A Modified Derivation of BET Isotherm in Statistical Mechanics*.

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(Received June 2, 1948.)

1. S. Brunauer, P. H. Emmett and E. Teller(1) have generalized the Langmuir's adsorption theory to multimolecular adsorption and obtained an adsorption isotherm (BET isotherm). This adsorption isotherm gives a fair agreement with experimental data, and is now widely utilized in obtaining informations on the surface area of adsorbent. The original derivation of the isotherm has been done on the basis of kinetic theory; while several authors(2) have studied this problem from the point of view of statistical mechanics. In this paper, the author will derive the same isotherm by the saddle point method of statistical mechanics, free from erroneous calculation of permutations and combinations. The model of the present theory is almost the same as the other authors.

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* Read at the 1st Annual Meeting of the Chemical Society of Japan held at Tokyo on April 3, 1948.

(1) S. Brunauer, P. H. Emmett, and E. Teller. *J. Am. Chem. Soc.* **60** (1938), 3309.

(2) T. L. Hill; *J. Chem. Phys.* **14** (1946), 263.

M. Dole; *J. Chem Phys.* **16** (1948), 25.

2. The model, on which the theory is based, is analogous to the one in Hill's paper⑵; on the flat surface of adsorbent there are S sites for adsorption, $S_0, S_1, S_2, \ldots. S_j, \ldots..$ which are covered, respectively, by $0, 1, 2, 3, \ldots. j, \ldots.$ layers of adsorbed molecules. In equilibrium, the ratio of these S_js will become a constant value. For the sake of simplicity, the possible positions of adsorbed molecules in multilayers are assumed to be in a vertical line from any sites, as shown in Fig. 1.

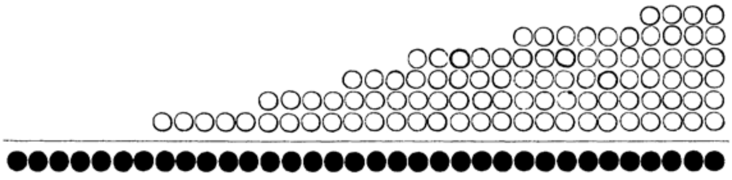

Fig. 1.

Now there are $S_1 + S_2 + S_3 + \cdots\cdots$ adsorbed molecules in the first layer, and therefore, the partition function for this layer is given by $f_1^{s_1+s_2+s_3+\cdots}$, where f_1 denotes the internal partition function of a molecule in the first layer. In the same manner, the partition function for the second layer is given by

$$f_2^{s_2+s_3+s_4+\cdots}$$

and so on.

It is assumed, as has been done in the BET theory, that the partition function of the j-th cell $(j > 1)$ is identical with each other, and they are denoted by f. The complete partition function for the adsorbed system is, then

$$\theta = \sum \frac{S!}{\prod\limits_0^\infty S_j!} f_1^{s_1+s_2+s_3+\cdots} f^{s_2+s_3+\cdots} f^{s_3+s_4+\cdots}$$

with the conditions $\sum\limits_0^\infty S_j = S$, $\sum\limits_0^\infty jS_j = N$; N means the total number of adsorbed molecules. θ may be rewritten as follows;

$$\theta = \sum \frac{S!}{\prod\limits_0^\infty S_j!} f_1^{s_1} (f_1 f)^{s_2} (f_1 f^2)^{s_3} \ldots (f_1 f^{j-1})^{s_j} \ldots$$

Putting $k_0 = 1,\ k_1 = f_1,\ k_2 = f_1 f,\ \ldots\ k_j = f_1 f^{j-1} (j \geq 1)$ .... (1)

then

$$\theta = \sum S! \prod_0^\infty \frac{k_j^{s_j}}{S_j!}$$

For calculating θ, then modular function ϕ is defined as

$$\phi = (\sum_0^\infty x^j k_j)^s$$

It is evident that θ is the coefficient of x^N in the expanded series of ϕ in x. According to the Cauchy's theorem,

$$\theta = \frac{1}{2\pi i}\oint \frac{(\sum x^j k_j)^s}{x^{N+1}}dx = \frac{1}{2\pi i}\int_{\alpha-i\infty}^{\alpha+i\infty} e^{s\log(\sum x^j k_j)-(N+1)\log x}dx$$

θ may be calculated approximately by the saddle point method. If the saddle point in integland is denoted by α, then it follows that

$$\log\theta \fallingdotseq S\log(\sum \alpha^j k_j) - N\log\alpha$$

where α can be determined by

$$\frac{d}{dx}\left\{S\,log\,(\sum x^j k_j) - (N+1)\,log\,x\right\} = 0$$

or

$$\frac{N}{S} = \frac{\sum_0^\infty j\alpha^j k_j}{\sum_0^\infty \alpha^j k_j} \quad \text{..................} \quad (2)$$

For the free energy F of the adsorbed system, it holds

$$-\frac{F}{kT} = \log\theta = S\log(\sum \alpha^j k_j) - N\log\alpha$$

For the partial potential μ of the molecules

$$\frac{\mu}{kT} = \frac{1}{kT}\frac{\partial F}{\partial N} = \log\alpha$$

For the abosolute activity of molecules is, then given by

$$\lambda = e^{\mu/kT} = \alpha$$

In the gaseous phase the absolute activily λ' is, as shown⁽³⁾, given by

$$\lambda' = \frac{p}{kT}\frac{h^3}{(2\pi mkT)^{3/2}j(T)}$$

In equilibrium, λ is equal to λ'; therefore,

$$\alpha = \frac{p}{kT}\frac{h^3}{(2\pi mkT)^{3/2}j(T)}$$

Substituting this value of α into equation (2), the adsorption isotherm are obtained in the form,

$$\frac{N}{S} = \frac{\sum j\alpha^j k_j}{\sum \alpha^j k_j}$$

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(3) R. H. Fowler and E. A. Guggenheim; "Statistical Thermodynamics", (1939).

From (1), it follows that

$$\frac{N}{S} = \frac{af_1}{(1-af)(1-af+af_1)}$$

or, in accordance with the BET's representation,

$$\frac{v}{v_m} = \frac{cx}{(1-x)(1-x+cx)}$$

where v is the total volume of adsorbed vapour, v_m the volume for the monolayer adsorption, respectively.

The constants c, x are respectively given by $c = \frac{f_1}{f}$ and $x = af$..

If it is assumed that the higher layers of adsorbed molecules other than the first are in liquid of soled state, then f can be represented by saturation pressure p_s, that is,

$$\frac{1}{f} = \frac{p_s}{kT}\frac{h^3}{(2\pi mkT)^{3/2}j(T)}$$

then

$$x = \frac{p}{p_s}$$

The constant c can be written in the following form,

$$c = \frac{f_1}{f} = Ke^{(E_1-E_L)/RT}$$

where E_1 and E_L are, respectively, the heat of adsorption to naked surface and the heat of vapourisation or sublimation.

Summary. (1) The BET adsorption isotherm was derived by statistical mechanics, using the saddle point method.

(2) The constants in BET isotherm can be represented by the internal partition functions of the adsorbed phase.

The author is indebted to Professor Dr. I. Sano, Dr. K. Suzuki and Dr. T. Sakaki for helpful comments.

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