

## 새로운 多分子層物理吸着理論에 依한 氣體吸着現象의 研究

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## Application of a New Theory of Multilayer Physical Adsorption to the Study of Adsorption of Gases

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**要約.** 이 論文에서는 著者들이 앞서 發展시킨 多分子層物理吸着理論을 修正하여 새로운 吸着理論을 提案하였다. 이 새로운 理論을 여러가지 adsorbent-adsorbate 系에 適用시켜 본 결과 Type II 와 Type III 吸着의 경우에는 理論値와 實驗値가 잘 一致하였다. 뿐만 아니라 이미 발표한 理論으로써는 說明할 수 없었던 Type I 吸着等溫式도 새로운 理論으로는 說明할 수 있었다. 이 理論에 包含되어 있는 두 parameter  $q/q_1$ 과  $a$ 는 吸着熱과 어떤 關聯性이 있는 것으로 推測된다.

**ABSTRACT.** In this paper a modified version of the theory of multilayer physical adsorption developed previously by the authors is presented. This new theory is applied to various adsorbent-adsorbate systems and excellent agreements between theoretical results and the observed data are obtained for Type II and Type III adsorption. In addition, the Type I isotherm, which was not accounted for previously, can also be explained in terms of the newly derived isotherm. It is conjectured that two parameters involved in this theory,  $q/q_1$  and  $a$ , are somehow related to the heat of adsorption.

### 1. INTRODUCTION

The BET theory for multilayer physical adsorption has two crucial defects by its nature: (a) the assumption 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 and (b) neglect of lateral intermolecular interactions. In a previous paper<sup>1</sup>

(hereafter, referred to as the Paper I) we have shown that the original BET theory can be drastically improved if we adopt the correct packing pattern for adsorbed molecules and thus have concluded that among the two defects of original BET theory mentioned above the former is more responsible for failure of the theory.

In the Paper I we have adopted the view that a second or higher layer molecule will be adsorbed above the center of a square or trian-

gular array of molecules, rather than on top of molecules themselves, in the next lower layer. The proposed theory has been based on the following three assumptions:

(1) The number of adsorption sites available to the  $i$ -th layer molecules,  $M_i$ , is given by

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

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

(2) 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

$$N_1/M_1 \equiv x, N_2/M_2 = N_3/M_3 = \dots \equiv y;$$

(3) The molecular partition function<sup>0</sup> for each layer is same for all but the first layer. That is,

$$q_1 \equiv q_2 = q_3 = \dots = q_i \equiv q.$$

The derived adsorption isotherm has been shown to take the following form:

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

where  $\omega$  is the average number of molecules per site on the adsorbent surface and  $x$  and  $y$  can be obtained by solving the equations

$$y = \frac{\xi}{\xi + (1-y) \frac{ny^{n-1}}{1+(n-1)y^n}} \quad (2)$$

and

$$x = \frac{\xi}{\xi + \frac{q}{q_1} (1-y) \frac{nx^{n-1}}{1+(n-1)y^n}} \quad (3)$$

$\xi$  in Eqs. (2) and (3) represents the relative pressure,  $p/p_0$ .

In the Paper I we have adopted the assumption that  $y$  tends to the value of 1 as  $\xi$  appro-

aches to unity. Later we have found that lift of this restriction could lead to a more versatile and widely applicable form of adsorption isotherm. We have applied the thus derived adsorption isotherm to various adsorbate-adsorbent systems and the results have shown excellent agreements with experimental data nearly over all the range of  $\xi$  (from 0 to 1). Furthermore the newly derived isotherm has been found to be able to account for the Type I adsorption, not to mention the Type II and Type III.

## 2. THEORY

In the Paper I [see Eqs. (15) and (19)] we have shown that at equilibrium the following two relations hold:

$$\ln(1-x) - \ln x + \ln \frac{q_1}{q} - \ln(1-y) + \ln y + \frac{ny^{n-1} - nx^{n-1}}{1+(n-1)y^n} \ln(1-y) = 0 \quad (4)$$

and

$$-\ln y + \left[ 1 - \frac{ny^{n-1}}{1+(n-1)y^n} \right] \ln(1-y) + \ln q = -\frac{\mu_g^0}{kT} - \ln \xi \quad (5)$$

where  $\mu_g^0$  is the standard chemical potential for the vapor phase and  $\xi$  means the relative pressure,  $p/p_0$ .

