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ESTIMATION OF THE SURFACE AREA OF ADSORBENTS FROM THE THIRD GAS–SOLID VIRIAL COEFFICIENT

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SUMMARY

A new method is proposed for the estimation of the surface area of adsorbents from the second and third gas–solid virial coefficients. The method is based on a three-dimensional model of physical adsorption, and is in addition an extremely simple one. The data needed can be easily obtained by gas chromatography.

INTRODUCTION

Virial expansion is at the present time the most promising and descriptive formula in the theory of physical adsorption of gases on solids. Virial expansion of the adsorption isotherm is the kind of expansion most often considered. This is due to the fact that the relationship obtained when the number of molecules adsorbed is treated as a function of the adsorbate density is the relationship most often investigated in experimental works concerning adsorption phenomena.

In the virial treatment of physical adsorption, the number of adsorbed molecules is expanded in a power series with respect to the density of the adsorbate phase, the coefficient at the $(n - 1)$th power of the density being called the nth gas–solid virial coefficient.

In the theoretical and experimental work done in this field so far, only the first two terms of this expansion are taken into account, these being the second and the third gas–solid virial coefficients, respectively.

The second gas–solid virial coefficient introduces the effect of the interaction between a single molecule and the adsorbent surface, while the third represents the effect of the interaction between two adsorbate molecules and the adsorbent surface. Since virial treatment is a most accurate expression, the properties of the adsorption systems determined on using this equation should also be accurate. In particular, one would expect that the use of the virial equation to estimate the surface area of an adsorbent will lead to good results.

The first theoretical papers along these lines were by BARKER AND EVERETT[1], followed by SAMS *et al.*[2]. They have shown how the second and third gas–solid virial coefficients may be used to determine the surface area of an adsorbent, and also to obtain information about the forces between the adsorbed particles. They were, simultaneously, the first to investigate three-body effects, *i.e.* of two adsorbate molecules plus adsorbent, in the virial data, with respect to the problem of estimation of surface area.

The theoretical calculations of SINANOGLU AND PITZER[3], YARIS[4] and MCLACHLAN[5] have shown that three-body effects can contribute considerably to the total interactions between the adsorbed molecules.

All three derivations lead to the same conclusion, *viz.* that the third-order interaction can be taken into account by introducing an additional term proportional to r^{-8} in the pair interaction potential valid for the bulk phase. The fluctuation, or dispersion part, of this third-order interaction is shown by them to yield a repulsion between the two molecules in a monolayer that amounts to 20–40% of the gas phase LJ (12, 6) potential minimum. The same energy, yields an additional attraction of about 10–20% LJ (12, 6) potential minimum when the two molecules are on top of one another, as in multilayer formation.

KRIZAN AND CROWELL[6] were the first to investigate the contribution of the three-body effects to the thermodynamic properties of adsorption systems. They rather considered adsorption systems as two-dimensional ones, the deviations from planar configurations of molecules being treated as a small parameter only.

JOHNSON AND KLEIN[7] also have presented analyses of experimental data in terms of a two-dimensional model, using the LJ (12,6,3) potential derived by SINANOGLU AND PITZER. The difference between the two papers lies only in the mode of evaluation of the proportionality constant η in the SINANOGLU AND PITZER calculations. The calculations of η made by KRIZAN AND CROWELL are of a purely theoretical nature, whereas JOHNSON AND KLEIN found η by using a "best-fit" procedure with experimental data.

Comparison of the two lots of result shows that the values of η calculated by KRIZAN AND CROWELL are in general two to five times higher than the best-fit values obtained by JOHNSON AND KLEIN. Furthermore, the surface area calculated from these data seems to depend strongly on the factor η. Thus, there should be strong discrepancy between the surface areas obtained by means of the two procedures mentioned above.

The procedure of JOHNSON AND KLEIN has been next criticized by WOLFE AND SAMS[8] on the basis that the best-fit values of η are probably quite sensitive to one's choice of potential parameters for the bulk phase. Their object was to investigate the consistency between theoretical results obtained in three different ways, and the results obtained by using the best-fit procedure. The most interesting result obtained by them is that, although η is extremely sensitive to the choice of bulk potential parameters, any reasonable choice of the bulk parameters will lead to substantially the same value for the surface area.

