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물리흡착에 관한 통계열역학적 연구

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Statistical Thermodynamical Approach to Physical Adsorption

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要 約. 多分子層 物理吸着에 있어서 第二分子層이나 또는 그 以上의 分子層이 形成될 때에는 分子들은 바로 아래 層의 分子들이 이루는 三角形 또는 四角形 配列의 中心部위에 吸着될 것이라는 前提下에 새로운 物理吸着理論을 提案하고 이 때의 吸着等溫式을 誘導하였다. 誘導된 吸着等溫式에는 monolayer capacity를 나타내는 v_m, 第二層 以上의 層에 대한 分子分配函數와 첫째層 分子의 그것間의 比를 나타내는 q/q_1 및 吸着된 分子들의 쌓이는 樣相을 나타내는 n이란 3개의 調節可能한 파라미터가 들어있다. 誘導된 吸着等溫式을 argon이 "Carbolac" carbon 上에 吸着되는 경우와 nitrogen이 Linde silica 上에 吸着되는 경우에 適用시켜 보면 p/p_0가 0.8에 이를때까지 理論値와 實驗値가 잘 一致함을 볼 수 있다. 이 두 경우에 있어서 $n=3$이라 놓으면 理論値와 實驗値가 가장 잘 一致하므로 이로부터 吸着된 分子들이 아마도 密集方式으로 쌓이게 되는 것이라 結論지을 수 있다.

ABSTRACT. In this paper we propose a new theory of multilayer physical adsorption based on the view that a second or higher layer molecule will be adsorbed above the center of a square or triangular array of molecules, rather than on top of molecules themselves, in the next lower layer and the corresponding adsorption isotherm is derived. The derived isotherm contains three adjustable parameters; v_m (monolayer capacity), q/q_1 (ratio of the molecular partition function for the second or higher layer *vs.* that for the first layer) and n (a parameter characterizing the piling pattern of adsorbed molecules). When applied to adsorption of argon on "Carbolac" carbon and nitrogen on Linde silica, excellent agreements between observed and calculated values are obtained up to $p/p_0=0.8$. In both cases $n=3$ gives the best fit and this probably indicates that adsorbed molecules are piled up in a closest packing pattern.

1. INTRODUCTION

One of the basic problems in the subject of multilayer physical adsorption of gases on the uniform surface of a solid adsorbent is the derivation of a theoretical adsorption isotherm based on an appropriate model which can reproduce experimental data over a wide range of temperature and pressure. To this end numerous theories and their modifications have been published,[1~20] but at the present time it seems that a theoretical isotherm capable of describing the observed results for various adsorbate–

adsorbent systems over an appreciable range of temperature and pressure has yet to appear.

Among so many theories proposed thus far it is the one due to Brunauer, Emmett and Teller[1], usually referred to as the BET theory, that is best known and has been playing the central role in the postwar study of multilayer physical adsorption. The BET theory, though useful and widely used, has several inherent shortcomings originating from oversimplified nature of the proposed model on which it is based. At the same time it has also some advantages over other theories in that it gives a clear picture of multilayer adsorption phenomena and is mathematically simple. Moreover, the parameters involved in it can be correlated to some physically measurable quantities without much difficulty. Thus it seems desirable for us to develop a new theory in the direction that can lead to an improved form of adsorption isotherm while maintaining the mathematical simplicity of the BET theory.

Comparison of experimental data with those calculated from the BET isotherm usually reveals that the latter deviates from the former at very low values and comparatively high values of the relative pressure, p/p_0. The deviation at very low values of p/p_0 is known to be mainly due to the surface heterogeneity, but the discrepancies at high values of p/p_0 (usually greater than 0.35) becomes greater as p/p_0 increases and its origin obviously lies in the oversimplified nature of the BET model itself.

