ANNALES

UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA LUBLIN – POLONIA

VOL. XXXI/XXXII, 23

SECTIO AA

1976/1977

Instytut Chemii UMCS Zakład Chemii Teoretycznej Kierownik: doc. dr hab. Władysław Rudziński

Władysław RUDZIŃSKI, Stefan SOKOŁOWSKI

Evaluation of the Energy Distribution Function in Physical Adsorption as the Problem of Laplace Transform. II. Spatial Distribution of Adsorption Energy Evaluated from the Third Gas—Solid Virial Coefficient

Wyznaczanie różniczkowego rozkładu energii adsorpcji jako problem transformaty Laplace'a. II. Określenie przestrzennego rozkładu energii adsorpcji z trzeciego współczynnika wirialnego gaz—ciało stałe

Определение дифференциального распределения энергии адсорбции как проблемы трансформации Лапласа. II. Определение пространственного распределения энергии адсорбции из третьего вириального коэффициента газ—твердое тело

INTRODUCTION

As in the first part of this publication series, we shall consider here the simple case, when the state of adsorbate molecule is fully described by the coordinates of the center of mass of adsorbate molecule. The evaluation of the energy distribution function provides, though quantitative, only a total description of gas—solid interactions, without giving any information about the macroscopic structure of adsorbent. Such a knowledge of gas—solid interactions is sufficient in the adsorption region, where interaction between adsorbed molecules can be negated. At higher adsorbate pressures, however, the contributions from the states in which two, three, or more adsorbate molecules are near each other, to the thermodynamics properties of adsorption systems, become considerable. Therefore, the full knowledge of the gas—solid interactions requires not only the energy distribution, but also the spatial distribution of adsorption energies.

In terms of localized adsorption this means the knowledge of the spatial distribution for pairs, triples, etc., of adsorption sites. These spatial distributions are included in appropriate gas—solid virial coefficients [1]. B_{3s}

involves the function $\omega_2(r_1, r_2)$, corresponding to the potential of the force between two adsorbate molecules, one located at $\overrightarrow{r_1}$, and the other at $\overrightarrow{r_2}$. This is a more complicated situation. Not only the energy distribution of sites but the spatial distribution for a pair of sites are required.

Barker and Everett [2] were the first to investigate the heterogeneity effects, using the virial description formalism. This problem has been considered in the last years by Steele [3] and Hill [4].

The purpose of this paper is to propose some methods for investigating the spatial energy distribution, on the basis of the real energy distribution $\chi(\varepsilon)$ evaluated in the first part of this publication series.

as goilg to be last of the THEORETICAL

Let us consider the expression for the third gas—solid virial coefficient B_{3s} [1, 5]

$$B_{35} = \iint_{V} \left[\left(1 + f_{1} \right) \left(1 + f_{2} \right) \widetilde{\omega}_{2} - \widetilde{\omega}_{2}^{\circ} \right] dr_{1} dr_{2}$$
(1)

$$f_{i} = \exp\left[-\mathcal{E}\left(\vec{r}_{i}\right)/kT\right] - 1, \quad \widetilde{\omega}_{2} = \exp\left[-\omega_{2}\left(\vec{r}_{1},\vec{r}_{2}\right)/kT\right] - 1$$

$$\widetilde{\omega}_{2}^{0} = \exp\left[-\omega_{2}^{0}\left(r_{12}\right)/kT\right] - 1$$
(2)

and $\omega_2^0 = \omega_2^0(r_{12})$ is the pair interaction energy in bulk phase, r_{12} is the intermolecular distance. The eq. (1) can be rewritten to the form [6]

$$B_{3s} = \iint_{V_s} \exp\left[-\frac{\mathcal{E}(\vec{r_1}) + \mathcal{E}(\vec{r_2})}{kT}\right] \exp\left[-\frac{\omega_2(\vec{r_1}, \vec{r_2})}{kT}\right] d\vec{r_1} d\vec{r_2} \quad (3)$$

Above V and V_s are the volumes of adsorbate and adsorbed phase, respectively, defined in the first part of this paper. The eq. (3) follows from the fact that out the surface phase V_s , the integrand in the integral (1) is equal to zero. Next, the contribution from the states in which the functions $(1+f_i)$ are near maximum to the integral (1), are predominant, when considering the positions within the surface phase V_s . Thus, the first term $(1+f_1)$ $(1+f_2)\tilde{\omega}_2$ is about 10¹⁰ times higher than the second term for typical adsorption systems at room temperatures [7].