Previously, in order to simplify Eq. (5) we have assumed that  $y$  tends to the value of 1 as  $\xi$  approaches to unity. This assumption, however, is useful only in the limit that the partition function  $q$  is independent of  $\xi$ . Thus it is desirable to remove this restriction to make allowance for the effect of  $\xi$  on  $q$ .

Rearranging Eq. (5), we obtain

$$y = \frac{a\xi}{a\xi + (1-y) \frac{ny^{n-1}}{1+(n-1)y^n}} \quad (6)$$

where

$$a = qe^{\mu_g^0/kT} \quad (7)$$

Substitution of Eq. (6) back into Eq. (4) and slight rearrangement produce another important equation

$$x = \frac{a\xi}{a\xi + \frac{q}{q_1}(1-y)^{\frac{nx-1}{1+(n-1)y}}} \quad (8)$$

$y$  can be calculated from Eq. (6) by iterative process for a given set of values of  $\xi$ ,  $n$ , and  $a$ . By making use of thus determined value of  $y$  we can obtain  $x$  from Eq. (8) for a given set of values of  $\xi$ ,  $q/q_1$ ,  $n$  and  $a$ . [Eq. (6) always has a trivial solution  $y=1$  and this must be abandoned.]

Substitution of the values of  $x$  and  $y$  obtained from Eqs. (6) and (8) into the adsorption isotherm given by Eq. (1) can yield the value of  $\omega$  for a given set of values of  $\xi$ ,  $q/q_1$ ,  $n$ , and  $a$ .

### 3. CALCULATIONS AND RESULTS

For illustrative purposes we have calculated theoretical isotherms for various values of  $n$ ,  $a$ , and  $q/q_1$ , and the results have been presented in Fig. 1 through Fig. 12. From these we see that various types of adsorption isotherms can be generated by varying the values of three parameters  $n$ ,  $a$ , and  $q/q_1$ . Unlike the case of Paper I, we see that the Type I isotherm can also be accounted for if we take small value of  $a$ .

To convert the reported adsorption data to those expressed in terms of monolayers adsorbed we have to know the monolayer capacity,  $v_m$ . To calculate the value of  $v_m$  we follow the procedure described in Paper I. First we take two data points in the lower region of  $\xi$  and calculations similar to those made in Paper I are performed for a given set of  $n$  and  $a$ . We repeat such calculations for various sets of values of  $n$  and  $a$  until the best overall fitting of theoretical results into experimental data is obtained. Such calculations have been made for

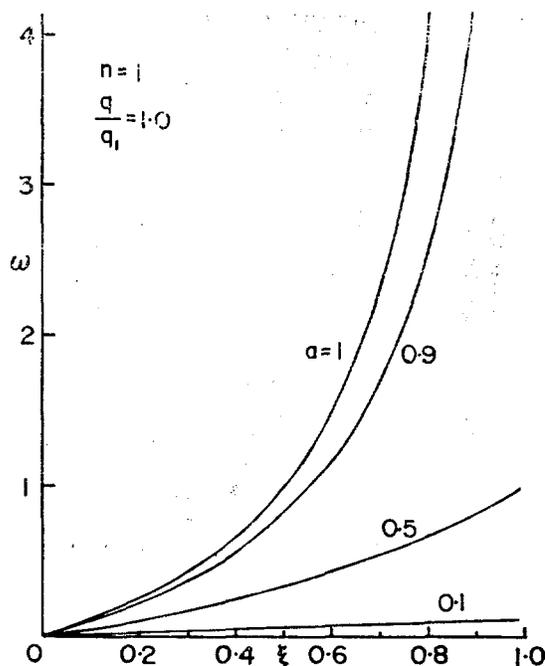


Fig. 1. Theoretical adsorption isotherms for  $n=1$  and  $q/q_1=1.0$ .