In the BET model it is assumed that when the second or higher layer is formed one molecule may be adsorbed right on top of another molecule in the layer just below yielding the full energy of liquefaction. In view of the nature of van der Waals intermolecular force such a model seems to be highly untenable and a more reasonable model must be sought. Though Hill[21] has suggested that introduction of lateral intermolecular interactions into the BET model could yield a considerable improvement over the original theory, the present authors believe that adoption of the correct packing pattern for adsorbed molecules is more important than this. In this paper the authors have developed a new theory of multilayer physical adsorption based on the view that, as Halsey once noted[10], a second or higher layer molecule is much more likely to be adsorbed adove the center of a square or triangular array of molecules in the next lower layer, rather than right on top of molecules themselves, and thus obtained theoretical results have been found to agree with the observed data very well up to $p/p_0=0.8$.

2. THEORETICAL DERIVATION OF ADSORPTION ISOTHERM

Suppose that the adsorbent surface can provide a regular square array of M equivalent but distinguishable sites for adsorption, as shown in *Fig.* 1. If the four sites A, B, C and D in *Fig.* 1 are all occupied each by a first-layer molecule, the point S located right above the center of a square formed by these four points can become an adsorption site available to the second layer molecules. Then we may ask, "How many points such as S can be formed when there are N_1 molecules in the first layer randomly distributed over M sites?" This question can be answered if we find the probability that the four sites A, B, C and D are simultaneously occupied each by a first-layer molecule. This probability can be expressed in terms of M and N_1 as

$$\frac{(M-4)!}{(M-N_1)!\ (N_1-4)!}\Big/\frac{M!}{N_1!\,(M-N_1)!}=\frac{N_1(N_1-1)(N_1-2)(N_1-3)}{M(M-1)(M-2)(M-3)} \quad (1)$$

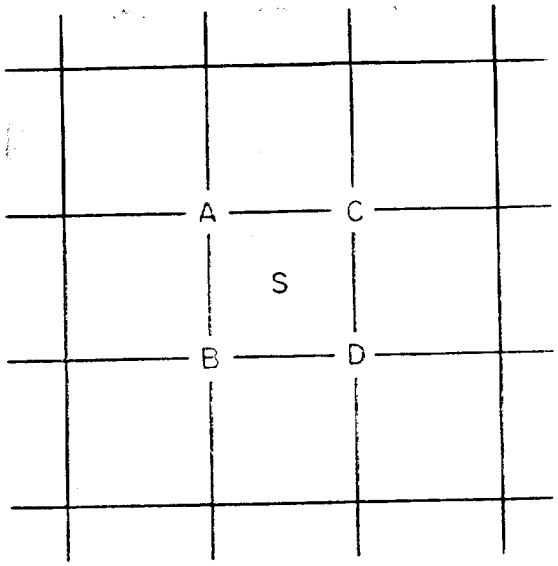

Fig. 1. Square array of adsorption sites and the possibility that an adsorption site available to a second layer molecule may be formed.

Since both M and N_1 are usually much larger than 1, the above becomes equal to $(N_1/M)^4$. In other words the probability that the point S can act as an adsorption site for the second-layer molecules is given by $(N_1/M)^4$. Since there are M such points, we can say the total number of sites offered by the first-layer molecules is on the average equal to

$$(N_1/M)^4\times M=N_1(N_1/M)^3 \tag{2}$$

By the same logic we can show that, if the sites on the adsorbent surface form a triangular array and the adsorbed first-layer molecules are randomly distributed over these sites, the average number of sites available to the second-layer molecules is given by $N_1(N_1/M)^2$.

The above rationale has led us to propose that the number of adsorption sites available to the ith-layer molecules, M_i, may be written as

$$M_i=N_{i-1}(N_{i-1}/M_{i-1})^{n-1} \tag{3}$$

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.

Thus we may write

$$\begin{aligned}&M_1=M\\&M_2=N_1(N_1/M_1)^{n-1}\\&M_3=N_2(N_2/M_2)^{n-1}\\&\vdots\\&M_i=N_{i-1}(N_{i-1}/M_{i-1})^{n-1}\end{aligned} \tag{4}$$

and so forth.