There have been made many attempts to evaluate the integral (3). Apart from difficilties involved by heterogeneity, it is a very complicated problem. It is due to the fact that the interactions between two adsorbed molecules are perturbed by the presence of a solid surface.

Steele and Halsey [8] and next Freeman and Halsey [9] were the first to evaluate theoretically B_{3s} , but without taking into account the third-order interactions. Freeman [10] has pointed out experimentally the existence of the third-order effects in the adsorption of rare gases on graphitized black carbon. The first quantum-mechanical calculations of the third-order interactions are due to Sinanoglu and Pitzer [11].

Recent results are due to Wolfe and Sams [12] who have found that surface area calculations are rather insensitive to these threebody effects. The problem of evaluating the surface area in the presence of these three-body effects has been recently considered by Rudziński et al. [13] by using the more realistic three-dimensional model of adsorption.

We shall continue this point of view in the present paper, and consider the adsorption potential $\varepsilon(r)$, in the following form

$$\mathcal{E}(\vec{r}) = \begin{cases} \infty & \text{for } \vec{r} \in V_{d} \\ \mathcal{E}(\vec{r}) & \text{for } \vec{r} \in V_{S} \\ 0 & \text{for } \vec{r} \in V_{f} \end{cases}$$
(4)

Above V_a , V_s and V_f are volumes of adsorbent, of surface phase and of free gas phase, respectively. Let us assume later that for $r \in V_s$, the potential ε has the form

$$\mathcal{E}(\vec{r}) = \begin{cases} \infty & \text{for } - d \leq x < 0 \\ \mathcal{E}(\vec{r}_{s}) & \text{for } 0 \leq x < \Delta \\ 0 & \text{for } \Delta \leq x < \infty \end{cases}$$
(5)

Władysław Rudziński, Stefan Sokołowski

where r_s is the position on the adsorbent surface, considered as a plane. It is like a square-well potential, the γ value being simply the slow-collision distance between admolecule and adsorbent surface. By choosing the adsorption potential in the form as given in eq. (5), we assume that heterogeneity does not change the interactions depths γ and Δ , but only the strength of the gas—solid interactions. Now, we would like to explain the reason, for which such an assumption seems to be a good approximation.

Let us assume for instance the adsorbate molecules uniformly distributed in the adsorbent volume V. Then, in the case of identical adsorbent molecules interacting via LJ(n - n) potential with an admolecule, one gets the following results [1]

$$\mathcal{E}(x_{s}) = \left(\frac{n-3}{n-m}\right) \left(\frac{n-3}{m-3}\right)^{\frac{m-3}{n-3}} \mathcal{E}^{*}\left[\left(\frac{x^{*}}{x_{s}}\right)^{n-3} - \left(\frac{x^{*}}{x_{s}}\right)^{m-3}\right]$$
(6)

where

$$\mathcal{E}^{*} = \frac{2\pi N_{o} \omega^{*} (s^{*})^{m}}{m (m+1)}$$
(7)

In the above x_s is the distance from adsorbent surface, n, m, x^*, ω^* and s^* are parameters in the adsorbent-adsorbate interaction, and r_{12} is the appropriate intermolecular distance, N_0 being the number density (in atom/cm³) of the adsorbent, and

$$X = \left(\frac{1}{15}\right)^{\frac{1}{6}} S$$
(8)

It is well-known that the functions of LJ(m-n) type are not very sensitive to the choice of n and m. The interaction depth in the gas-solid interaction potential should therefore depend predominantly upon the value of x^* , and through it upon s^* . Next, it seems that, while the parameters describing the attraction strength between the pair of gas—solid molecules may change considerably the other parameters describing the slow-collision distances, change to a lower degree. For instance, it has been found by Crowell and Steele that for rare gases interacting with graphite, the interaction between an individual gas-solid pair, can be presented by a potential of the form

$$\omega(r_{12}^{*}) = -A\left[\left(r_{12}^{*}\right)^{-6} - \frac{1}{2}\left(s^{*}\right)^{6}\left(r_{12}^{*}\right)^{-12}\right]$$
(9)

From the values tabulated by Crowell and Steele, one sees, that, for example, s^* value for pair C—CH₄ is about 10% higher than that for pair C—Ne, whereas A value is higher by about 350%.

