ON THE POSSIBILITY OF SIMULTANEOUS FORMATION OF THE FIRST AND SECOND ADSORPTION LAYERS (QUASI-CHEMICAL METHOD)

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The work is devoted to the following problem: is it possible for the first and second adsorption layers to be formed simultaneously? Using the quasi-chemical method and the square-site model it is shown that under some physical conditions the simultaneous formation of the first and second layers can take place. Especially favorable conditions for such formation exist in the case of adsorption of rare gases on metals and ionic crystals.

1. Introduction

The question of whether or not the first and second adsorption layers can be formed simultaneously is a very important one in many adsorption problems. In the first accepted theory of adsoption isotherm by Brunauer, Emmett and Teller (1938) (BET) a mathematically flat surface of the crystal and the single-particle-site model was assumed. Therefore, it was assumed thet the simultaneous formation of the first and the next adsorption layers is possible. The BET theory was replaced by the more rigorous triangular-site model of Halsey (1952), who assumed that a particle cannot be adsorbed in upper layer unless there is a triangular array of three adsorbed particles forming a site for adsorption. The physical-adsorption isotherm based on the triangular-site model was given by Taylor, Longley and Bryant (1965) using the idea of Halsey and the Bragg-Williams (BW) approximation. Two-layer adsorption models were also given by Ballentine (1964) and by Betts and Hunter (1965). These two papers are based on the single-site-single-particle model. In the present paper we shall consider the possibility of simultaneous formation of the first and second adsorption layers in the description of the square-site model and the quasi-chemical method, which is more refined than the BW approximation. We shall give the adsorption isotherm and a qualitative discussion of the conditions under which it is possible to form the first and second layers on crystals simultaneously.

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2. The model

In order to answer the question stated in the Introduction it is necessary to know the number of particle groups which in the state of thermodynamical equilibrium are adsorbed in the first layer and may form a site for adsorption in the second (upper) layer. The arrangement of particles in the first layer forming such a group and also the number of particles in the group depends on the geometry of adsorption sites of the given adsorbent. The one-layer adsorption isotherm based on the square-site model was given by Hill (1950). In order to calculate, in the state of thermodynamical equilibrium, the number of squares occupied by four particles, he used the quasi-chemical method. Since the square occupied by four particles in the first layer may be regarded as the adsorption site of the second layer, we shall use the Hill model in the present paper. The characteristic of the square-site model is given in Fig. 1, where the first five columns are the same as in Hill's paper. The last two

Type of square	· · · ·	⊙ · · ·	⊙ ⊙ · ·	⊙ · · ⊙	⊙ ⊙ ⊙ ·	⊙ ⊙ ⊙ ⊙	⊙ ⊙ ⊗ ⊙ ⊙
Number of equivalent arrangements	1	4	4	2	4	1	1
Number of squares of this type	N_0	N_1	N_2'	N_2''	N_3	N_4'	N_4''

Fig. 1

columns characterize the possibility of the second layer being formed when the first layer is formed. The squares in columns 1 to 5 contain zero, one, two and three particles, respectively. The square in the sixth column has four particles and the square in the seventh has five of which four are adsorbed in the first layer and the fifth is adsorbed in the second layer on the site marked by the crosslet.

The number of adsorption sites (per unit area) B^* depends on the surface coverage θ in the first layer, and equals the number of sites on the surface of the adsorbent plus the number B' of sites which are formed by the adsorbed square in the first layer. Therefore

$$B^* + B + B', \tag{1}$$

and

$$B' = N_4/4. \tag{2}$$

N_4 denotes the number of squares occupied by four particles in the first layer and the number of squares occupied by five particles: four in the first layer and one in the second. Therefore

$$N_4 = N_4' + N_4''. \tag{3}$$

For the present case the equations (1) and (2) from Hill's paper take the following form

$$B^* = B + N'/4 + N''/4, \tag{4}$$

$$4N = N_1 + 2N_2' + 2N_2'' + 3N_3 + 4N_4' + 5N_4'', \tag{5}$$

where N denotes the number of adsorbed particles.