At this stage we introduce an assumption that the degree of occupation for each layer, N_i/M_i, is same for all but the first layer. This assumption is equivalent to writing

$$\begin{aligned}&x\equiv\frac{N_1}{M_1}\\&y\equiv\frac{N_2}{M_2}=\frac{N_3}{M_3}=\cdots\cdots\cdots=\frac{N_i}{M_i}=\cdots\cdots\\&\qquad\qquad(x\neq y)\end{aligned} \tag{5}$$

This seemingly intuitive assumption may be derived via the kinetical considerations, as has been done in the BET theory, but further theoretical investigations of its validity may be necessary. In our next publication we intend to report under what conditions the above assumption is valid. Anyway this assumption has turned out to facilitate the mathematical formulation of our adsorption model and has yielded quite a useful isotherm.

Combination of Eqs. (4) and (5) gives us

$$\begin{aligned}&M_1=M\\&M_2=x^nM\\&M_3=y^nM_2=x^ny^nM\\&\vdots\\&M_i=y^nM_{i-1}=y^{(i-2)n}x^nM\\&\vdots\end{aligned} \tag{6}$$

and

$$\begin{aligned}&N_1=xM_1=xM\\&N_2=yM_2=x^nyM\\&N_3=yM_3=x^ny^{n+1}M\\&\vdots\\&N_i=yM_i=x^ny^{(i-2)n+1}M\\&\vdots\end{aligned} \tag{7}$$

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

$$\omega=\sum_{i=1}^{\infty} N_i/M$$
$$=x+x^n y+x^n y^{n+1}+x^n y^{2n+1}+\cdots\cdots$$
$$=x+\frac{x^n y}{1-y^n} \qquad (8)$$

Therefore, the problem is reduced to the calculation of x and y for a given value of p/p_0 and this in turn requires the statistical mechanical study of the system under consideration.

Let us now suppose there are N_i molecules in the ith layer distributed over M_i sites. Neglecting the lateral intermolecular interactions and assuming the localized adsorption model, the canonical partition function for the ith layer may be written as

$$Q_i(M_i,\ N_i\ T)$$
$$=\frac{M_i!}{(M_i-N_i)!\ N_i!}\, q_i(T)^{N_i} \qquad (9)$$

where $q_i(T)$ is the average molecular partition function for a molecule in the ith layer. Note that $q_i(T)$ is in general a function of temperature. Hence we may write

$$\ln Q_i=M_i\left[-\left(1-\frac{N_i}{M_i}\right)\ln\left(1-\frac{N_i}{M_i}\right)-\frac{N_i}{M_i}\ln\frac{N_i}{M_i}+\frac{N_i}{M_i}\ln q_i\right] \qquad (10)$$

where we have used the Stirling's formula

$$\ln N!\cong N\ln N-N$$

which is valid for a large number N.

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

$$\frac{1}{M}\ln Q=\frac{1}{M}\sum_{i=1}^{\infty}\ln Q_i \qquad (11)$$

As in the case of BET model, we assume

$$q_1\neq q_2=q_3=\cdots\cdots=q \qquad (12)$$

Then it follows from Eqs. (10) and (11) that

$$\varphi\equiv -A/MkT$$
$$=\frac{1}{M}\ln Q$$
$$=-(1-x)\ln(1-x)-x\ln x+x\ln q_1+\frac{x^n}{1-y^n}\left[-(1-y)\ln(1-y)-y\ln y+y\ln q\right] \qquad (13)$$

where A is the Helmholtz free energy and k the Boltzmann constant.