Moreover, they are of the opinion that the three-body effects in physical adsorption may be smaller than was previously supposed.

The last conclusion is in strong contradiction to the earlier suggestions of KRIZAN AND CROWELL and JOHNSON AND KLEIN. Thus, it seems that the determination of the surface area from the third gas–solid virial coefficient still remains an unresolved problem because of the difficulties involved due to the three-body effects.

In the current paper we once more consider this problem, using a three-dimensional model of physical adsorption. The existence of the third-order interaction permits some approximations which then lead to an exceptionally simple expression for the surface area. The experimental data needed can be easily obtained by gas chromatography.

THEORETICAL

It has been shown in our previous paper[9] that the second and third gas-solid virial coefficients B_{2s} and B_{3s} may be written in the following form:

$$B_{2s} = \iint\limits_{V_s}\left\{\exp\left[\frac{W_1(\boldsymbol{r}_1)}{-kT}\right]\right\}\mathrm{d}\boldsymbol{r}_1 \tag{1}$$

$$B_{3s} = \iint\limits_{V_s}\left\{\exp\left[\frac{W_1(\boldsymbol{r}_1)+W_1(\boldsymbol{r}_2)}{-kT}\right]\right\} \times \left\{\exp\left[\frac{\omega_2(\boldsymbol{r}_1,\boldsymbol{r}_2)}{-kT}\right]-1\right\}\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2 \tag{2}$$

where

V_s = volume of surface phase

$W_1(\boldsymbol{r}_i)$ = potential energy of adsorption of a single molecule, whose centre is at point $\boldsymbol{r}_i$

$\omega_2(\boldsymbol{r}_1, \boldsymbol{r}_2)$ = interaction energy between two adsorbate molecules in the presence of solid

k = Boltzmann constant

T = absolute temperature.

Next, by using an algebraic method, the following expression has been obtained for the average density ϱ_1 in the adsorbed phase[10]:

$$\bar{\varrho}_1 = \frac{\bar{P}}{kT} + \frac{b_2}{b_1^2}\left(\frac{\bar{P}}{kT}\right)^2 + \ldots \tag{3}$$

where $\bar{P}$ is the average pressure in the adsorbed phase and b_1 and b_2 are cluster-type integrals, dependent on configuration integrals[11]. For example:

$$b_1 = \frac{1}{V_s} B_{2s} \tag{4}$$

$$b_2 = \frac{1}{2V_s} B_{3s} \tag{5}$$

The basic idea of our method is to consider the retention data from a region of as small as possible concentration of solute. We have suggested in our previous paper that for this region the simplest form of the retention equation of CONDER AND PURNELL[12] may be used. Thus:

$$jV_R = V_f + V_s \frac{\bar{\varrho}_1}{\varrho_0} \tag{6}$$

where

j = James–Martin compressibility factor

V_f = free gas phase volume

ϱ_0 = adsorbate density in free gas phase.

Using this expression, the following relationship between the adsorbate density ϱ_0 and the retention data has been developed, and is believed to be valid at very small concentrations of solute:

$$jV_R - V_f = B_{2s} + \varrho_0 B_{3s} \tag{7}$$

However, the above equation is in fact valid only for the case of infinite dilutions of solute. To establish the connection between the retention data and the gas–solid virial coefficients for the case of finite concentrations of solute, we consider the retention equation of CONDER AND PURNELL[12] in the form valid for all concentrations of solute:

$$V_R - V_f = F \cdot y \cdot V_s \frac{\partial \bar{\varrho}_1}{\partial \varrho_0} \tag{8}$$

where

F = compressibility factor depending upon column conditions
y = mole fraction of solute in free gas phase.