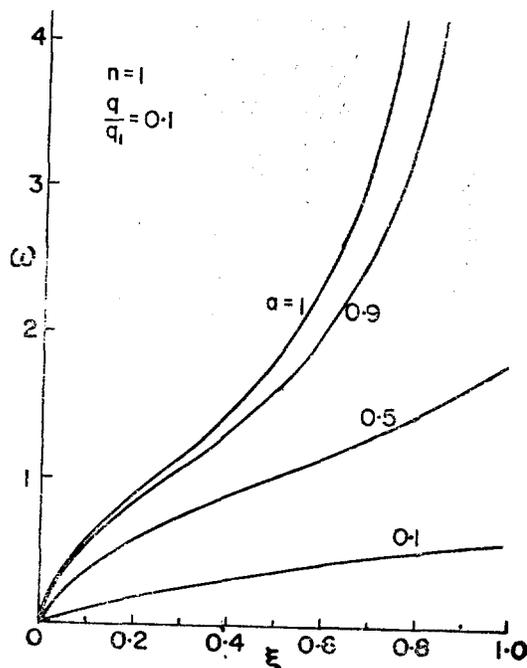


Fig. 2. Theoretical adsorption isotherms for  $n=1$  and  $q/q_1=0.1$ .

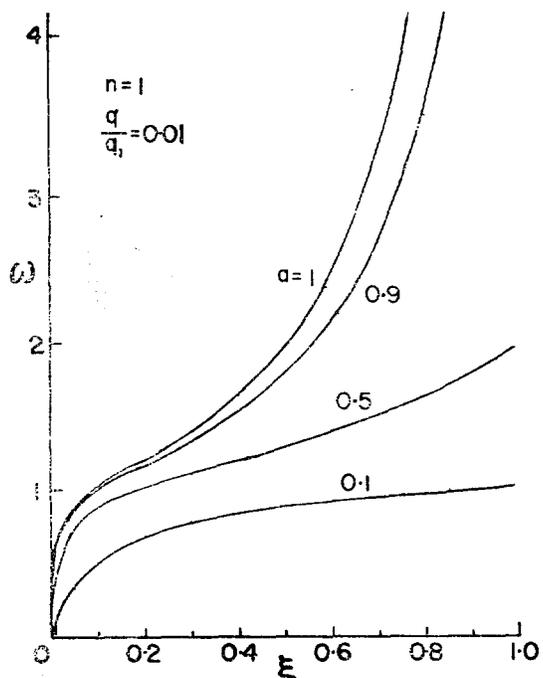


Fig. 3. Theoretical adsorption isotherms for  $n=1$  and  $q/q_1=0.01$ .

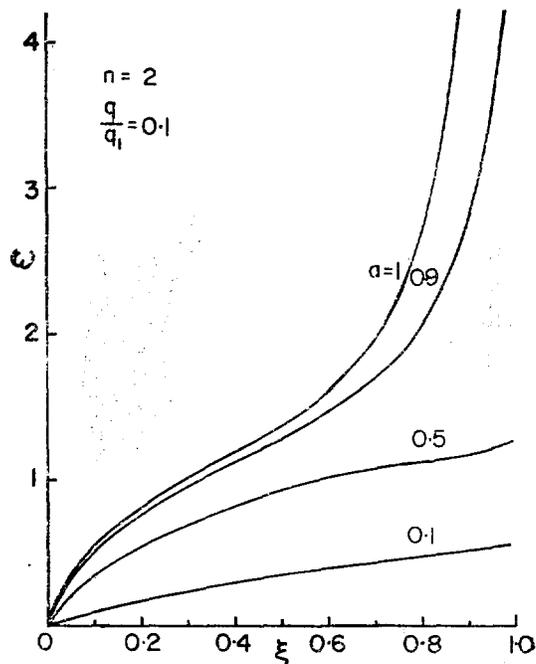


Fig. 5. Theoretical adsorption isotherms for  $n=2$  and  $q/q_1=0.1$ .