Let us introduce a new quantity g defined by

$$g\equiv(\partial\varphi/\partial x)_{\omega} \qquad (14)$$

At equilibrium g must be equal to zero since then the free energy A is minimized. From this condition and Eq. (13) we obtain the following equation:

$$\ln(1-x)-\ln x+\ln\frac{q_1}{q}-\ln(1-y)+\ln y+\frac{ny^{n-1}-nx^{n-1}}{1+(n-1)y^n}\ln(1-y)=0 \qquad (15)$$

We introduce another thermodynamic quantity ψ given by

$$\psi\equiv-\mu_A/kT \qquad (16)$$

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

$$\psi\equiv-\mu_A/kT=(\partial\varphi/\partial\omega)_g$$
$$=(\partial\varphi/\partial\omega)_x+(\partial\varphi/\partial x)_{\omega}(\partial x/\partial\omega)_g. \qquad (17)$$

At equilibrium the above quantity is equal to $(\partial\varphi/\partial\omega)_x$ since the second term on the right-hand side of Eq. (17) vanishes. Thus we have

$$\psi_{eq}=-(\mu_A/kT)_{eq}=(\partial\varphi/\partial\omega)_x$$
$$=\ln(1-y)-\ln y+\ln q-\frac{ny^{n-1}}{1+(n-1)y^n}\ln(1-y) \qquad (18)$$

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. (18) may be rewritten as

$$-\ln y+\left[1-\frac{ny^{n-1}}{1+(n-1)y^n}\right]\ln(1-y)$$
$$+\ln q=-\frac{\mu^\circ_g}{kT}-\ln\xi \qquad (19)$$

where μ°_g is the standard chemical potential for the vapor phase and ξ means the relative pressure, p/p_0.

If we assume y tends to 1 as ξ approaches to unity, then we have from Eq. (19)

$$\ln q=-\mu^\circ_g/kT \qquad (20)$$

Substitution of Eq. (20) into Eq. (19) yields the relation

$$-\ln\xi=-\ln y+\left[1-\frac{ny^{n-1}}{1+(n-1)y^n}\right]\ln(1-y) \qquad (21)$$

Rearranging Eq. (21), we obtain

$$y=\frac{\xi}{\xi+(1-y)^{\frac{ny^{n-1}}{1+(n-1)y^n}}} \qquad (22)$$

from which y can be calculated by iterative process for a given set of values of ξ and n.

Substitution of Eq. (21) into Eq. (15) and slight rearrangement yield another important relation

$$x=\frac{\xi}{\xi+\frac{q}{q_1}(1-y)^{\frac{nx^{n-1}}{1+(n-1)y^n}}} \qquad (23)$$

from which, using the previously determined value of y, we can calculate x for a given set of values of ξ, q/q_1 and n. [Note that Eq. (22) always has a trivial solution $y=1$ and this must be disregarded.]

In summary our adsorption isotherm may be written in the form

$$\omega=x+\frac{x^n y}{1-y^n} \qquad (8)'$$

where x and y can be obtained by solving the equations

$$y=\frac{\xi}{\xi+(1-y)^{\frac{ny^{n-1}}{1+(n-1)y^n}}} \qquad (22)'$$

and

$$x=\frac{\xi}{\xi+\frac{q}{q_1}(1-y)^{\frac{nx^{n-1}}{1+(n-1)y^n}}} \qquad (23)'$$

for a given set of values of ξ, q/q_1 and n.

It should be pointed out in passing that in case $n=1$ our adsorption isotherm (8)′ reduces to the 'simple' or '∞-form' BET equation. When $n=1$, we have from Eqs. (22)′ and (23)′

$$y=\xi \quad \text{and} \quad x=\frac{\xi}{\xi+\frac{q}{q_1}(1-\xi)}$$

Substituting these results into Eq. (8)′, we obtain

$$\omega=\frac{x}{1-y}=\frac{\xi}{(1-\xi)[\xi(1-q/q_1)+q/q_1]} \qquad (24)$$

which is nothing but the BET equation itself. Thus we may say that the BET equation is a special case of our general isotherm.