We then follow the procedure described in our previous paper. According to this procedure, we substitute the term $\bar{P}/kT$ in eqn. 3 with its value for the adsorbate phase considered to be that for an ideal gas, *viz.*

$$\frac{\bar{P}}{kT} = B_{2s} \frac{P_0}{kT} \tag{9}$$

where P_0 is the average pressure in the free gas phase. Next, we assume that at very small concentrations of solute, the free gas phase can still be considered as an ideal one. Inserting eqn. 9 into eqn. 3, we get a first correction for the non-ideality of the adsorbed phase. We are of the opinion that this correction is satisfactory for the region of very small concentrations considered here. Thus, we get:

$$\bar{\varrho}_1 = \frac{B_{2s}}{V_s} \varrho_0 + \frac{B_{3s}}{2V_s} \varrho_0^2 + \cdots \tag{10}$$

Inserting eqn. 10 into eqn. 8 we get:

$$V_R - V_f = F \cdot y \cdot (B_{2s} + \varrho_0 B_{3s}) \tag{11}$$

It follows from eqn. 11 that the plot $(V_R - V_f)$ *versus* ϱ_0 should yield a straight line, having a slope of FyB_{3s}, and intercept FyB_{2s}.

Now, we want to show how the surface area S can be calculated from the virial coefficients B_{2s} and B_{3s}. To do this, we assume the adsorption surface to be a plane (let it be an xy plane), and the adsorption potential $W_1(\mathbf{r}_i)$ to depend on the distance z from the surface. Next, we approximate the adsorption potential $W_1(\mathbf{r})$ by the following square-well function:

$$W_1(\mathbf{r}) = W_1(z) = \begin{cases} +\infty & \text{for } 0 \leqslant z < a \\ W_{\text{min.}} & \text{for } a \leqslant z < b \\ 0 & \text{for } b \leqslant z < +\infty \end{cases} \tag{12}$$

It is well-known that the above function is a good approximation for adsorption potentials when the parameters a, b, and $W_{\text{min.}}$ are suitably chosen. In addition, the above function allows for a very precise definition of the surface volume V_s, and therefore for its accurate determination. This problem has been largely discussed in our previous paper.

Next, we shall consider the interaction energy to have the form:

$$\omega_2(\mathbf{r}_1,\mathbf{r}_2) = \begin{cases} +\infty & \text{for } O \leqslant /\mathbf{r}_1 - \mathbf{r}_2/ < D \\ \omega_{\text{min.}} & \text{for } D \leqslant /\mathbf{r}_1 - \mathbf{r}_2/ < RD \\ O & \text{for } RD \leqslant /\mathbf{r}_1 - \mathbf{r}_2/ < +\infty \end{cases} \tag{13}$$

Let us now use functions 12 and 13 to evaluate coefficients B_{2s} and B_{3s}. We must first remark, however, that the result of the integration depends on the relations between the parameters $(b - a)$, D, and R. We shall later assume that $(b - a) \approx 0.1\, D$, and $R \approx 2$ (ref. 13). This is in accordance with the true physical situation in the majority of adsorption systems investigated in practice. Let us introduce the following notations:

$$\begin{aligned} \Omega_{1D} &= 6D^2(b-a)^2 - (b-a)^4 \\ \Omega_{1RD} &= 6R^2D^2(b-a)^2 - (b-a)^4 \\ \Omega_{2D} &= 3D^3(b-a) - \frac{7}{2}D^2(b-a)^2 - \frac{5}{3}D(b-a)^3 - \frac{1}{4}(b-a)^4 \\ \Omega_{2RD} &= 3R^3D^3(b-a) - \frac{7}{2}R^2D^2(b-a)^2 - \frac{5}{3}RD(b-a)^3 - \frac{1}{4}(b-a)^4 \end{aligned} \tag{14}$$

With the above notation, integration of eqns. 1 and 2 yields:

$$B_{2s} = S(b-a)\exp\left(\frac{W_{\text{min.}}}{-kT}\right) \tag{15}$$

$$\begin{aligned} B_{3s} = &-\left\{\frac{\pi S}{6}\,\Omega_{1D}\exp\left[\frac{2W_{\text{min.}}}{-kT}\right] + \frac{\pi S}{3}\,\Omega_{2D}\exp\left[\frac{W_{\text{min.}}}{-kT}\right]\right\} + \\ &\left\{\frac{\pi S}{6}(\Omega_{1RD} - \Omega_{1D})\exp\left[\frac{2W_{\text{min.}}}{-kT}\right] + \right. \\ &\left.\frac{\pi S}{3}(\Omega_{2RD} - \Omega_{2D})\exp\left[\frac{W_{\text{min.}}}{-kT}\right]\right\}\left\{\exp\left[\frac{\omega_{\text{min.}}}{-kT}\right] - 1\right\} \end{aligned} \tag{16}$$

