

Study of Effect of Adsorbate-Adsorbent Interaction in Multilayer Physical Adsorption of Gases on Solids

Sung Ju Park, Jo W. Lee, Hyungsuk Pak and Seihun Chang

Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151, Korea
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In this paper a further generalization of the theory of multilayer physical adsorption previously developed by the authors is attempted so that the effect of vertical interactions between adsorbent and adsorbate can be explicitly taken into account. In this attempt we have to discard the previously adopted assumption that the molecules in the second layer or above are all in the same physical state. In order to estimate the effect of vertical interactions on the adsorption isotherm the interaction energy between an adsorbed molecule and the adsorbent surface is assumed to vary as r^{-3} where r is the distance that the molecule under consideration is separated from the adsorbent surface. Resulting adsorption isotherm is applied to interpret the adsorption data of tetramethylsilane vapor on iron film and good agreements between observed and calculated values are obtained over wide range of pressure.

Introduction

A number of authors¹⁻⁶ have sought to refine the BET model by taking into account the layer by layer decrease in the heat of adsorption. As is well known, the BET formulation implies that $E_1 \neq E_2 = E_3 = \dots = E_i = \dots$, where E_i is the heat of adsorption for i -th layer. Replacing such a simple postulate by a more realistic one $E_1 > E_2 > E_3 > \dots$ comes from the current views of van der Waals forces and from measurements of the heat of adsorption as a function of the amount adsorbed^{7,8}. The first treatment incorporating the postulate $E_1 > E_2 > E_3 > \dots$ was due to Dole¹ whose generalization of the Hill-Cassie statistical derivation^{9,10} of the BET equation also took lateral interaction forces into account. No explicit isotherm equations emerged, but Dole was able to indicate the conditions under which multilayer adsorption led to various modified BET isotherms. The refined BET treatment due to Cook^{5,6} takes interactions and variable heat of adsorption with successive layer into account and it gives good agreement with typical type II isotherm. Nonetheless, such theories still suffer from the original BET assumption that one molecule is adsorbed right above the molecule underneath.

In this work we discuss a modified version of the theory due to Chang *et al.*^{11,12} by considering the effect due to the layer by layer decrease in the vertical interaction that an adsorbed molecule experiences. It is conjectured that the vertical interaction energy of an adsorbed molecule can be divided into two parts. The first is the interaction between the molecule under consideration and the adsorbent surface. This energy is attractive and can be shown to vary as r^{-3} where r is the distance of the molecule from the surface of the adsorbent¹³. The second is the interaction between the molecule of the question and other molecules in its neighboring layers. This kind of energy tends to be leveled as r increases. In formulating the theory such properties of the vertical interactions will be incorporated into the molecular partition function as is shown in the next section.

Theory

As we have shown previously,^{11,12,14} the number of adsorption sites available to the i -th layer molecules, M_i , may be written as

$$M_i = N_{i-1} (N_{i-1} / M_{i-1})^{n-1} \quad (1)$$

where N_{i-1} and M_{i-1} are, respectively, the number of molecules in the $(i-1)$ -th layer and the number of sites available to these molecules, and n signifies a parameter to be determined by the piling pattern of adsorbed molecules.

The ratio N_i / M_i represents the degree of occupation for the i -th layer and will henceforth be denoted by x_i ; that is,

$$x_i \equiv N_i / M_i \quad (2)$$

At this stage we introduce an assumption that the degree of occupation is same for all the layers above the k -th layer. This assumption is rather intuitive and comes from the fact that the adsorbed phase becomes more or less uniform as the distance from the adsorbent surface increases. Then we may write

$$y \equiv x_{k+1} = x_{k+2} = x_{k+3} = \dots \quad (3)$$

If the number of adsorption sites on the adsorbent surface is denoted by M , it follows from Eqs. (1), (2), and (3) that

$$\begin{aligned} M_1 &= M \\ M_2 &= x_1^n M \\ M_3 &= x_1^n x_2^n M, \\ &\vdots \\ M_k &= x_1^n x_2^n \dots x_{k-1}^n M, \\ M_{k+1} &= x_1^n x_2^n \dots x_k^n M, \\ &\vdots \\ M_i &= x_1^n x_2^n \dots x_k^n y^{(i-k)n} M, \\ &\vdots \end{aligned} \quad (4)$$