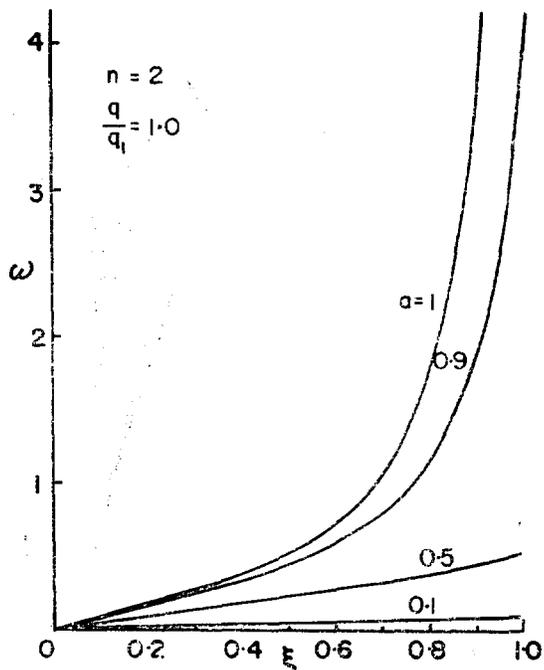


Fig. 4. Theoretical adsorption isotherms for  $n=2$  and  $q/q_1=1.0$ .

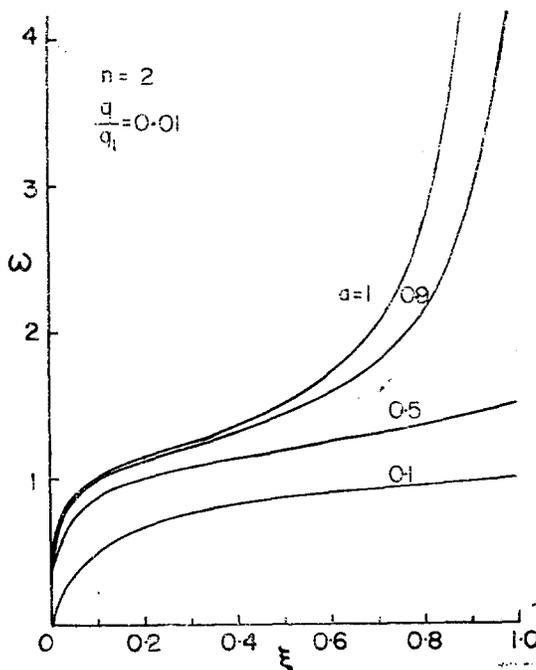


Fig. 6. Theoretical adsorption isotherms for  $n=2$  and  $q/q_1=0.01$ .

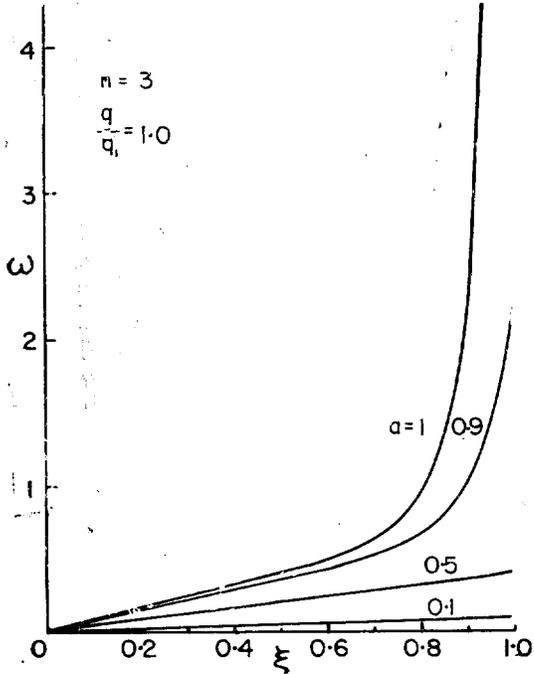


Fig. 7. Theoretical adsorption isotherms for  $n=3$  and  $q/q_1=1.0$ .