The heterogeneity of adsorbents arises from the presence of different molecules in the adsorbent volume V_s , or from the presence of molecules groupped in different ways. An interaction between an admolecule and a group of adsorbent molecules may be approximately treated as an interaction with some new chemical individuals. In both cases, the slow-collision parameters should not change considerably, when compared with the changes in attractive forces. Since the interaction depths, as pointed out, depend predominantly upon the slow-collision parameter s^* , hence the heterogeneity does not affect remarkably the interaction depth Λ . The heterogeneity effects should appear as rather different attraction energies in the surface phase V_s .

Now let us return to the third gas-solid virial coefficient. When evaluating the integral (3), we shall neglect contributions from all other admolecules configurations, except for the "quasi-planar" configurations, in which both admolecules are within surface phase V_s , i.e., in which both $0 \le x_1 \le \Delta$ and $0 \le x_2 \le \Delta$. According to the discussion given above, and according to the results of the papers [6, 7], the contributions from the configurations in which x_1 . $x_2 \in V_s$ are of order 10^{10} higher than those in which admolecules are out of surface phase V_s .

The theoretical investigations of B_{3s} , for homogeneous surface based on two-dimensional models of adsorption, lead to satisfactory agreement with the experiments. Consequently the deviations from planarity in adsorbed molecules are very small. This is possible when the interaction depth Δ is small. Thus, interaction energy ω_2 can be considered with good approximation as a function of intermolecular distance r_{12} only, between the adsorbed molecules [14]

$$\omega_2(r_{12}) = 4 \,\omega_0^3 \left[\left(\frac{s'}{r_{12}} \right)^{12} \left(\frac{s^3}{r_{12}} \right)^6 \right] \tag{10}$$

where:

$$\omega_{0}^{1} = \xi_{0}^{2} , \quad s = \xi_{0}^{-\frac{1}{6}} , \quad \frac{2}{3} \leq \xi \leq 1$$

It means that the slow-collision diameter remains practically unchanged, and therefore we shall take later s'=s.

Next, we shall accept this type of interaction for the case of heterogeneous surfaces, by introducing the concept of an "effective parameter ω_{eff} ", being a kind of average value of ω_0 averaging over all possible configurations of two adsorbed molecules on the adsorbent surface. With this concept we have

$$\omega_2(r_{12}) = 4 \omega_{eff} \left[\left(\frac{s}{r_{12}} \right)^{12} - \left(\frac{s}{r_{12}} \right)^6 \right]$$
(11)

Let us consider the two spatial distributions: 1) the fully patchwise spatial distribution, 2) the fully random spatial distribution. The patchwise spatial distribution means, that for the majority of configurations, in which two admolecules are at interaction distances, the both admolecules have the same adsorption energy. In such a case eq. (3) may be written in the form

$$B_{3s} = \int_{0}^{\infty} \chi(\varepsilon') \varepsilon \times \rho \left[\frac{2\varepsilon'}{kT}\right] d\varepsilon'$$

$$2\pi\Delta \int_{0}^{\infty} r_{12} \left\{ \exp\left[-\frac{4\omega eff}{kT} \left[\left(\frac{s}{r_{12}}\right)^{42} \left(\frac{s}{r_{12}}\right)^{6}\right] \right] - 1 \right\} dr_{12}$$
 (12)