and

$$\begin{aligned} N_1 &= x_1 M, \\ N_2 &= x_1^n x_2 M, \\ N_3 &= x_1^n x_2^n x_3 M, \\ &\vdots \end{aligned}$$

$$\begin{aligned} N_k &= x_1^n x_2^n \dots x_k M, \\ N_{k+1} &= x_1^n x_2^n \dots x_k^n y M, \\ &\vdots \\ N_i &= x_1^n x_2^n \dots x_k^n y^{(i-k-1)n+1} M, \\ &\vdots \end{aligned} \quad (5)$$

Thus the average number of molecules per site on the adsorbent surface, ω , may be given as follows:

$$\begin{aligned} \omega &= \sum_{i=1}^{\infty} N_i / M \\ &= \sum_{j=1}^k (x_k^{n-j+1})^{-1} \prod_{i=1}^{k-j+1} x_i^n + y(1-y)^{-1} \prod_{i=1}^k x_i^n \end{aligned} \quad (6)$$

Therefore, the problem is reduced to the calculation of $x_1, x_2, x_3, \dots, x_k$, and y for given values of the relative pressure p/p^0 and this in turn requires the statistical mechanical study of the system under consideration.

Suppose that there are N_i molecules in the i -th layer distributed over M_i sites. Assuming the localized model, the canonical partition function for the i -th layer may be written as

$$Q_i(N_i M_i, T) = \frac{M_i! q_i(T)^{N_i}}{(M_i - N_i)! N_i!} \quad (7)$$

where $q_i(T)$ is the average molecular partition function for a molecule in the i -th layer. Note that $q_i(T)$ is in general a function of temperature T . Taking the logarithm of Eq.(7) and using the Sterling approximation, we have

$$\ln Q_i = M_i [-(1-x_i) \ln(1-x) - x_i \ln x_i + x_i \ln q_i] \quad (8)$$

Since the canonical partition function for the entire adsorbed phase, Q , may approximately be set equal to $\prod_{i=1}^{\infty} Q_i(N_i M_i, T)$, we have

$$M^{-1} \ln Q = M^{-1} \sum_{i=1}^{\infty} \ln Q_i, \quad (9)$$

In parallel with the assumption represented by Eq.(3) we also assume

$$q_1 \neq q_2 \neq q_3 \neq \dots \neq q_{k+1} = q_{k+2} = \dots = q. \quad (10)$$

Then, the quantity ϕ defined as $-A/MkT$, where A is the Helmholtz free energy for the adsorbed phase and k the Boltzmann constant, may be rewritten as

$$\begin{aligned} \phi &\equiv -A/MkT = M^{-1} \ln Q \\ &= -(1-x_1) \ln(1-x_1) - x_1 \ln x_1 + x_1 \ln q_1, \\ &\quad + x_1^n [-(1-x_2) \ln(1-x_2) - x_2 \ln x_2 + x_2 \ln q_2] \\ &\quad \vdots \\ &\quad + x_1^n x_2^n \dots x_{k-1}^n [-(1-x_k) \ln(1-x_k) - x_k \ln x_k + x_k \ln q_k] \\ &\quad + \frac{x_1^n x_2^n \dots x_{k-1}^n x_k^n}{1-y^n} [-(1-y) \ln(1-y) - y \ln y + y \ln q] \end{aligned} \quad (11)$$

Let us introduce a quantity q_i defined by

$$q_i \equiv (\partial \phi / \partial x_i)_{\omega, x_{j \neq i}} \quad (12)$$

Since the system has a minimum value of Helmholtz free energy at equilibrium under the condition of constant M and T ,

$$g_i = 0 \quad (1 \leq i \leq k) \quad (13)$$

at equilibrium,

As has been shown in our previous works^{11,12,14}, we introduce another thermodynamic quantity given by

$$\phi \equiv -\mu_A/kT \quad (14)$$

where μ_A is the chemical potential for the adsorbed phase. This quantity can be calculated by making use of the relation

$$\begin{aligned} \phi &\equiv -\mu_A/kT = (\partial \phi / \partial \omega)_{g_1, g_2, \dots, g_k} \\ &= (\partial \phi / \partial \omega)_{x_1, x_2, \dots, x_k} + (\partial \phi / \partial x_1)_{\omega, x_{j \neq 1}} (\partial x_1 / \partial \omega)_{g_1, g_2, \dots, g_k} \\ &\quad + \dots + (\partial \phi / \partial x_k)_{\omega, x_{j \neq k}} (\partial x_k / \partial \omega)_{g_1, g_2, \dots, g_k} \end{aligned} \quad (15)$$