Considering the second term in eqn. 16, let the first $W_{\text{min.}}$ be unperturbed, *i.e.* the same as in the bulk phase, then for the majority of the adsorption systems investigated in practice $\omega_{\text{min.}}/-k$ is from about 100° K, for simple gases, to about 400° K, for many organic compounds[14]. The adsorbates which are most often used in surface area measurements are simple gases, so that we shall later use $(\omega_{\text{min.}}/-k) = 100°$ K in our considerations. In addition, according to the theoretical results of SINANOGLU AND PITZER, the value $\omega_{\text{min.}}$ in the adsorbed phase should be about 50% smaller than that for the bulk phase, because of the third-order interactions. The last argument decreases our estimated value of $\omega_{\text{min.}}/-k$ to about 50° K.

The temperature regions which are most often investigated in practice are close to room temperature, *i.e.* they are about 300° K. Thus, to underestimate the most probable value of exp $[\omega_{\text{min.}}/-kT]$, we can reckon that $(\omega_{\text{min.}}/-kT) \approx 1/6$, so that $\exp[\omega_{\text{min.}}/-kT] \approx 1.10$, and the total factor $\{\exp[\omega_{\text{min.}}/-kT] - 1\}$ will be of the order 10^{-1}. The remaining factor in the second term in eqn. 16 is of the same order as the first term in the equation. Therefore, we shall neglect the second term in comparison with the first.

Now consider once more the first term in eqn. 16. The value $W_{\text{min.}}/-k$ for the majority of simple gases on typical adsorbents is of the order of about 6000° K (ref. 13). Thus, at room temperature the total factor $\exp[W_{\text{min.}}/-kT]$ will be of the order 10^5. This enables us to neglect the second component in the first term of eqn. 16, by comparison with the first, containing the second power of $\exp[W_{\text{min.}}/-kT]$. With the above approximations, the expression for B_{3s} reduces to the following:

$$B_{3s} = -S\pi D^2(b-a)^2 \exp\left[\frac{2W_{\text{min.}}}{-kT}\right] \tag{17}$$

Dividing B_{3s} given as above by $B_{2s}{}^2$ given by eqn. 15, we get:

$$S = -\pi D^2 \frac{B_{2s}{}^2}{B_{3s}} \tag{18}$$

Thus, we have obtained an extremely simple formula for the surface area, and the presence of the third-order interaction is here rather a favourable circumstance.

The value D which is used in eqn. 18 remains to be discussed, since third-order interaction effects also change the slow-collision diameter, though only to a small extent according to SINANOGLU AND PITZER's theory. The above assumptions are additionally supported by the results obtained by WOLFE AND SAMS. Accordingly, the value for D for the bulk phase may be used in eqn. 18, which (apart from simplicity) is an additional advantage of this equation.

EXPERIMENTAL

To illustrate our method, we have measured the surface area of the Schuchardt silica gel, which is acceptable for cyclohexane and carbon tetrachloride. In these measurements we used a 2 m-long chromatographic column, containing 4 g of 80–120 mesh silica gel, produced by Schuchardt in Munich, G.F.R.

To plot $V_N = V_N(\varrho_0)$, we used the following sample sizes of solute: 0.1 µl, 0.2 µl, 0.3 µl, 0.5 µl, 0.8 µl, and 1.0 µl. It was found that the concentrations of solute in our chromatographic column, obtained with these sample sizes vary from about 10^{-5} to about 10^{-4} mole/l.

The measurements were performed with the Polish apparatus "Chromatoprep N-502", using a katharometer as detector. Hydrogen was used as carrier gas, with a flow-rate of about 50 ml/min.

RESULTS AND DISCUSSION

The results of our measurements and calculations are presented in Tables I and II.