3. Theory

Commencing thermodynamical considerations, we introduce the following notation:

$-U$ — the first-layer-particle-adsorbent interaction energy;

$-U'$ — the second-layer-particle-adsorbent interaction energy;

W — the interaction energy of two nearest neighbour particles in the first layer;

W' — the interaction energy of two second neighbour particles in the first layer;

W'' — the interaction energy between two nearest neighbour particles from which one is in the first layer and the other in the second;

$$u = e^{U/kT}, \quad v = e^{U'/kT},$$

$$y = e^{-W/kT}, \quad t = e^{-W'/kT}, \quad z = e^{-W''/kT}; \tag{6}$$

μ — the electrochemical activity of particles in the gas phase;

λ — the absolute activity of adparticles;

$$\mu = \ln \lambda. \tag{7}$$

By $g^* (N_2', N_2'', N_3, N_4', N_4'', N, B^*)$ we denote the number of distinguishable arrangements of N adparticles on B^* sites which yield N_2' squares of type $2'$, N_2'' squares of type $2''$ and so on, to N_4'' squares of type $4''$. Then, the grand partition function Ω^* can be written in the form

$$\Omega^* = \sum_N \sum_{N_2'} \cdots \sum_{N_4''} g^* y^{(N_2' + 2N_3 + 4N_4' + 4N_4'')/2} t^{(N_2'' + N_3 + 2N_4' + 2N_4'')} \times$$
$$\times z^{4N_4''} (a_1\lambda)^{N-N_4''/4} (a_2\lambda)^{N_4''/4}, \tag{8}$$

where a_1 and a_2 are the partition functions of isolated adsorbed particle in the first and second layers, respectively. Following Hill, we assume

$$g^* = \sqrt{P^* Q^*}, \tag{9}$$

with

$$P^* = \frac{(B^* - N)! \, N!}{N_0! \, [(N_1/4)!]^4 \, [(N_2'/4)!]^4 \, [(N_2''/2)!]^2 \, [(N_3/4)!]^4 N_4'! \, N_4''!}, \tag{10}$$

$$Q^* = \frac{(B^* - N)! \, N!}{B^*!}, \tag{11}$$

where N_0 and N_1 are to be eliminated by use of (4) and (5). The maximum term in Ω^* is found by differentiating $\ln \Omega^*$ (replacing Ω^* by the expression standing under the summation sign in (8)) with respect to $N_2', \ldots, N_4''$, N.

The differentiation with respect to N gives

$$a_1\lambda = \alpha^2(1-\theta^*)/\theta^*, \tag{12}$$

where

$$\theta^* = N/B^*, \tag{13}$$

$$\alpha = N_1/4N_0. \tag{14}$$

The other differentiations (which lead to (15)), when combined with (12), give the adsorption isotherm.

We have

$$4\theta^* = \frac{4\alpha + 8\alpha^2 y + 4\alpha^2 t^2 + 12\alpha^3 y^2 t^2 + \left(\dfrac{4+5\beta}{1+\beta}\right)\alpha^4 y^4 t^4}{1 + 4\alpha + 4\alpha^2 y + 2\alpha^2 t^2 + 4\alpha^3 y^2 t^2 + \dfrac{5}{4}\alpha^4 y^4 t^4}, \tag{15}$$

where

$$\beta = \alpha Z^8 (a_2/a_1)^{1/2}. \tag{16}$$

From (16) we obtain

$$\alpha = \alpha(\theta^*, y, t, z, u, v).$$

It should be noted that differentiation with respect to N'_4 and N''_4 gives

$$N''_4 = \beta N'_4 \tag{17}$$

what, when combined with (3), gives

$$N'_4 = \frac{1}{1+\beta} N_4, \tag{18}$$

$$N''_4 = \frac{\beta}{1+\beta} N_4. \tag{19}$$

Therefore, we have determined the constants C' and C'' in the intuitive relations