At equilibrium the above quantity is equal to $(\partial \phi / \partial \omega)_{x_i}$ since the rest terms on the righthand side of Eq.(15) are vanishing. [cf. Eq. (14).] Thus we have

$$\begin{aligned} \phi_{eq} &= -(\mu_A/kT) = (\partial \phi / \partial \omega)_{x_i} \\ &= -\ln y + \ln(1-y) + \ln q \\ &\quad - \frac{ny^{n-1}}{1+(n-1)y^n} \ln(1-y) \end{aligned} \quad (16)$$

If we take into account the fact that at equilibrium the chemical potential for the adsorbed phase is equal to that for the vapor phase, Eq.(16) may be rewritten as

$$\begin{aligned} -\ln y + \ln(1-y) \frac{ny^{n-1}}{1+(n-1)y^n} \ln(1-y) \\ + \ln q = -\mu_g^0/kT - \ln \xi \end{aligned} \quad (17)$$

where μ_g^0 is the standard chemical potential for the vapor phase and ξ means the relative pressure, p/p^0 .

Rearrangement of Eq.(17) will lead us to a more convenient form

$$y = \frac{a\xi}{a\xi + (1-y) \frac{ny^{n-1}}{1+(n-1)y^n}} \quad (18)$$

where $a = q \exp(\mu_g^0/kT)$.

The conditions $g_1=0, g_2=0, \dots, g_k=0$ will give us a set of equations from which we can obtain x_1, x_2, \dots, x_k as in our previous works. In this case, however, the derivation of such equations is a little more difficult because of many independent variables. A detailed procedure for derivation is given in Appendix. From the conditions $q_i=0 (i=1, \dots, k)$ the following set of hierarchy equations results:

$$x_k = \frac{a\xi}{a\xi \dots \frac{q}{q_k} (1-y) \frac{nx_k^{n-1}}{1+(n-1)y^n}} \quad (19)$$

and

$$\begin{aligned} x_i &= a\xi / \left\{ a\xi + \frac{q}{q_i} \prod_{j=i+1}^k (1-x_j) \frac{j-1}{i} n(1-y)^{j-1} x_j^{(n-\delta_{ij})} \right. \\ &\quad \left. \frac{n(1-n)^{k-i}}{1+(n-1)y^n} \prod_{l=i}^k x_l^{(n-\delta_{il})} \right\} \\ &\quad \times (1-y) \end{aligned} \quad (20)$$

where $1 \leq i \leq k-1$ and δ_{ij} is the symbol that equals unity if $l=i$ and is zero otherwise.

To find theoretical isotherms we first calculate y from Eq.(18) by iterative method for a given set of values of ξ, n , and a . Thus obtained value of y is then substituted into Eq. (19) and the iterative method is used again to calculate x_k for

a given set of values of $\xi, q/q_k, n,$ and a . The values of y and x_k are then substituted into the equation for x_{k-1} and again use is made of the iterative method to find the value of x_{k-1} for a set of values of $\xi, q/q_k, q/q_{k-1}, n,$ and $a,$ and such process can be followed repeatedly until all the solutions for y, x_1, x_2, \dots, x_k are found. Thus obtained values of $y, x_1, x_2, \dots,$ and x_k are then substituted into Eq.(6) to find ω .

To investigate the effect of vertical interactions on the adsorption isotherm we assume q_i can be written as follows:

$$q_i = q_i^0 \exp(-\varepsilon_i/kT) \tag{21}$$

where ε_i is the vertical interaction energy of a molecule in the i -th layer and q_i^0 is the part of molecular partition function that is insensitive to the variation of vertical interactions.