First, we shall explain how the values B_{2s} and B_{3s} were obtained. The experimental function $V_N = V_N(\varrho_0)$ was interpolated by means of a polynome of the second order, *viz.* $V_N = B_{2s} + B_{3s}\varrho_0 + B_{4s}\varrho_0{}^2$. The calculations were performed numerically, and the procedure of the smallest areas was included in the program, to

TABLE I

RESULTS OF MEASUREMENTS AND CALCULATIONS FOR CYCLOHEXANE ADSORBED ON SCHUCHARDT'S SILICA GEL

Temperature (°K)	B_{2s} *(l/g)*	B_{3s} *(l²/mole·g)*	B_{2s}^2/B_{3s} *(moles/g)*	*Surface area from virial expansion (m²/g)*	*Surface area from BET method (m²/g)*
359.8	$2.73 \cdot 10^{-2}$	-10.59	$-7.03 \cdot 10^{-5}$	58.6	11.9
368.9	$2.19 \cdot 10^{-2}$	-5.13	$-9.30 \cdot 10^{-5}$	77.5	16.1
374.5	$1.93 \cdot 10^{-2}$	-4.33	$-8.58 \cdot 10^{-5}$	71.5	18.3
383.9	$1.54 \cdot 10^{-2}$	-2.63	$-9.02 \cdot 10^{-5}$	75.2	15.6
410.5	$8.53 \cdot 10^{-3}$	-0.94	$-7.77 \cdot 10^{-5}$	64.7	13.2
426.2	$6.49 \cdot 10^{-3}$	-0.59	$-7.05 \cdot 10^{-5}$	58.7	12.4
Average values (over temperature)			$-8.12 \cdot 10^{-5}$	67.7	14.6

analyse experimental deviations. The function $V_N = V_N(\varrho_0)$ was measured chromatographically, using the method recommended by CONDER[15], *i.e.* by considering the positions of peak maxima.

Next the values B_{2s}^2/B_{3s} for different temperatures were considered. According to the results obtained in the theoretical section, they should be temperature-independent ones. It can be seen from Tables I and II that there is no regular relationship between these values and the absolute temperature. The differences between them are probably due to experimental uncertainties. Thus, even when temperature dependence exists, it is smaller than the changes due to experimental errors.

Finally, we have calculated the surface areas S, and compared them with the areas calculated by the BET method, being the one most widely known and most often used so far.

Before presenting the results of these calculations, we want to explain how the values of D for carbon tetrachoride and cyclohexane were found. The value of D used for carbon tetrachloride was $D = 6.1$ Å, found earlier by LAUGER[16] from the transport properties of gaseous carbon tetrachloride. The appropiate value for cyclohexane was calculated from liquid densities, by using the WASSENBERG–BALLANDIN formula[17], and has been found to be equal to 6.6 Å.

TABLE II

RESULTS OF MEASUREMENTS AND CALCULATIONS FOR CARBON TETRACHLORIDE ADSORBED ON SCHUCHARDT'S SILICA GEL

Temperature (°K)	B_{2s} *(l/g)*	B_{3s} *(l²/mole·g)*	B_{2s}^2/B_{3s} *(moles/g)*	*Surface area from virial expansion (m²/g)*	*Surface area from BET method (m²/g)*
359.8	$4.30 \cdot 10^{-2}$	-20.77	$-8.9 \cdot 10^{-5}$	62.6	13.1
374.5	$2.85 \cdot 10^{-2}$	-8.87	$-9.1 \cdot 10^{-5}$	64.0	13.9
393.0	$2.25 \cdot 10^{-2}$	-2.94	$-9.9 \cdot 10^{-5}$	69.6	14.3
410.5	$1.20 \cdot 10^{-2}$	-2.09	$-7.0 \cdot 10^{-5}$	49.2	9.9
419.5	$9.85 \cdot 10^{-3}$	-1.24	$-7.8 \cdot 10^{-5}$	54.7	12.0
426.2	$8.69 \cdot 10^{-3}$	-0.79	$-9.5 \cdot 10^{-5}$	66.8	13.6
Average values (over temperature)			$-8.9 \cdot 10^{-5}$	62.7	12.8

To use the BET method, we first calculated the adsorption isotherms for each temperature by considering them to be equal to ($B_{2s}\varrho + B_{3s}\varrho^2 + B_{4s}\varrho^3$). In this way six adsorption isotherms were obtained both for cyclohexane and for carbon tetrachloride. The BET values of the areas, calculated from these isotherms, are presented in Tables I and II. It is seen that like the virial expansion values, they are not temperature-dependent, though they do differ a little because of experimental errors.