$$N'_4 = C' N_4, \; N''_4 = C'' N_4.$$

For the first layer surface coverage θ we have

$$4\theta = \frac{4N - N''_4}{B^* - B'} = \frac{4N - N''_4}{B^*}, \tag{20}$$

whence

$$4\theta^* = \frac{B\theta + N''_4}{B^*} = \frac{4N}{B^*}. \tag{21}$$

Combining (15), (19) and (21) we have

$$4\theta + 4(4\theta - 1)\alpha + 2(4\theta - 2)(2y + t^2)\alpha^2 + 4(4\theta - 3)y^2 t^2 \alpha^3 + 4(\theta - 1)y^4 t^4 \alpha^4 = 0, \tag{22}$$

where

$$0 \leqslant \theta \leqslant 1. \tag{23}$$

Information on how the coverage θ will change the adsorption process after the simultaneous formation of the first and second layers is taken into account is given by the adsorption isotherm. However, acknowledging the approximative character of the adsorption

model, it seems that the use of the rate N_4'/N_4'' is adequate for obtaining qualitative information about second layer formation. From (18) and (19) we have

$$N_4''/N_4' = \beta. \tag{24}$$

For a_1 and a_2 appearing in β we have

$$a_1 = u a_{\text{osc}}^{(1)}, \tag{25}$$

$$a_2 = v a_{\text{osc}}^{(2)}, \tag{26}$$

with

$$a_{\text{osc}}^{(i)} = e^{-T_c^{(i)}/2T}(1 - e^{-T_c^{(i)}/T})^{-1}, \quad i = 1, 2; \tag{27}$$

where $T_c^{(i)} = h\nu^{(i)}/k$ and $\nu^{(i)}$ is the frequency of oscillations of particle in the first $(i = 1)$ and second $(i = 2)$ layers, respectively. We assume further that

$$a_{\text{osc}}^{(1)} = a_{\text{osc}}^{(2)},$$

therefore

$$(a_2/a_1)^{1/2} = (v/u)^{1/2} = e^{\frac{U'-U}{2kT}} \equiv e^{-s/2}, \tag{28}$$

where

$$s = (U - U')/kT \geqslant 0. \tag{29}$$

4. Numerical computations

The numerical compuions of $\beta(\theta)$ were carried out with the Elliott 803 computer in the Depertment of Numerical Methods of the University of Wrocław. For $\beta(\theta)$ from (24) and (28) we have

$$\beta(\theta) = \alpha(\theta) e^{-(8x'' + s/2)}, \tag{24a}$$

where

$$\alpha = \alpha(x, x'), \quad x = |W|/kT, \quad x' = |W'|/kT, \quad x'' = |W''|/kT,$$

and s is given by (29). The parameters x and x' appeared independently only in α, whereas the parameters x and s form a linear combination in the exponent of (24a). Therefore, for the purpose of numerical computations it was convenient to fix the value of the sum $c = 8x'' - \dfrac{s}{2}$, and then to determine one of the parameters x'' or s with the other one fixed. The values of the parameters x and x' are determined as follows. Taking into account that at room temperature $kT \simeq 0.03$ eV, we have accepted the following values of $|x|$ and $|x'|$: : $|x| = 0; 1; 10; 33$, and $|x'| = 0; 1; 10$. The value $|x| = |x'| = 0$ means that the adparticles in the first layer are noninteracting objects; the case $|x| = |x'|$ corresponds to the interaction energy of particles from the first layer, which is equal to kT (hence at room temperature $|x| = |x'| \simeq 0.03$ eV); the case $|x| = |x'| = 10$ corresponds to the interaction energy of the order of 0.3 eV and $|x| = 33$ to the interaction energy of the order of 1 eV.