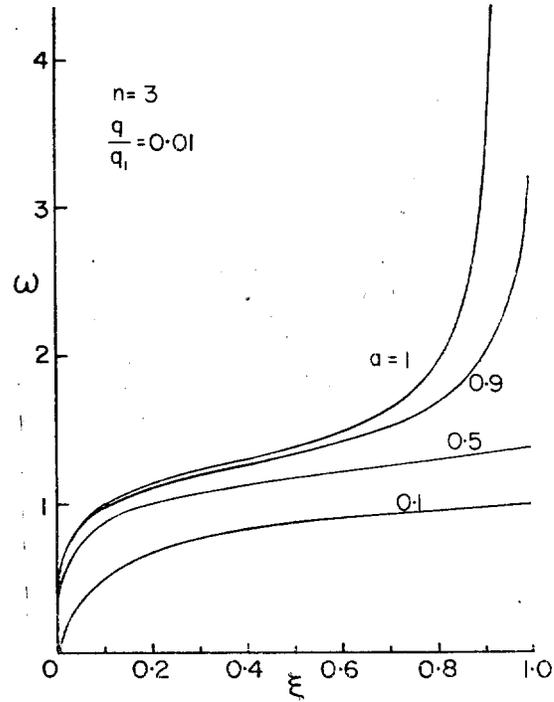


Fig. 9. Theoretical adsorption isotherms for  $n=3$  and  $q/q_1=0.01$ .

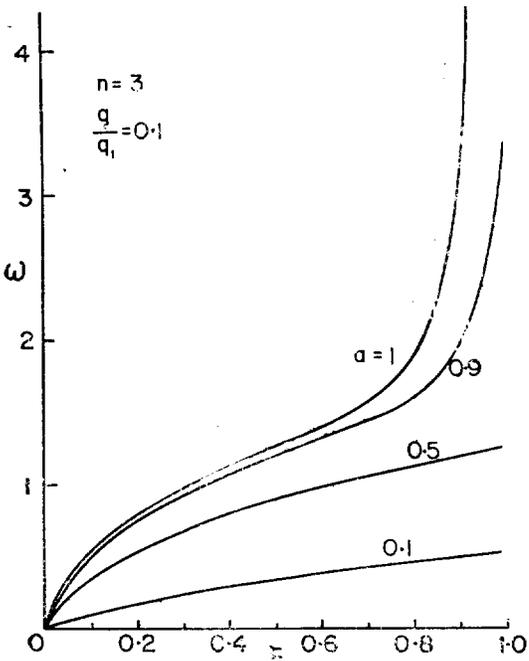


Fig. 8. Theoretical adsorption isotherms for  $n=3$  and  $q/q_1=0.1$ .

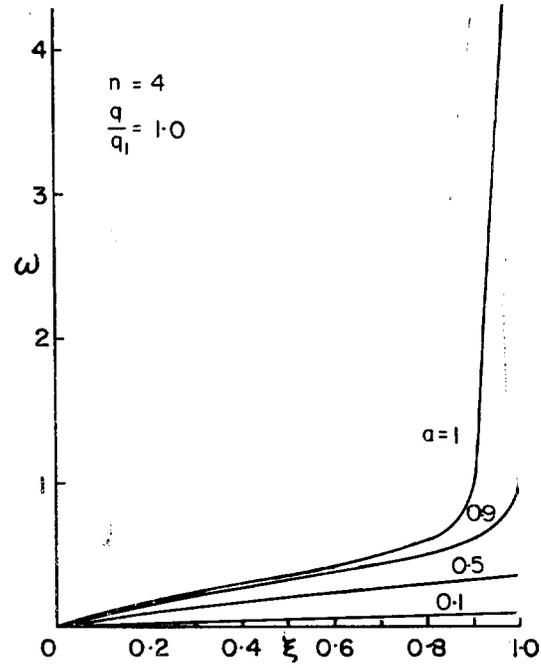


Fig. 10. Theoretical adsorption isotherms for  $n=4$  and  $q/q_1=1.0$ .

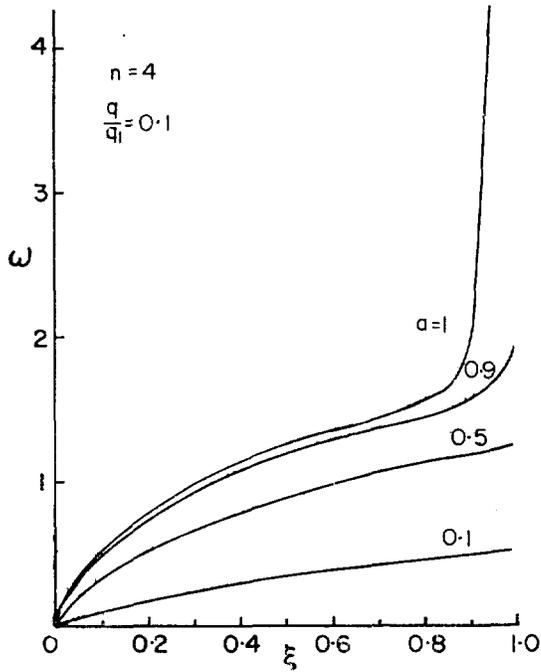


Fig. 11. Theoretical adsorption isotherms for  $n=4$  and  $q/q_1=0.1$ .