As mentioned briefly in the introductory section, ε_i can be divided into two parts. The first is the interaction of the molecule with the surface of adsorbent and this interaction energy may be assumed to vary as r^{-3} where r is the distance from the adsorbent surface¹³. The second part is the interaction of the molecule with other molecules in the neighboring layers. Though the latter interaction may show the layer by layer variation depending on the degree of occupation for each layer, we will simply assume that they are constant throughout the adsorbed phase except for the first layer. Such assumption greatly alleviates the difficulty involved in treating the effect of adsorbent surface on the adsorption isotherm. Thus, except for the first layer, we may write

$$\frac{q}{q_i} \cong \exp\left[b\left(\frac{1}{(k+1)^3} - \frac{1}{i^3}\right)\right] \tag{22}$$

where the parameter b describes strength of interaction between an adsorbate molecule and the adsorbent surface. In case of the first layer q/q_1 will simply be treated as being described by a different value of b . Let us denote this parameter by b' .

In Figure 1 through Figure 3 we have provided the illustrative examples of adsorption isotherms for various situations. In these examples k is assumed to be fixed, either 12 or 2, and b is set equal to b' .

Result and Discussion

It is clear from Eqs.(6), (18), (19), and (20) that in case $k=1$ our adsorption isotherm reduces to the previous one¹². For comparison with experimental data we have calculated the theoretical isotherms as follows. First, we set k equal to 1 and obtain the values of y, x_1, x_2, \dots, x_k for a given set of values of ξ, n, a, b and b' by solving Eqs.(18), (19), and (20) numerically and then calculate ω using Eq.(6). Then we increase the value of k by one and repeat the same procedure. If these two calculated isotherms differ from each other substantially, we increase the value of k again by one and repeat the same calculations. We continue such process until the calculated isotherm shows no further change. Then we repeat the same procedure for another set of parameters. In this way we can find a theoretical isotherm sufficiently close to the experimental one.

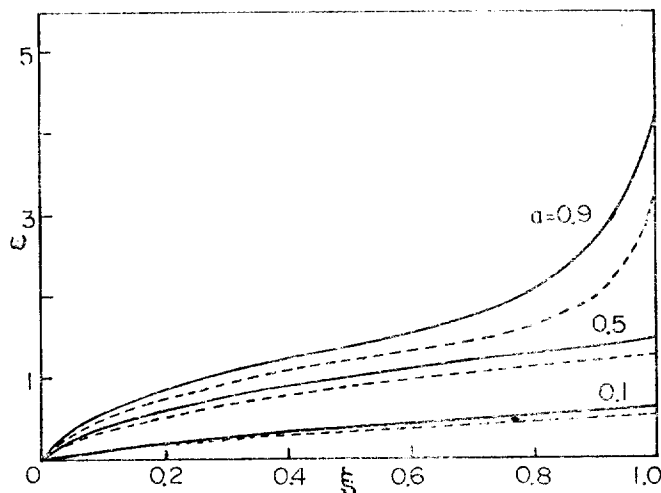


Figure 2. Theoretical adsorption isotherms for $n=3$ and $q/q_{12}=0.1$ (—) and $q/q_2=0.1$ (---).

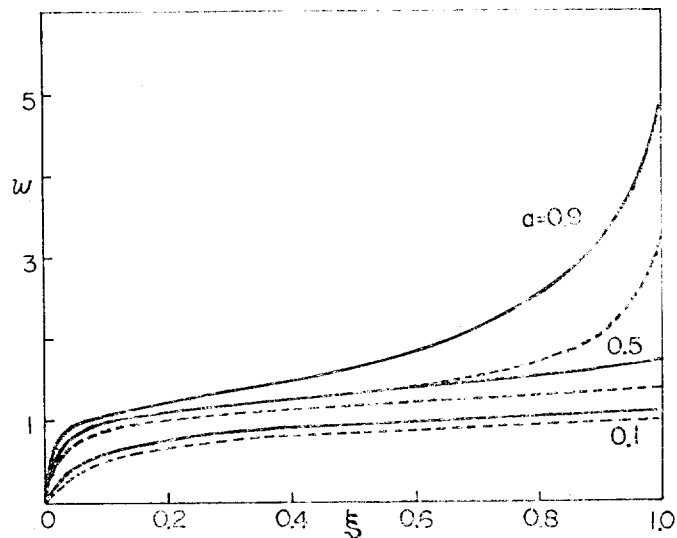


Figure 1. Theoretical adsorption isotherms for $n=3$ and $q/q_{12}=0.01$ (—) and $q/q_2=0.01$ (---).

