

CHROM. 5747

STUDY ON THE POSSIBILITY OF DETERMINING THE THIRD GAS-SOLID VIRIAL COEFFICIENT IN PHYSICAL ADSORPTION BY GAS CHROMATOGRAPHY

W. RUDZIŃSKI*, Z. SUPRYNOWICZ AND J. RAYSS

Department of Physical Chemistry, Institute of Chemistry, UMCS, Lublin, Nowotki 10 (Poland)
(Received August 30th, 1971)

SUMMARY

Definitions of virial coefficients used in the theory of physical adsorption of gases are discussed. A new method of evaluating the third virial coefficient is developed, based on gas chromatographic measurements. To illustrate this method, the third virial coefficient for carbon tetrachloride adsorbed on graphite was evaluated.

INTRODUCTION

For many cases of physical adsorption, there exist regions of pressure and temperature where the adsorbate phase may be considered to be a real gas in the presence of an external field due to the solid surface.

Many attempts have been made to interpret adsorption data by using the statistical mechanics of imperfect gases. The first theoretical work was carried out by ONO^{1,2}, who extended the Ursell-Mayer theory for the presence of an external solid surface field. ONO³, HALSEY and co-workers⁴, HILL^{5,6}, and BARKER AND EVERETT⁷ later extended the theory to include both gas mixtures and heterogeneity.

In all these attempts, the concept of "gas-solid virial coefficients" is of great importance, as these coefficients are a source of information about gas-solid interactions.

HALSEY and co-workers^{4,8} were the first to calculate the potential energy curve for a single molecule in the presence of a solid from the temperature-dependence of the first gas-solid virial coefficient. HANLAN AND FREEMAN⁹ showed that this virial coefficient can be easily obtained from gas chromatographic data.

Recently, HANSEN *et al.*^{10,11} have developed a new theoretical method for calculating the potential energy curve from chromatographic data obtained at low temperatures.

The interaction of a single molecule of adsorbate with a solid surface is called the "second-order gas-solid interaction", while the interaction between two molecules and the solid surface is called the "third-order gas-solid interaction".

* This work is based in part on a dissertation submitted by W. Rudziński to the Department of Theoretical Chemistry, Jagiellonian University, in fulfillment of the requirements of the degree of Doctor of Chemistry, Cracov, 1970.

Many attempts have been made, both experimental^{12,13} and theoretical¹⁴, to investigate this third-order gas-solid interaction. SINANOGLU AND PITZER¹⁴ were the first to calculate the potential energy curves for two molecules in the presence of a solid. However, this work is of no practical use until some empirical coefficients are known for the adsorption system under consideration, these coefficients being simply related to the third gas-solid virial coefficient^{4,14}.

Thus the simple, rapid and accurate evaluation of this virial coefficient is of great importance, as the third-order gas-solid interactions contribute considerably to the total adsorption effect.

In this paper we propose a new method of evaluating the third gas-solid virial coefficient from simple chromatographic data.

THEORETICAL

We would like first to draw attention to the two different types of virial coefficients that are used in the theory of physical adsorption. The first are the "gas-solid virial coefficients" discussed above. Here the $(i + 1)$ th gas-solid virial coefficient $B_{i+1,s}$ is the coefficient of the i th power of the adsorbate activity, when expanding the number of adsorbed molecules in the activity series. For example:

$$B_{2,s} = \int_v \left\{ \exp \left[\frac{W_1(\mathbf{r}_1)}{-kT} \right] \right\} d\mathbf{r}_1 - \int_v d\mathbf{r}_1 \quad (1)$$

$$B_{3,s} = \int_v \int \left\{ \exp \left[\frac{W_1(\mathbf{r}_1) + W_1(\mathbf{r}_2)}{-kT} \right] \right\} \left\{ \exp \left[\frac{\omega_2(\mathbf{r}_1, \mathbf{r}_2)}{-kT} \right] - 1 \right\} d\mathbf{r}_1 d\mathbf{r}_2 \\ - \int_v \int \left\{ \exp \left[\frac{U_2(\mathbf{r}_1, \mathbf{r}_2)}{-kT} \right] - 1 \right\} d\mathbf{r}_1 d\mathbf{r}_2 \quad (2)$$

Where V is the volume of the adsorption space; $W_1(\mathbf{r})$ is the adsorption potential of a single molecule, whose centre is at the point \mathbf{r} ; $\omega_2(\mathbf{r}_1, \mathbf{r}_2)$ is the interaction energy between two molecules in the presence of a solid; $U_2(\mathbf{r}_1, \mathbf{r}_2)$ is the interaction energy between two isolated molecules; k is the Boltzmann constant; and T is the absolute temperature.