The results of numerical computations may be divided into two groups: *I* and *II*, accor ding to the value of $|x|$. Group *I* includes the results for $|x| = 33$ and for differen values of the remaining parameters. In this group the values of $\beta(\theta)$ are very small (of the order of 10^{-20}). Group *II* comprises the results for $|x| = 0; 1; 10$. In this group $\beta(\theta)$ is greater than 10^{-2} for some values of c. In both groups there are some solutions without any physical
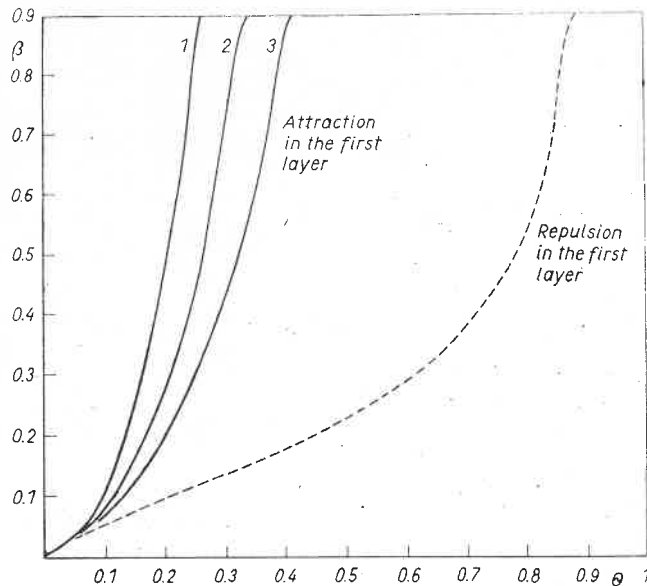

Fig. 2

meaning (for $x'' > 0$ and $s < 0$). The physically sensible results (for $c = -0.5$) are depicted in Fig. 2. This Figure exhibits two cases: 1) repulsion in the first layer (dashed curve), and attraction between particles in the first and second layers ($x, x' > c, x' < 0$); 2) attraction in the first layer (full curves), and attraction between layers.

5. Discussion of results

Generally speaking, the case 1) may correspond to the adsorption of: a) alkaline atoms on metals and ionic crystals; and b) polar molecules on nonmetal crystals. The case 2) may correspond to atomic adsorption on metals and semiconductors. A more detailed analysis of curves in Fig. 2 may be made. The dashed curve corresponds to the case 1) and was obtained for $x = 1$ and $x' = 0$; hence for $c = -0.5$ it follows that when $x'' < 0$ one must have $s > 1$. Therefore, this curve corresponds to an interaction energy between adparticles of the order of kT and to an adsorption energy greater than kT. This is the case of adsorption which at a given temperature T is associated with weak repulsion between adparticles in the first layer and with stronger binding of the first layer with the adsorbent. Hence this may be the case of adsorption of rare gases on metals when adatoms are polarized and are interac-

ting with weak electrostatic forces. This case may also correspond to the adsorption of rare gases on ionic crystals because the situation is now similar to the preceding one. The same physical conditions are also fulfilled in the adsorption of alkaline adatoms on metals, but in this case it is not very reasonable to suppose that the interaction between image dipoles would be of the order of kT. Therefore, in the former case we cannot state whether the second layer is formed simultaneously with the first layer.

The full curves in Fig. 2 correspond to various values of the parameters, namely: 1) $x = -10$, $x' = -1$, $s > 1$; 2) $x = -10$, $x' = 0$, $s > 1$; 3) $x = -1$, $x' = 0$, $s > 1$. These three curves correspond to successively weaker attraction between adparticles. These may be said to describe the cases of atomic adsorption on metals and semiconductors (for instance, Ge on W). The shape of these curves implies that the weaker attraction of adparticles in the first layer involves a slower formation of the second layer with increasing θ.

The foregoing shows that under some physical conditions simultaneous formation of the first and second adsorption layers may be observed. Therefore, it seems important for both theory and experiment to have more detailed studies performed along these lines.

REFERENCES

Ballentine, L. E., *Physica*, **29**, 1231 (1964).
Betts, D. H., Hunter, D. L., *Canad. J. Phys.*, **43**, 980 (1965).
Brunauer, S., Emmett, P., H., Teller, E., *J. Amer. Chem. Soc.*, **60**, 309 (1938).
Halsey, G., *J. Chem. Phys.*, **16**, 931 (1948).
Hill, T. L., *J. Chem. Phys.*, **18**, 988 (1950).
Taylor, L. H., Longley, W.W. Jr., Bryant, P. J., *J. Chem. Phys.*, **43**, 1184 (1965).