3. CALCULATIONS AND RESULTS

For illustrative purposes we have calculated ω for various values of ξ setting $q/q_1=0.01$, 0.1, 1.0 and $n=1$, 2, 3, 4, and the results have been presented in *Fig.* 2, 3 and 4. We see from these that theoretical curves resemble the Type III isotherm when q/q_1 has the value close to unity. As q/q_1 gets smaller than unity, the knee bends of curves become more apparent and for the value of q/q_1 less than 0.1 the curve shape comes close to that of a typical Type II isotherm.

Experimental data are usually reported in terms of total volume of the gas adsorbed, v, as

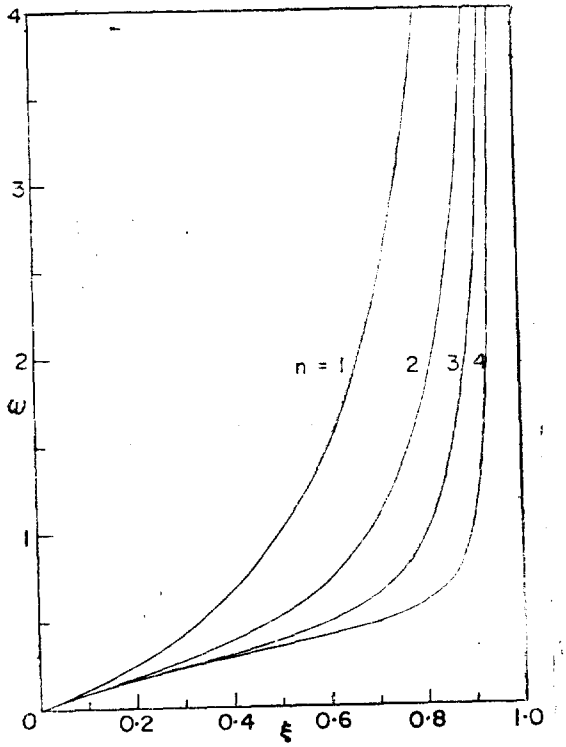

Fig. 2. Theoretical isotherms for $q/q_1=1.0$.

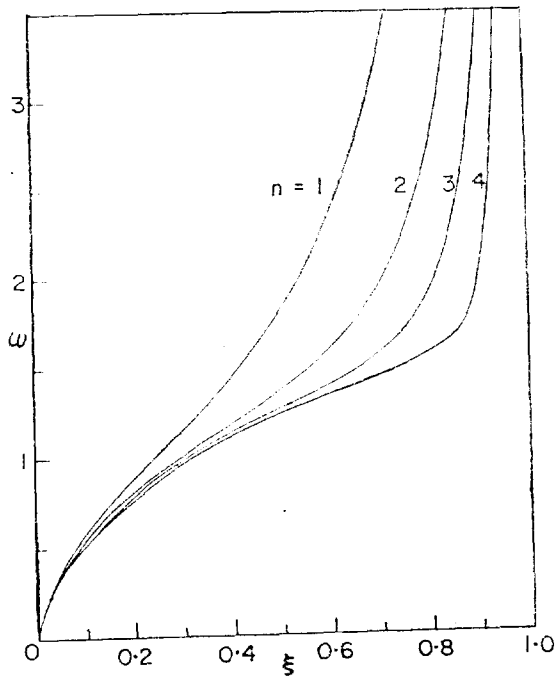

Fig. 3. Theoretical isotherms for $q/q_1=0.1$.