The random spatial distribution means that if one admolecule is located anywhere on the adsorbent surface, the second one will have an average energy ε' , equal to

$$\bar{\mathcal{E}}^{'} = \int_{\mathcal{B}} \mathcal{E}^{'} \mathcal{X} \left(\mathcal{E}^{'} \right) d\mathcal{E}^{'}$$
(13)

where Ω is the range of possible variations of ε' . In this case the eq. (3) may be rewritten in the form

$$B_{3s} = \exp\left(\frac{\bar{\varepsilon}'}{kT}\right) \int_{0}^{\infty} \exp\left(\frac{\varepsilon'}{kT}\right) \mathcal{Z}\left(\varepsilon'\right) d\varepsilon' \cdot 2\pi \Delta \int_{0}^{\infty} r_{12} \left\{ \exp\left[-\frac{4\omega eff}{kT} \left[\left(\frac{s}{r_{12}}\right)^{12} - \left(\frac{s}{r_{12}}\right)^{6}\right]\right] - 1 \right\} dr_{12}$$
(14)

The two spatial distributions discussed above are some ideal cases, the real spatial distribution being only their better or worse approximations. The eqs. (12) and (14) provide a method of detection, if an investigated

adsorption system obeys the patchwise spatial distribution rather than the random one. For this purpose we notice that both the integral and

 $\int \exp\left(\frac{\mathcal{E}'}{KT}\right) \mathcal{K}\left(\mathcal{E}'\right) d\mathcal{E}'$

the average ε' can be easily calculated, by the method developed in the first part of this paper. Thus, the expression for B_{3s} from eqs. (12) and (14) can be regarded as two-parameter function of temperature, with unknown parameters Δ and ω_{eff} . These parameters may be found when fitting best the expressions (12) and (14), with respect to experimental values of B_{3s} . Although parameters Δ and ω_{eff} are chosen optimally the expressions (12) and (14) will approximate the experimental values of B_{3s} to a various degree. By comparing the experimental deviations one may detect whether the expression (12) or (14) is more adequate to describe the experimental behaviour of B_{3s} , and consequently, either the patchwise or the random spatial distribution is a more appropriate model for the investigated system.

NUMERICAL RESULTS AND DISCUSSION

In order to demonstrate the applicability of the procedure proposed above, we shall consider the experimental results of Sams et al. [15] concerning the adsorption of argon on graphitized carbon P33 (2700).

As it was mentioned in the first part, these are most accurate experimental data reported thus so far. It will be interesting to compare the results obtained here with the earlier theoretical results [12, 13, 16, 17], obtained with the assumption that the graphite P33 (2700) is a homogeneous adsorbent. Table 1 presents the results of our calculations, performed on the computer ODRA-1204 in the UMCS Department of Numerical Calculations. The numerical results show that the assumption of the patchwise spatial distribution of adsorption energies leads to negative values for both Δ and ω_{eff} which are of course physically meaningless. The physical meaning of the parameters Δ and ω_{eff} suggests that they must have still positive values.

Now, let us consider the values for Δ and ω_{eff} , obtained by assuming the fully random spatial distribution. From the values tabulated by Hirschfelder et at. [18] one sees, that parameter ω for two argon atoms in bulk phase interacting via LJ (12—6) potential is about 240 cal/ /mole. Johnson and Klein [17] assumed that the surface of graphite Władysław Rudziński, Stefan Sokołowski

The assumed model of adsorption	The gas-solid interaction depth Δ	The gas-solid interaction energy ω_{eff}
Patchwise distribution	$-2.65 \ 10^{-5} \ \text{\AA}$	-478 cal/mole
Random distribution	1.60 Å	226 cal/mole

Table 1. The results of numerical calculations for the experimental results of Sams, Constabaris and Halsey

P33 (2700) was fully uniform, and accepted the Sinanoglu-Pitzer potential. They obtained the value $\omega = 220$ cal/mole and s = 3.45 Å, whereas in bulk phase 3.41 Å. The theoretical analysis of Wolfe and Sams [12] yields the values 220 cal/mole and 3.43 Å, respectively, when accepting the Sinanoglu-Pitzer interaction potential, and 118.8 cal/mole and 3.46 Å, when accepting the LJ (12-16) potential. The small differences, which appear are, in our opinion, due to heterogeneity of the surface. The above results show that the spatial energy distribution for argon on graphite P33 (2700) is a highly random one. The best-fit results for the effective slow-collision diameter s, obtained by Johnson and Klein, and Wolfe and Sams, justify its identification with appropriate value for bulk phase, made in our calculations. Both Johnson and Klein, and Wolfe and Sams have found that the calculation of surface area for this adsorption system is insensitive to the three-body effects. According to theoretical results of Steele [3] and Hill [4], such a situation is characteristic of the adsorption systems with random energy distribution. Now let us consider the interaction depth Δ . It is equal to 0.47s = 1.60 Å. Thus, it is in fact a small parameter, as it was assumed by us.