It can be seen that the coefficients $B_{i+1,s}$ have significant values only in the space where adsorption forces exist, and that the last (second) integrals in eqns. 1 and 2 may be neglected in comparison with the first integrals.

Following MUSUKAWA AND KOBAYASHI¹⁵, the volume V_s where the adsorption forces exist will be called later the "volume of surface phase", while the volume V_f equal to $(V - V_s)$ will be called the "free gas-phase volume".

From eqns. 1 and 2, expressions for $B_{2,s}$ and $B_{3,s}$ can be written in the following form:

$$B_{2,s} = \int_{v_s} \left\{ \exp \left[\frac{W_1(\mathbf{r}_1)}{-kT} \right] \right\} d\mathbf{r}_1 \quad (3)$$

$$B_{3,s} = \int_{v_s} \int \left\{ \exp \left[\frac{W_1(\mathbf{r}_1) + W_1(\mathbf{r}_2)}{-kT} \right] \right\} \left\{ \exp \left[\frac{\omega_2(\mathbf{r}_1, \mathbf{r}_2)}{-kT} \right] - 1 \right\} d\mathbf{r}_1 d\mathbf{r}_2 \quad (4)$$

In addition to the first type of virial coefficients there exists a second type, introduced by KRIZAN^{16,17}. KRIZAN expanded the equation of state for the adsorbate phase in powers of average density of the adsorbate phase, similar to the virial expansion for a common free gas phase.

As in the theory of imperfect gases, the coefficient at the $(n-1)$ th power of average density is called the " n th virial coefficient".

To distinguish between these two types of virial coefficients, we shall later call the coefficients introduced by KRIZAN the "surface virial coefficients". The second surface virial coefficient, C_2 , was defined by KRIZAN as follows:

$$C_2 = \frac{1}{2 \int_v \left\{ \exp \left[\frac{W_1(r_1)}{-kT} \right] \right\} dr_1} \int_v \int_v \left\{ \exp \left[\frac{W_1(r_1) + W_1(r_2)}{-kT} \right] \right\} \times \left\{ \exp \left[\frac{\omega_2(r_1, r_2)}{-kT} \right] - 1 \right\} dr_1 dr_2 \quad (5)$$

However, in our opinion, there is an error in KRIZAN's definition of C_2 . If the two following obvious equations are written for the adsorbate phase:

$$\frac{\bar{p}}{kT} = \sum_{i \geq 1} b_i z^i \quad (6)$$

$$\bar{\rho} = \sum_{i \geq 1} i b_i z^i \quad (7)$$

where z , \bar{p} and $\bar{\rho}$ are the activity, average pressure and average density, respectively, in the adsorbate phase and b_i are cluster-type integrals, dependent upon configuration integrals. For example:

$$b_1 = \frac{1}{V} \int_v \left\{ \exp \left[\frac{W_1(r_1)}{-kT} \right] \right\} dr_1 \quad (8)$$

$$b_2 = \frac{1}{2V} \int_v \int_v \left\{ \exp \left[\frac{W_1(r_1) + W_1(r_2)}{-kT} \right] \right\} \left\{ \exp \left[\frac{\omega_2(r_1, r_2)}{-kT} \right] - 1 \right\} dr_1 dr_2 \quad (9)$$

To eliminate parameter z from eqns. 6 and 7, taking

$$z = \sum_{n \geq 1} d_n \bar{\rho}^n \quad (10)$$

where d_n is the coefficient in the expansion of activity in the density powers one obtains:

$$\sum_{i \geq 1} i b_i \left(\sum_{n \geq 1} d_n \bar{\rho}^n \right)^i - \bar{\rho} = 0 \quad (11)$$

By comparison of the coefficients at equal powers of $\bar{\rho}$, one obtains:

$$d_1 = \frac{1}{b_1}; \quad d_2 = -\frac{2b_2}{b_1^3}; \quad d_3 = \frac{8b_2^2 - 3b_3b_1^2}{b_1^5} \quad (12)$$