One would expect the virial expansion values for surface area to be greater than those calculated by the BET method. The explanation for this is very simple as in the BET theory the lateral interactions are completely neglected. These lateral interactions have an effect of decreasing the effective area of adsorbent, since the repulsive part of these interactions contributes predominantely to the total interaction effect. This effective area is identified with the real area in the BET theory.

The most interesting result obtained here is, in our opinion, the degree of influence of the lateral interactions on the calculated surface areas. It seems that this effect is much greater than previously supposed.

TABLE III

RESULTS OF MEASUREMENTS AND CALCULATIONS FOR THE DATA OF SAMS *et al.*[2] CONCERNING ADSORPTION OF ARGON ON GRAPHITIZED CARBON BLACK P33.

Temperature (°K)	B_{2s} *(cm³/g)*	B_{3s} *(cm⁶/mole·g)*	*Surface area from three-dimensional treatment according to eqn. 18 (m²/g)*	*Surface area from two-dimensional treatment of* SAMS *et al. (m²/g)*
240.019	0.0812	− 91.1	—	
220.393	0.1158	− 123.5	—	
207.773	0.1508	− 136.5	—	
175.082	0.3650	− 425.7	—	
166.135	0.4933	− 442.9	—	
158.077	0.6720	− 248.7	—	
150.140	0.9421	631.9	—	
145.114	1.1850	2052.0	—	
140.607	1.4802	5215.0	15.8	9.0

Our results are now compared with the results obtained by SAMS *et al.* for argon adsorbed on graphitized Carbon Black P33 (ref. 2). The calculations of SAMS *et al.* are based on a two-dimensional model where lateral interactions are taken into account. They are included in Table III. In addition, the ratio $B_{2s}{}^2/B_{3s}$ has been plotted as a function of absolute temperature in Fig. 1. It is seen from this figure that one may observe a temperature dependence of $B_{2s}{}^2/B_{3s}$ when investigating wider temperature regions, especially at low temperatures. This is due to the fact that at low temperatures the second term in eqn. 16, which includes the factor $\{\exp[(\omega_{\text{min.}}/-kT)] - 1\}$ cannot be neglected. On the other hand, at higher temperatures, the value $B_{2s}{}^2/B_{3s}$ in Fig. 1 depends only slightly on temperature, *i.e.* this is the temperature region for which our assumptions are valid. One may extract from this a simple test for choosing the temperature region which is appropriate for surface area measurements, when using eqn. 18. This is the region of the plateau in the plot $B_{2s}{}^2/B_{3s}$ *versus* T. However, it is not recommended that regions of very high temperatures are