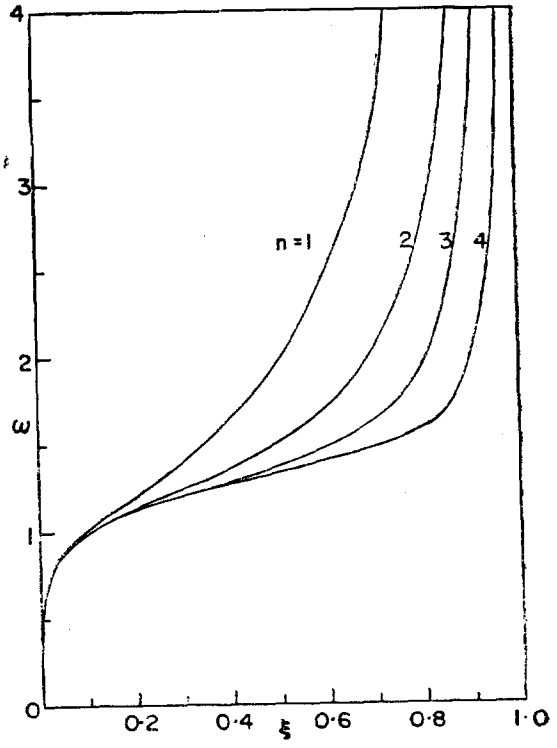

Fig. 4. Theoretical isotherms for $q/q_1=0.01$.

a function of the relative pressure, ξ. Therefore, in order to use Eq. (8)′ to interpret the observed results one must convert the reported data to those expressed in terms of monolayers adsorbed and this requires the knowledge of monolayer capacity, v_m. The calculation of v_m using our adsorption isotherm can be done as follows. First, we take two data points v_1 and v_2 at two different values of relative pressure ξ_1 and ξ_2. Then we may write for a given value of n

$$\frac{v_1}{v_m}=x_1+\frac{x_1{}^n y_1}{1-y_1{}^n} \tag{25}$$

and

$$\frac{v_2}{v_m}=x_2+\frac{x_2{}^n y_2}{1-y_2{}^n} \tag{26}$$

where x_1, x_2, y_1 and y_2 are the values of x and y corresponding to the values of relative

pressure ξ_1 and ξ_2, respectively. Dividing Eq. (26) by Eq. (25), we have

$$\frac{v_2}{v_1}=\frac{x_1+x_1^n y_1/(1-y_1^n)}{x_2+x_2^n y_2/(1-y_2^n)} \qquad (27)$$

The value of q/q_1 satisfying the relation (27) for a given value of n can be calculated numerically with the aid of Eqs. (22)′ and (23)′. Once the value of q/q_1 is determined, it is rather straightforward to calculate v_m either from Eq. (25) or Eq. (26).

To test the validity of our theory we have applied the new isotherm [Eq. (8)′] to the following two systems: argon on "Carbolac" carbon[22] and nitrogen on Linde silica.[23] In both cases n has been set equal to 3 and the value of q/q_1 has been determined from Eq. (27) by taking two data points in the lower region of ξ so that the calculated curve can give the best fit in this region. The results, as shown in *Fig.* 5 and 6, are in satisfactory agreement with the observed data up to $\xi=0.8$. This confirms that we are on the right track in pursuing the correct model of multilayer physical adsorption. For comparison the BET isotherm is also shown in the same plot (by a dashed curve) for the given value of q/q_1.

4. CONCLUSIONS AND DISCUSSIONS

The results of this work show that in the BET model the number of adsorption sites avail