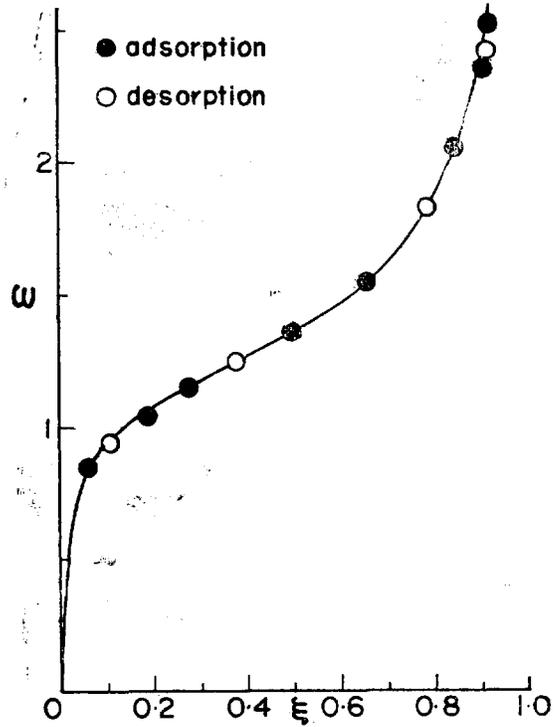


Fig. 13. Adsorption of argon on "Carbolac" carbon at  $-195.6^\circ\text{C}$ ;  $n=3.0$ ,  $a=0.90$ ,  $q/q_1=0.014$ .  
○, ●: experimental, —: theoretical.

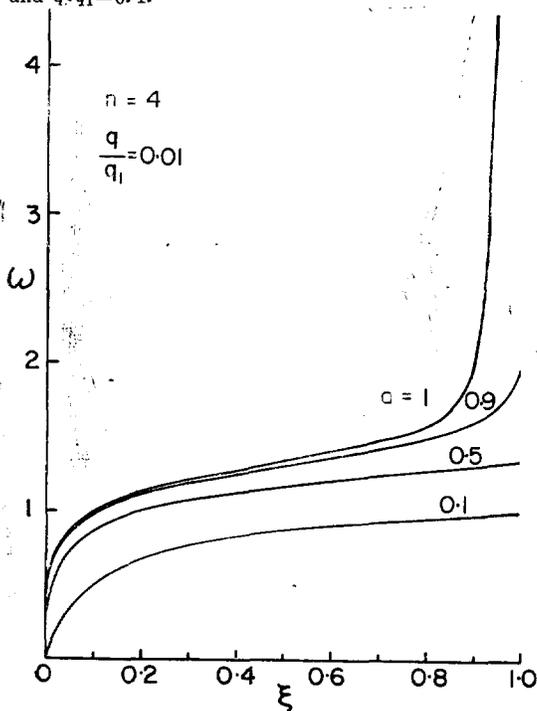


Fig. 12. Theoretical adsorption isotherms for  $n=4$  and  $q/q_1=0.01$ .

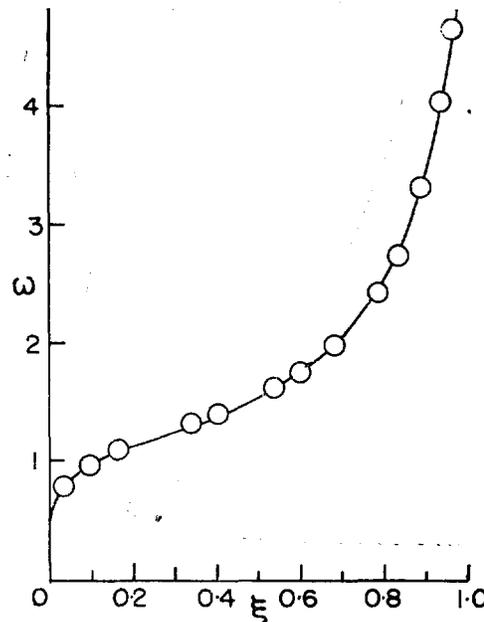


Fig. 14. Adsorption of nitrogen on alumina at  $-196^\circ\text{C}$ ;  $n=1.5$ ,  $a=0.89$ ,  $q/q_1=0.01$ .  
○: experimental, —: theoretical.