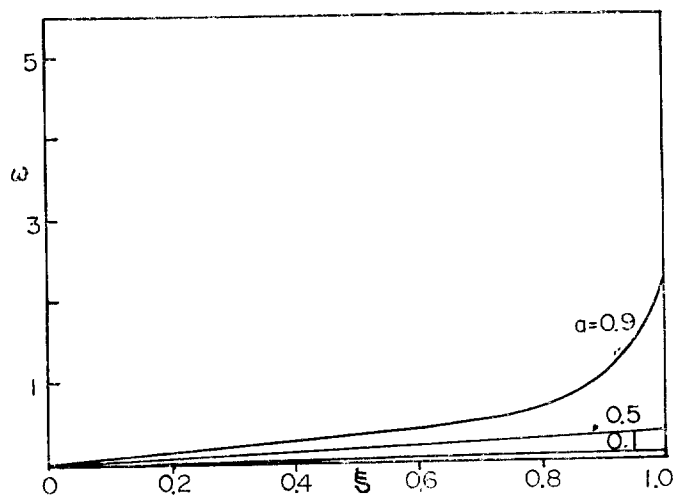


Figure 3. Theoretical adsorption isotherms for $n=3$ and $q/q_{12}=q/q_2=1$.

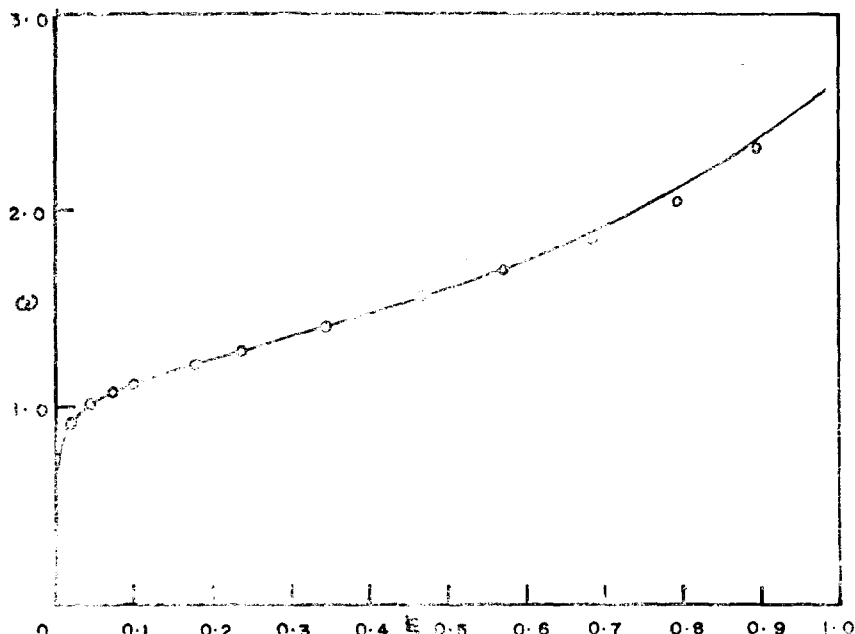


Figure 4. Adsorption isotherm of tetramethylsilane on iron film at 23.3 °C. $k=12$, $n=3$, $a=0.7$, $b=7.0$ and $b'=6.3$ Experimental(○), Theoretical(—).

In Figure 4 we have compared a theoretical isotherm with the experimental one obtained for tetramethylsilane on clean iron film¹⁵. In this case we have found that $k=12$ is an adequate value for the description of the system. Calculated isotherm is in good agreement with the observed one as shown in Fig.4, even in the region of $\xi > 0.7$ where we have failed in a previous work¹⁴.

In this work the lateral interactions among adsorbate molecules have not been considered to focus ourselves on the effect of vertical interactions; however, inclusion of lateral interactions in our theory along with vertical interactions will no doubt give the far reaching results.

In summary we may conclude that the effect of vertical interaction is significant in case the adsorbate-adsorbent interaction is strong and that the variation of such interaction with distance from the adsorbent surface must be explicitly taken into account. In view of our result the assumption that the adsorbent-adsorbate interaction varies as r^{-3} seems reasonable for the case of TMS vapor on iron film.