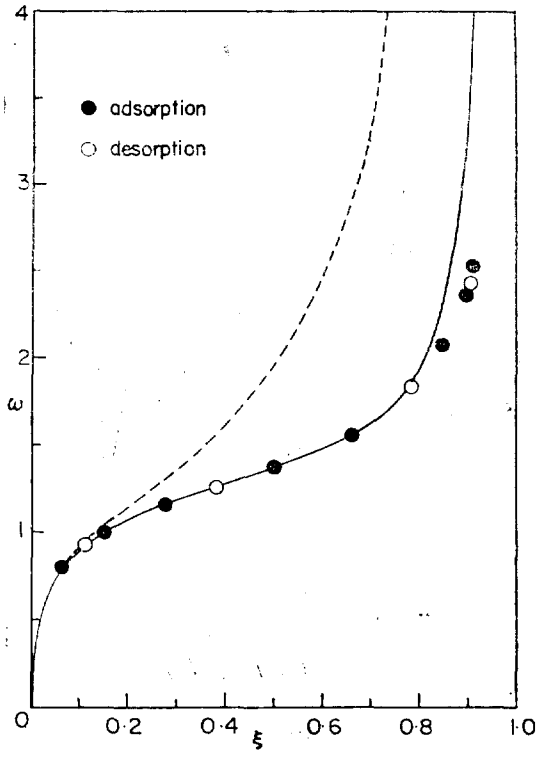

Fig. 5. Adsorption of argon on "Carbolac" carbon (free powder) at −194°C. Solid curve is the theoretical isotherm calculated from Eq. (8)′ while the BET isotherm is shown by a dashed curve, both for $q/q_1=0.023$.

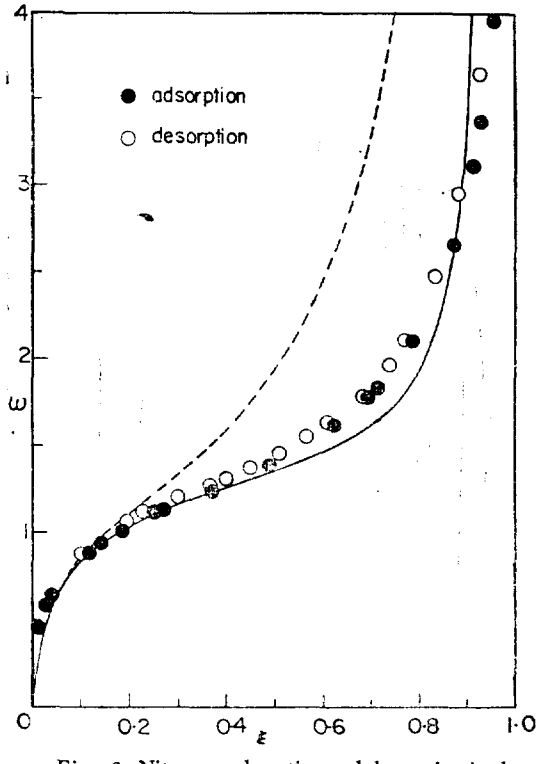

Fig. 6. Nitrogen adsorption and desorption isotherms for Linde silica at −195 °C. Average particle radius is 63 Å and the specific surface area is reported to be 180 m^2/g. Theoretical isotherm is represented by a solid curve while the BET isotherm is drawn by a dashed curve, both for $q/q_1=0.030$.

able to the second or higher layer molecules has been obviously overestimated and, if a correct way of counting the number of sites is employed, the observed results can be properly interpreted. It can also be seen that neglect of lateral intermolecular interactions between adsorbed molecules is not too serious a problem as far as the Type II and Type III adsorption isotherms are concerned.

In the case of adsorption of argon on "Carbolac"carbon, theoretical curve begins to deviate from experimental data at $\xi=0.8$, but this deviation may be considered to arise from our assumption that the number of adsorption sites available to second or higher layer molecules is given by Eq. (3). At present we have some evidences that if more exact way of counting the number of available adsorption sites is employed the discrepancies at $\xi>0.8$ can be corrected.

In the case of nitrogen-Linde silica system agreement between experimental data and calculated values may not look as impressive as in the argon-"Carbolac" carbon system. However, we think that deviation in the region $\xi=0.5\sim 0.8$ is apparent one. The adsorption data for this system have been obtained using the fine powder of Linde silica with the average radius of particles *ca.* 60 Å, and the pendular ring condensation phenomena would make an appreciable contribution in this case. Though not explicitly reported here, we have strong evidences that if allowance is made for the effect of pendular ring condensation the result can be as good as that for the argon-"Carbolac" carbon system.

Finally, we have to remark here that other values of n, besides 3, were also tested for the above two cases but the results have not been as satisfactory as in the case of $n=3$. This would probably indicate that both argon and nitrogen molecules are piled up in a closest packing pattern in these cases.

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