On the basis of the above discussion we may conclude that the distribution of adsorption centers on graphite P33 (2700) surface must be described by the random distribution function.

REFERENCES

1. Pierotti R. A., Thomas H. E.: Physical Adsorption: The Interaction of Gases with Solids. J. Willey, New York 1971.

- 2. Barker J. A., Everett D. H.: Trans. Faraday Soc. 58, 1080 (1962).
- 3. Steele W. A.: J. Phys. Chem. 67, 2016 (1963).
- 4. Hill T. L.: J. Chem. Phys. 17, 762 (1949).
- 5. Pierotti R. A.: Chem. Phys. Letters 3, 385 (1968).
- 6. Rudziński W., Suprynowicz Z., Rayss J.: J. Chromatogr. 66, 1 (1972).
- Rudziński W., Waksmundzki A., Suprynowicz Z., Rayss J.: J. Chromatogr. 72, 221 (1972).

- 8. Steele W. A., Halsey G. D.: J. Phys. Chem. 59, 57 (1955).
- 9. Freeman M. P., Halsey G. D.: J. Phys. Chem. 59, 181 (1955).
- 10. Freeman M. P.: J. Phys. Chem. 62, 729 (1958).
- 11. Sinanoglu O., Pitzer K. S.: J. Chem. Phys. 32, 1279 (1960).
- 12. Wolfe R., Sams J. R.: J. Chem. Phys. 44, 2181 (1966).
- 13. Rudziński W.: Phys. Letters 42A, 519 (1973).
- 14. McLachlan A. D.: Mol. Phys. 7, 381 (1964).
- Sams J. R., Constabaris G. D., Halsey G. D.: J. Chem. Phys. 36, 1334 (1962).
- 16. Kirzan J. E., Crowell A. D.: J. Chem. Phys. 41, 1322 (1964).
- 17. Wolfe R., Sams J. R.: J. Chem. Phys. 44, 2181 (1966).
- Hirschfelder J. O., Curtis C. F., Bird R. B.: Molecular Theory of Gases and Liquids. J. Willey, New York 1954.

STRESZCZENIE

W części pierwszej pracy wskazano metodę wyznaczania funkcji dystrybucji energii adsorpcji z temperaturowej zależności drugiego współczynnika wirialnego gaz—ciało stałe. W niniejszej części wskazano, w jaki sposób można z temperaturowej zależności trzeciego współczynnika wirialnego gaz—ciało stałe uzyskać dodatkowe informacje na temat przestrzennego rozkładu energii adsorpcji.

РЕЗЮМЕ

В первой части работы был указан новый метод определения дифференциального распределения энергии адсорбции из второго вириального коэффициента газ—твердое тело. В следующей части показано, каким образом можно получить дальнейшие информации на тему пространственного распределения энергии адсорбции из третьего вириального коэффициента.

ivaluation of the Energy Distribution Constiction With Scient

as it was assumed by us.

On the basis of the above discussion we may conclude that the distribution of adsorption centers on graphily P33 (2700) surface must be described by the random distribution function

REFERENCES-

 Pieretti R. A. Thomari H. R. Physical Adsorption: The Interaction of Game with Solids J. Willey, New York 1979
 Sarker J. A. Everett D. H. Trans. Frankey Soc. 28, 1988 (1982).
 Stevie W. A. J. Phys. Chem. 57, 2016 (1963)
 Hill T. L. J. Chem. Phys. 17, 762 (1969)
 Pieretti L. A. Chem. Phys. Letters 3, 585 (1963).
 Hadathell W. Bupry no with Z. Bartet J. J. Chromatogr. 55, 1 (1972).
 Sudatesti W. Makemundzki A. Supry no with Z. Sayss J.7 J. Chromatogr. 75, 201 (1972).