the following systems: argon on "Carbolac" carbon,<sup>2</sup> nitrogen on alumina,<sup>3</sup> propanol on oxidized iron film,<sup>4</sup> water on anatase,<sup>5</sup> butane on Iceland spar,<sup>6</sup> and nitrogen on Saran chars.<sup>7</sup> In all of these systems excellent agreements between theoretical results and observed data have been obtained and the results have been diagrammatically presented in Fig. 13 through Fig. 18.

#### 4. CONCLUSION AND DISCUSSION

The results of this work show that if the assumption that  $\gamma \rightarrow 1$  as  $\xi \rightarrow 1$ , which was adopted in Paper I, is discarded the previously developed theory can be made more versatile and flexible. Instead, one more parameter,  $a$ , is involved in the theory, which is given by Eq. (7). It is easy to see that the BET theory corresponds to

the case of  $n=a=1$ .

Though it is difficult to understand the direct physical meaning of  $a$ , it is conceivable that  $a$  depends on both the properties of adsorbate and adsorbent and characterizes the type and nature of adsorptions. Due to this the applicability of the theory developed here is not considered to be restricted to the physical adsorption only. Also, we think that two parameters  $q/q_1$  and  $a$  are by some means related to the heat of adsorption, which is not clear at this stage.

In this paper lateral intermolecular interactions are still not considered and the theoretical results are not expected to be good for the case where the effect of lateral interactions is appreciable. In fact we have tested the theory for adsorption of tetramethylsilane on oxidized iron film, but the result has shown that the theoretical isotherm

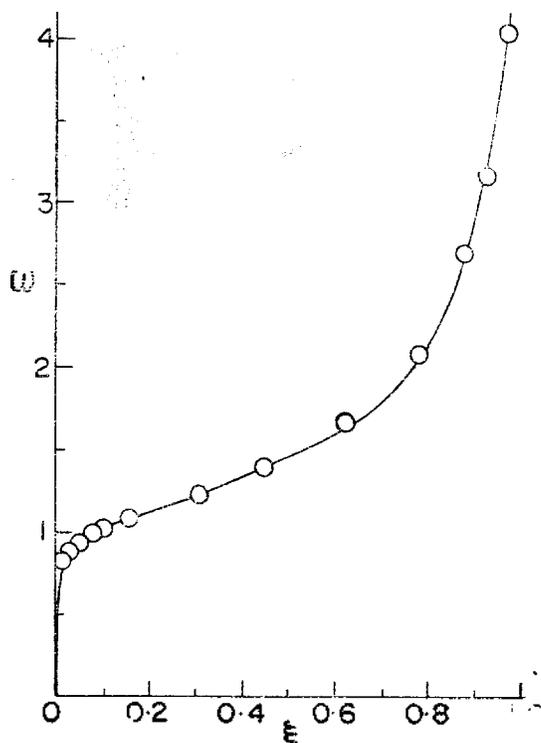


Fig. 15. Adsorption of propanol on oxidized iron film at 24.1°C;  $n=2.0$ ,  $a=0.90$ ,  $q/q_1=0.005$   
○: experimental, —: theoretical.