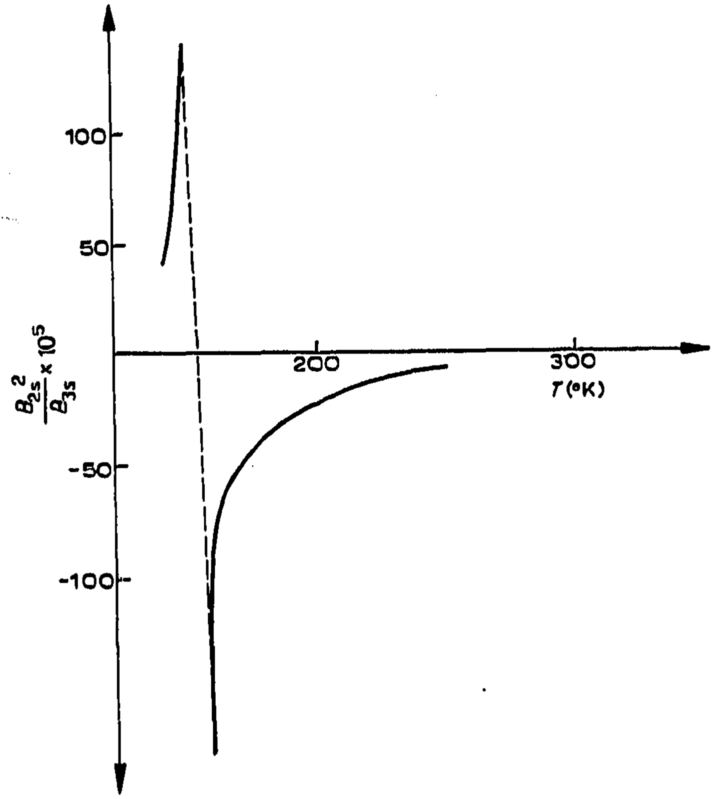

Fig. 1. Plot of B_{2s}^2/B_{3s} *versus* T for the data of Sams *et al.* obtained for adsorption of argon on graphitized Carbon Black P33.

investigated, since the accuracy of the measurements decreases because of the small retention volumes.

If we now calculate the surface area of graphitized Carbon Black P33, using our method and the data of Sams *et al.*, for the highest temperature under investigation, we get the value 15.8 m²/g, whereas the value obtained from the Kirkwood–Miller formula (second-order interaction) gives a value of 8.64 m²/g. It is of additional interest to compare our value with that obtained by Sams *et al.* on the basis of the two-dimensional model, with lateral interactions taken into account. The value obtained by Sams *et al.* is about 9 m²/g. It follows that there is a considerable difference between our results, obtained by using the three-dimensional model of adsorption, and the results of Sams *et al.* obtained using the two-dimensional model.

It is obvious that the finite thickness of the adsorbed layer considered by us introduces a much greater effect of repulsive interactions than is the case in a two-dimensional layer.

It now remains for us to decide which values for the surface areas are more suited to the real physical situation. In our opinion, in spite of a number of approximations made by us, our values should be closer to the true physical ones, since the three-dimensional model of adsorption is generally assumed to be the most realistic picture of physical adsorption.

REFERENCES

1 J. A. Barker and D. H. Everett, *Trans. Faraday Soc.*, 58 (1962) 1608.
2 J. R. Sams, G. Constabaris and G. D. Halsey, *J. Chem. Phys.*, 36 (1962) 1334.
3 O. Sinanoglu and K. S. Pitzer, *J. Chem. Phys.*, 32 (1960) 1279.
4 R. Yaris, *Thesis*, University of Washington, Seattle, 1962.
5 A. D. McLachlan, *Mol. Phys.*, 7 (1964) 381.
6 J. E. Krizan and A. D. Crowell, *J. Chem. Phys.*, 41 (1964) 1322; see also J. E. Krizan, *J. Chem. Phys.*, 42 (1965) 2923.
7 J. D. Johnson and M. L. Klein, *Trans. Faraday Soc.*, 60 (1964) 1964.
8 R. Wolfe and J. R. Sams, *J. Chem. Phys.*, 44 (1966) 2181.
9 W. Rudziński, Z. Suprynowicz and J. Rayss, *J. Chromatogr.*, 66 (1972) 1.
10 T. L. Hill, *Statistical Mechanics*, McGraw-Hill, New York, 1960.
11 R. A. Pierotti, *Chem. Phys. Lett.*, 2 (1968) 385.
12 J. R. Conder and J. H. Purnell, *Trans. Faraday Soc.*, 64 (1968) 3100.
13 A. D. Cromwell, in E. A. Flood (Editor), *The Gas–Solid Interface*, Marcel Dekker, New York, 1967, Ch. V.
14 J. O. Hirschfelder, C. F. Curtis and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954.
15 J. R. Conder, *Progr. Gas Chromatogr.*, 6 (1968) 209.
16 P. Lauger, *Helv. Chim. Acta*, 45 (1962) 1109.
17 W. E. Wassenberg, A. A. Ballandin and M. P. Maximova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 10 (1962) 1865.

J. Chromatogr., 72 (1972) 221–230