By inserting series 10 into series 6, and regrouping, one obtains the expression for the equation of state for the adsorbate phase:

$$\frac{\bar{p}V}{NkT} = 1 - \frac{b_2}{b_1^2} \bar{\rho} + O\bar{\rho}^2 + \dots \quad (13)$$

Eqn. 13 implies that the expression for the second surface virial coefficient C_2 is:

$$C_2 = -\frac{b_2}{b_1^2} \quad (14)$$

instead of that defined by KRIZAN:

$$C_2 = -\frac{b_2}{b_1}$$

By using the algebraic method presented above, two following additional equations may be obtained:

$$\bar{\rho} = \frac{\bar{P}}{kT} + \frac{b_2}{b_1^2} \left(\frac{\bar{P}}{kT} \right)^2 + \dots \quad (15)$$

$$\frac{\bar{P}}{kT} = \bar{\rho} - \frac{b_2}{b_1^2} \bar{\rho}^2 + \dots \quad (16)$$

The starting point for the essential part of our theory is the well-known equation:

$$V_R = V_f + V_s \frac{\bar{\rho}_1}{\rho_0} \quad (17)$$

where V_R is the retention volume under the column conditions and ρ_0 and $\bar{\rho}_1$ are the densities of the adsorbate in volumes V_f and V_s , respectively. Consequently:

$$V = V_f + V_s \quad (18)$$

Following the work of many authors, we now consider the simple case, when the adsorption surface may be approximated by a plane (YZ) and the potential energy of adsorption for a single molecule $W_1(r)$ is a function of the distance from the surface only (coordinate X).

Now, if $\rho_0 \rightarrow 0$, then $\bar{\rho}_1 \rightarrow 0$ also. At infinitely small concentrations of the adsorbate, the adsorbate phase may therefore be considered to be an ideal gas in the presence of the external solid surface field. In this case:

$$\lim_{\rho_0 \rightarrow 0} \frac{\bar{\rho}_1}{\rho_0} = \frac{B_{2,s}}{V_s} \quad (19)$$

The proof of this is very short. As $\rho_1 = \rho_1(X)$, and from the ideality of the adsorbate phase, the following equation can be written:

$$\frac{{}^{id}\rho_1(X_1)}{{}^{id}\rho_0(X_2)} = \exp \left[\frac{W_1(X_1) - W_1(X_2)}{-kT} \right] \quad (20)$$

In eqn. 20 $X_1 \in V_s$ and $X_2 \in V_f$. In addition, *id* represents the situation where the adsorbate can be considered to be an ideal gas. The potential energy scale is now chosen so that in the free gas-phase volume $W_1(X) = 0$. Then:

$${}^{id}\rho_1(X) = {}^{id}\rho_0 \exp \left[\frac{W_1(X)}{-kT} \right] \quad (21)$$

Integration over the volume V_s and division by V_s yields the following result:

$${}^{id}\bar{\rho}_1 = \frac{{}^{id}\rho_0}{V_s} \int_{V_s} \left\{ \exp \left[\frac{W_1(X_1)}{-kT} \right] \right\} dr_1 = \frac{{}^{id}\rho_0}{V_s} B_{2,s} = \frac{{}^{id}p}{V_s kT} B_{2,s} \quad (22)$$

Here *id**p* is the pressure in the free gas-phase. If measurements are made of the function $V_R = V_R(p/kT)$ for a number of very small samples of adsorbate, (very small p/kT), and this function is extrapolated to zero sample size of adsorbate, then:

$$\lim_{p \rightarrow 0} V_R \left(\frac{p}{kT} \right) = V_R^e \quad (23)$$

where *p* is the pressure in the free gas phase. By using V_R^e , eqn. 17 may be rewritten in the form:

$$V_R^e - V_f = B_{2,s} \quad (24)$$

In this way the simple expression for the second gas-solid virial coefficient is obtained. To obtain the expression for the third gas-solid virial coefficient, eqn. 15 is inserted into eqn. 17.