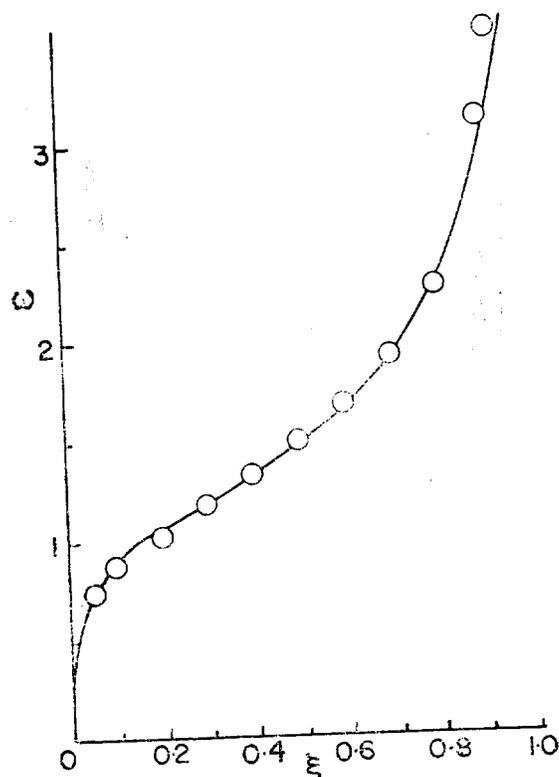


Fig. 16. Adsorption of water on  $\text{TiO}_2$  (anatase) at 25°C;  $n=1.5$ ,  $a=0.84$ ,  $q/q_1=0.02$ .  
○: experimental, —: theoretical.

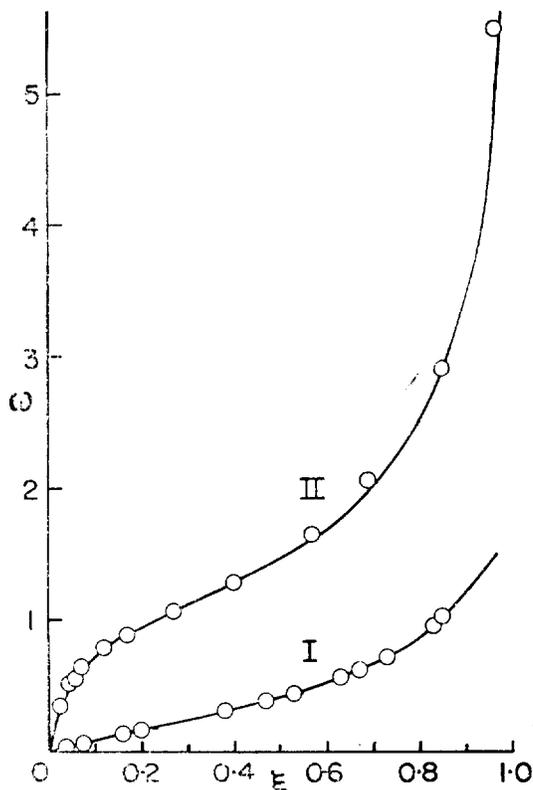


Fig. 17. Adsorption of butane on Iceland spar at 0°C.  
 I. the solid was outgassed at 25°C:  $n=2.0$ ,  $\alpha=0.78$ ,  $q/q_1=0.90$ ;  
 II. the solid was outgassed at 150°C:  $n=1.5$ ,  $\alpha=0.89$ ,  $q/q_1=0.05$ .  
 ○:experimental, —:theoretical.

deviates from the experimental one in the region  $\xi > 0.5$ . Since TMS molecules are quite large in size, one must expect that the effect of lateral interactions is substantial in this case.

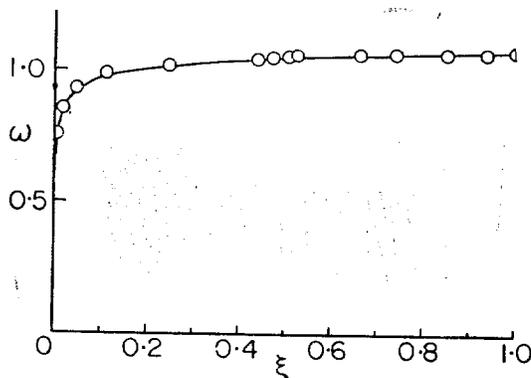


Fig. 18. Adsorption of nitrogen on a sample of Saran chars with no burn-off at  $-195.6^\circ\text{C}$ ;  $n=3.0$ ,  $\alpha=0.10$ ,  $q/q_1=0.0001$ .  
 ○:experimental, —:theoretical.

#### ACKNOWLEDGEMENTS

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