorption language. For most the word “law” would be more appropriate and for generalized proposals the word “hypothesis” is more appropriate. We will stick to “hypothesis” since we are talking in generalities. [↑](#footnote-ref-1)
2. Why is this being stated. It is because reviewers and other researchers unfortunately get deceived by the language. To emphasize the point ”Henry’s Law” will continue to be placed in quotes. [↑](#endnote-ref-1)
3. J. Silvestre-Albero, A. M. Silvestre-Albero, Philip L. Llewellyn, and Francisco Rodríguez-Reinoso, J. Phys. Chem., C (2013,) **117**, 16885−16889 [↑](#endnote-ref-2)
4. C. Nguyen and D. D. Do, Carbon **39** (2001) 1327–1336 [↑](#endnote-ref-3)