Since $\bar{\rho}_1$ is the average density in the volume V_s , the integrals b_1 and b_2 in eqns. 15 and 16 are in this case equal:

$$b_1 = \frac{B_{2,s}}{V_s}; \quad b_2 = \frac{B_{3,s}}{2V_s} \quad (25)$$

Thus:

$$V_R - V_f = \frac{V_s}{\rho_0} \left[\frac{\bar{p}}{kT} + \frac{B_{3,s}}{B_{2,s}^2} V_s \left(\frac{\bar{p}}{kT} \right)^2 + \dots \right] \quad (26)$$

Next, \bar{p}/kT in the above equation is approximated by the appropriate expression for the adsorbate phase treated as an ideal phase. According to eqn. 19:

$$\frac{\bar{p}}{kT} = \frac{{}^{id}\bar{p}}{kT} = \frac{{}^{id}\rho_0}{V_s} B_{2,s} \quad (27)$$

The following approximation is consistent with the one above:

$$\rho_0 = {}^{id}\rho_0 \quad (28)$$

Inserting eqns. 27 and 28 into eqn. 26:

$$V_R - V_f = B_{2,s} + \rho_0 B_{3,s} \quad (29)$$

Eqn. 29 shows that the plot of $(V_R - V_f)$ against ρ_0 should yield a straight line having a slope $B_{3,s}$ and intercept $B_{2,s}$.

However, in order to plot this line, one must know the volume of the surface phase, V_s , as the total volume, V , can be easily measured by means of inert gases. The problem of evaluating V_s is rather complicated¹⁵.

However, for the majority of adsorption systems, V_s is negligible in comparison with V_f . Thus one may use V instead of V_f in eqn. 29. Of course, there may exist adsorption systems where the approximation of V_f with V cannot be made without introducing a considerable error. In these cases the following procedure is proposed for evaluating V_s .

This procedure is a method of successive approximations. Before presenting this method, we would like to draw attention to the difficulties involved in the definition of the surface phase¹⁸.

The definition of the surface phase as the zone where adsorption forces exist is useful only for some types of adsorption potentials. For example, in the case of the 3-9-type adsorption potential, the adsorption forces exist theoretically over the whole adsorption space. On the other hand, the definition of the surface phase as the zone where the adsorption potential has a considerable value is not a precise one.

For this reason, $W_1(r)$ is approximated by the following function:

$$W_1(r) = W_1(X) = \begin{cases} +\infty & \text{for } 0 \leq X < \alpha \\ W_{\text{min.}} & \text{for } \alpha \leq X < \beta \\ 0 & \text{for } \beta \leq X \end{cases} \quad (30)$$

Here α and β are unknown, but it will be not necessary to know these values.

The above function fulfills the requirement for the precise definition of the surface phase, and in addition it is in our opinion a realistic approximation.

In the zero-order approximation, V_f is put equal to V . Then, from eqn. 17:

$$\ln(V_R^e - V_f) = \ln V_s - \frac{W_{\text{min.}}}{kT} \quad (31)$$

Thus the plot of $\ln(V_R^e - V_f)$ against $1/T$ should be a straight line having a slope $(-W_{\text{min.}}/k)$ and intercept $\ln V_s$. In this way the first-order approximation for V_s is obtained. Now, by inserting the first-order approximation for V_s into the left-hand side of eqn. 31, the second-order approximation for V_s is obtained. The method for evaluating the higher-order approximations is now obvious.

EXPERIMENTAL

Chromatographic measurements were made by means of the Chromatoprep N-502 apparatus. Graphite was used as the solid support, having particles about 0.25 mm in diameter. This support was cleaned with distilled water and methanol and then dried with hydrogen at 250° for 4 h. Carbon tetrachloride (P.O. Ch. Gliwice) was used as the adsorbate and was cleaned by means of a 5A-type molecular sieve. Hydrogen was used as the carrier gas, and was also cleaned by means of a 5A-type molecular sieve. The chromatographic column was 3 m long, with I. D. 4 mm, and contained 35.1 g of graphite. The flow-rate was about 50 ml ($\pm 5\%$) per minute.

RESULTS AND DISCUSSION

The results of our measurements and calculations are presented in Table I. In the first column are given the temperatures at which retention volumes were measured for evaluating V_R^e .

TABLE I

RESULTS OBTAINED USING CARBON TETRACHLORIDE AS ADSORBATE, WITH GRAPHITE SUPPORT AND HYDROGEN AS CARRIER GAS

Temperature (°K)	V_R^e (l)	V_f (l)	V_s (l)	$W_{min.}$ (cal/mole)	$B_{2,s}$ from eqn. 24	$B_{2,s}$ from eqn. 29	$B_{3,s}$
356.8	0.211	0.0463	0.0402	-5883	0.164	0.148	0.0000132
365.8	0.182	0.0460			0.136	0.115	0.0000066
375.6	0.148	0.0457			0.102	0.086	0.0000023
385.6	0.119	0.0456			0.074	0.069	0.0000008
396.1	0.093	0.0450			0.048	0.049	0.0000003

The value of V_s was calculated by using the procedure described in the theoretical section.