Appendix

The condition

$$g_i \equiv (\partial\phi/\partial x_i)_{x_{a+i}, \omega} = 0$$

means that the variation $\delta\phi=0$ under the constriction $\omega=\text{constant}$ for displacement of the variables x_i . That is,

$$\delta\phi = \sum_{i=1}^k (\partial\phi/\partial x_i)_{x_{a+i}, \omega} \delta x_i + (\partial\phi/\partial y)_{x_a} \delta y = 0 \quad (a-1)$$

and

$$\delta\omega = \sum_{i=1}^k (\partial\omega/\partial x_i)_{x_{a+i}, y} \delta x_i + (\partial\omega/\partial y)_{x_a} \delta y = 0 \quad (a-2)$$

Using the method of Lagrange undetermined multiplier, we obtain

$$\sum_{i=1}^k \left\{ \left(\frac{\partial\phi}{\partial x_i} \right)_{x_{a+i}, y} + \lambda \left(\frac{\partial\omega}{\partial x_i} \right)_{x_{a+i}, y} \right\} \delta x_i + \left\{ \left(\frac{\partial\phi}{\partial y} \right)_{x_a} + \lambda \left(\frac{\partial\omega}{\partial y} \right)_{x_a} \right\} \delta y = 0 \quad (a-3)$$

Now that an undetermined multiplier has been invoked, x_1, x_2, \dots, x_k , and y can all be considered as independent variables. Hence

$$\left(\frac{\partial\phi}{\partial x_i} \right)_{x_{a+i}, y} + \lambda \left(\frac{\partial\omega}{\partial x_i} \right)_{x_{a+i}, y} = 0 \quad (a-4)$$

and

$$\left(\frac{\partial\phi}{\partial y} \right)_{x_a} + \lambda \left(\frac{\partial\omega}{\partial y} \right)_{x_a} = 0 \quad (a-5)$$

We choose λ in such a way that

$$\lambda = - \frac{(\partial\phi/\partial y)_{x_a}}{(\partial\omega/\partial y)_{x_a}} \quad (a-6)$$

Then, from Eq.(a-4) we obtain,

$$\left(\frac{\partial\phi}{\partial x_i} \right)_{x_{a+i}, y} - \frac{(\partial\phi/\partial y)_{x_a}}{(\partial\omega/\partial y)_{x_a}} \left(\frac{\partial\omega}{\partial x_i} \right)_{x_{a+i}, y} = 0$$

which provides the basis for derivation of Eqs.(19) and(20).

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References

- (1) M. Dole, *J. Chem. Phys.*, **16**, 25 (1948).
- (2) R. B. Anderson, *J. Amer. Chem. Soc.*, **68**, 686 (1946).
- (3) R. N. Smith and C. Pierce, *J. Phys. Chem.*, **52**, 1115 (1948).
- (4) W. A. Steele, *J. Chem. Phys.*, **25**, 819 (1956)
- (5) M. A. Cook, *J. Amer. Chem. Soc.*, **70**, 2925 (1948).
- (6) M. A. Cook and D. H. Pack, *ibid.*, **71**, 791 (1949).
- (7) W. D. Harkins and G. Jura, *ibid.*, **66**, 919 (1944).
- (8) R. U. Culver and F. C. Tomkins, *Advan. Cat.*, **11**, 67 (1959).
- (9) A. B. D. Cassie, *Trans. Faraday Soc.*, **41**, 450 (1945).
- (10) T. L. Hill, *J. Chem. Phys.*, **15**, 767 (1947).
- (11) S. Chang, H. Pak, J. W. Lee and S. J. Park, *J. Korean Chem. Soc.*, **21**, 353 (1977).
- (12) S. Chang, J. W. Lee, H. Pak, and S. H. Han, *J. Korean Chem. Soc.*, **22**, 78 (1978).
- (13) T. L. Hill, "Introduction to Statistical Thermodynamics", Chap. 7, p. 126, Addison-Wesley, 1960.
- (14) S. H. Han, J. W. Lee, H. Pak, and S. Chang, *Bull. Korean Chem. Soc.*, **1**, 117 (1980)
- (15) S. Chang, unpublished results.