Abstract:

The Quantum Mechanical derivation (QM) of the physisorption equations uses the Hellmann-Feynman[i] Theorem. These equations were reported earlier using two methods, perturbation theory[ii] and the WKB[iii] approximation with, of course, the same results. The resultant equations can be readily used by someone not familiar with QM. However, an understanding of the origin is something the expert in physisorption should have. The QM followed by the Grand Canonical Partition Function (GCPF) yields the "simple" case, which is multilayered and uninhibited adsorption, with the Polanyi and London, with DeBoer and Zwikker, and with Fuller, et al., in Equation 1:

$$n_a/n_m = \theta = \Delta\chi\,\mathbf{U}(\Delta\chi) \quad \Delta\chi = \chi - \chi_\zeta$$
$$\text{where} \quad \chi = -\mathbf{ln}\left\{-\mathbf{ln}\left(P/P_{vap}\right)\right\} \quad \text{and} \quad \chi_\zeta = -\mathbf{ln}\left\{-\mathbf{ln}\left(P_\zeta/P_{vap}\right)\right\} \qquad \textit{Equation 1}$$

Where n_a in the "simple" case here is the amount adsorbed, n_m, is the monolayer equivalence. Thus θ is the projection of the total areal density. P_ς is the threshold pressure. $P_\varsigma = \mathbf{exp}(-\overline{E}_a/RT)$ yielding the preexponential for the **system internal energy function given in** *Equation* 2**:**

$$\Delta_l^a\,\mathbf{E}(-\chi) = E_a\,\mathbf{exp}(-\Delta\chi) \equiv E_a\,\mathbf{exp}(-n_a/n_m) \qquad \textit{Equation 2}$$

The QM also yields the following equations for the individual schicht[1] (or "layer") areal densities:

$$\begin{aligned}
\theta_1 &= 1 - \mathbf{exp}(-\Delta\chi)\\
\theta_2 &= 1 - \mathbf{exp}(-\Delta\chi + \theta_1)\\
&\vdots\\
\theta_{n+1} &= 1 - \mathbf{exp}\left(-\Delta\chi + \sum_{m=1}^{n}\theta_m\right)\\
\Rightarrow \theta &= \sum_{m=1}^{\infty}\theta_m \equiv \Delta\chi \geq 0
\end{aligned} \qquad \textit{Equation 3}$$

The first equation may be rearranged to the log-law, for steric restriction to a single monolayer:

$$n_{a,1} = n_m + \frac{n_m RT}{\overline{E}_a}\mathbf{ln}\left(\frac{P}{P_{vap}}\right) \qquad \textit{Equation 4}$$

These equations confirms the Dubinin "Thermodynamic criterion" where $\mathbf{\Delta}_l^a\mathbf{S} \approx 0$.

In the final section, the ESW hypothesis is presented, which is another way to start these equations.

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[1] The word "layers" has too much association with the classical meaning of a dense layer, so the word "schicht" is being used when individual positions in the stacking is being addressed and not the dense layers. Thus, the words "monolayer" and "monolayer equivalence" are retained with the meaning of amount as defined.

[i] R. P. Feynman, Forces in Molecules. *Phys. Rev*. **56,** 340-343 (1939).

[ii] J. B. Condon, "Chapter 4 p145" in *Surface Area and Porosity Determination by Physisorption.* (Elsevier Publishing, Amsterdam, ed. 2, 2020). ISBN 978-0-12-818785-2.

[iii] J. B. Condon, **Error! Main Document Only.**Equivalency of the Dubinin-Polanyi Equations and the QM Based Sorption Isotherm Equation - Part A, Simulations of Heterogeneous Surfaces. *Microporous Mesoporous Mat.* **38,** 359-3767 (2000).