It can be seen that there is a difference between the values of V_f calculated at different temperatures. The source of these differences lies in the fact that the values for $V = V_f + V_s$ measured with helium at different temperatures were not exactly equal (they decreased with increasing temperature.) In plotting $\ln(V_R^e - V_f)$ against $1/T$ for every temperature, the appropriate values of V for this temperature were used.

Of course, there exist two possibilities: either the volume V_f decreases with increasing temperature, or V_s decreases.

However, in our opinion, the changes in V are corrected rather by the dynamic effects of the chromatographic process, than by actual changes in V_s . These dynamic effects should take place in the volume V_f , where the transport of mass is much higher than in the volume V_s . For this reason, we have ascribed the effective changes in V to the volume V_f . Most interesting is the fact that the values of V_s and V_f are comparable. Thus our column represents the case of adsorption systems where the procedure of evaluating V_s must necessarily be used. It seems that the

evaluation of V_s is necessary for all adsorption systems with a large solid surface area, small particle diameter and close column packing.

The values of $B_{2,s}$ were calculated from both eqns. 24 and 29. The problem arises as to which values of $B_{2,s}$ are the more accurate. In our opinion, the values of $B_{2,s}$ calculated from eqn. 24 are the more accurate, as in developing eqn. 29 more approximations were introduced than in developing eqn. 24.

The values of $B_{3,s}$ were calculated from eqn. 29. As the values of V_R^c , V_f and V_s are expressed in litres, then according to the virial expansion, the density must be expressed in moles per litre and the value obtained for the number of adsorbed molecules will be in moles.

The sizes of adsorbate samples used in our measurements were about 0.1 – 10 μ l. At these sample sizes, the density ρ_0 of the adsorbate in our column was about 10^{-6} – 10^{-5} mole/l. These are rather small concentrations, and for this reason we hope that the values of $B_{2,s}$ and $B_{3,s}$ calculated by us are accurate.

REFERENCES

- 1 S. ONO, *Mem. Fac. Eng. Kyushu Univ.*, 12 (1950) 9.
- 2 S. ONO, *J. Chem. Phys.*, 18 (1950) 397.
- 3 S. ONO, *J. Phys. Soc. Japan*, 6 (1951) 10.
- 4 J. R. SAMS, G. CONSTABARIS AND G. D. HALSEY, *J. Chem. Phys.*, 36 (1962) 1334, with references to previous work beginning with W. A. STEELE AND G. D. HALSEY, *J. Chem. Phys.*, 22 (1954) 979.
- 5 T. L. HILL, *J. Chem. Phys.*, 18 (1950) 246.
- 6 T. L. HILL, *Statistical Mechanics*, McGraw-Hill, New York, 1956.
- 7 J. A. BARKER AND D. H. EVERETT, *Trans. Faraday Soc.*, 58 (1962) 1080.
- 8 W. A. STEELE AND G. D. HALSEY, *J. Phys. Chem.*, 59 (1955) 57.
- 9 J. F. HANLAN AND M. P. FREEMAN, *Can. J. Chem.*, 37 (1959) 843.
- 10 R. S. HANSEN AND J. A. MURPHY, *J. Chem. Phys.*, 39 (1963) 1642.
- 11 R. S. HANSEN, J. A. MURPHY AND T. C. GEE, *Trans. Faraday Soc.*, 60 (1964) 597.
- 12 J. H. DE BOER, *Adv. Catal.*, 8 (1956) 29.
- 13 M. P. FREEMAN, *J. Phys. Chem.*, 62 (1958) 729.
- 14 O. SINANOGLU AND K. S. PITZER, *J. Chem. Phys.*, 32 (1960) 1279.
- 15 S. MUSUKAWA AND R. KOBAYASHI, *J. Gas Chromatogr.*, 6 (1968) 257.
- 16 J. E. KRIZAN AND A. D. CROWELL, *J. Chem. Phys.*, 41 (1964) 1322.
- 17 J. E. KRIZAN, *J. Chem. Phys.*, 42 (1965) 2923.
- 18 E. A. GUGGENHEIM, *Mixtures*, Oxford University Press, Oxford, 1952, Ch. 9.

J. Chromatogr., 66 (1972) 1–8