

# Chromatographic Determination of the Second Gas-Solid Virial Coefficients for Argon, Nitrogen, and Carbon Dioxide with Carbon Powders

T. R. RYBOLT

Department of Chemistry  
University of Tennessee at Chattanooga  
Chattanooga, TN 37402

R. A. PIEROTTI

School of Chemistry  
The Georgia Institute of Technology  
Atlanta, GA 30332

A wide variety of chemical and physical phenomena including many processes of industrial importance, such as catalysis and corrosion, depend on the interaction of adsorbate gases with the surfaces of solid adsorbents. Changes in the distribution of adsorbate molecules between the solid and gas phases as a function of pressure and temperature have been used to study surface structures, surface areas, and gas-solid interactions. As an alternative to conventional adsorption techniques, gas-solid chromatography can be used to study physical adsorption. Although most previous investigations employing gas-solid chromatography to study physical adsorption have examined thermodynamic properties, there have been a few chromatographic studies, including work by Boucher and Everett (1971) and Rudzinski et al. (1972), which were used to determine gas-solid virial coefficients.

In the present investigation a direct chromatographic determination of the second gas-solid virial coefficients for 12 adsorbate-adsorbent systems over a temperature range from 265 to 365 K is used in conjunction with the virial coefficient theory of physical adsorption to ascertain the depth of the gas-solid interaction potentials and the surface areas of the adsorbents. In the current work argon, nitrogen, and carbon dioxide are used as adsorbates. The powders used as adsorbents include Mexican Graphite (No. 25 lubricating graphite from the United States Graphite Co.), Nuchar S-C, Nuchar S-A (provided by Kornegay of Westvaco, Chemical Div.), and Super Sorb (provided by Thomas O'Grady of Amoco Research). The virial surface areas of these powders are compared to areas obtained from the BET method.

As reviewed by Pierotti and Thomas (1971), the virial coefficient theory of physical adsorption introduced by Steele and Halsey (1954) offers the possibility of determining bulk information about the structure and surface area of the adsorbent as well as molecular information regarding the adsorbate-adsorbent and adsorbate-adsorbate interaction potentials. In the virial coefficient treatment of physical adsorption, the number of moles of gas adsorbed per gram of adsorbent is given by

$$n_{ad} = \sum_{i \geq 2} B_{is}(f/RT)^{i-1}. \quad (1)$$

The interaction of a single gas molecule with the surface is reflected in  $B_{2s}$ , while  $B_{3s}$  involves a pair of adsorbate molecules interacting with the surface,  $B_{4s}$  involves a triplet, etc. The virial treatment is most useful in the low coverage region where Henry's law and deviations from Henry's law dominate the adsorption isotherm. If adsorption isotherms are available for a given gas-solid system over a range of temperature then virial coefficients can be selected to model the adsorption isotherms. It is then possible to utilize the temperature dependence of the virial coefficients to

ascertain the parameters required to specify the exact form of the operative interaction potentials and also determine the surface area of the adsorbent. The complexity of the gas-solid system to be modeled with a virial treatment depends on the nature of both the adsorbate and adsorbent. Increasing complexity is introduced as one moves from monoatomic to diatomic, triatomic, and multiatomic adsorbates. Likewise, an exact virial treatment becomes more difficult as one moves from a homogeneous to a heterogeneous surface and still more difficult for a porous material.

Adsorption isotherms measured in the Henry's law region by either volumetric or gravimetric techniques can provide very precise values of the second gas-solid virial coefficients. However, the relative simplicity of gas-solid chromatography makes this technique a useful alternative to conventional adsorption experiments. In the pulse flow technique an adsorbate gas is injected into a flowing stream of a nonadsorbable carrier gas. The sample gas along with the carrier gas flows through a powder-packed column containing a solid adsorbent. The adsorbed gas is in a dynamic equilibrium with gas in the vapor phase. The residence time of the adsorbate gas in the powder-packed column depends on the magnitude of the adsorbate and vapor equilibrium. The second gas-solid virial coefficient for a gas-powder system depends on the flow rate of the carrier gas through the column, the retention time of the sample measured relative to a noninteracting reference gas, and the mass of the powder in the column.

## THEORETICAL BACKGROUND

The solution to the linear partial differential equation which describes the mass conservation between the adsorbed and desorbed phases in a pulse flow was found by Eberly and Spencer (1961) to be given by

$$n_g/n_a = (L/tv). \quad (2)$$

As shown by Ross et al. (1962), Eq. 2 may be rewritten as

$$n_g/n_a = (V_g/tF_1). \quad (3)$$

Using the ideal equation of state to model the behavior of the unadsorbed gas, one can write

$$n_g = (P_1 V_g)/(RT_1).$$

In the Henry's law region the virial equation of state for adsorption is given as

Correspondence concerning this paper should be addressed to T.R. Rybolt.

$$n_a = mB_{2s}(P_1/RT_1).$$

Substituting the previous two relations into Eq. 3 gives

$$B_{2s} = (tF_1/m). \quad (4)$$

Accurate values of  $B_{2s}$  can be found only if the proper values of the residence time and the flow rate inside the column are determined. The residence time of the adsorbate gas in the adsorbent powder is found by subtracting the measured retention time of a marker gas from the measured retention time of the sample gas. The difference in the time which passes from injection to detection of a sample gas and nonadsorbable marker gas may be attributed to the adsorption of the sample gas in the powder-packed column. The column flow rate must be calculated from the measured flow rate. Atkins and Curthoys (1978) have given the corrected column flow rate as

$$F_1 = F_m \frac{T_1}{T_f} \frac{3}{2} \left[ \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \right] \frac{P_o}{P_a} \quad (5)$$

## EXPERIMENTAL PROCEDURE

As described by Rybolt (1981), a gas chromatograph employing a thermal conductivity detector was used to ascertain the temperature dependence of the second gas-solid virial coefficients for 12 different adsorbate-powder systems. Equation 4 was used in conjunction with the experimental quantities  $t$ ,  $F_1$ , and  $m$  to calculate a value of  $B_{2s}$  at each temperature.

The packed columns were made from 6.35 mm o.d. copper tubing using plugs of corning pyrex wool to secure the powder in the tube. Columns were prepared using Mexican Graphite (6.09 g), Nuchar S-C filtered through a 177 micron wire mesh (1.9002 g), Nuchar S-A (1.240 g), and Super Sorb (0.9968 g). Prior to packing a column, the powder was degassed for two hours in vacuo at 400 K. Samples of Nuchar S-A (SA), Nuchar S-C (SC), Super Sorb (SS), and Mexican Graphite (MG) were found to contain 11, 7, 3.5 and 0.1% water by weight, respectively. Nitrogen BET surface areas were run on each of the powders using a Micromeritics Digisorb 2500 surface area analyzer. The areas were found to be 26, 903, 1661 and 3,169 ( $\text{m}^2/\text{g}$ ) for the MG, SC, SA and SS powders, respectively.

The selected packed-powder column was placed in a thermostated box where the desired column temperature was maintained with a model 71 YSI temperature controller and thermistor probe. The YSI controller was used to activate a resistance heater or to open a solenoid valve which allowed cool nitrogen vapor to be transferred into the thermostated chamber. A fan was used to circulate air within the chamber.

Reproducible volumes of gaseous samples were introduced into the flowing carrier gas stream by means of a gas sampling valve. The Gas Sampling Valve contained a sample tube with an internal volume of 0.25  $\text{cm}^3$ . Using an attached glass manifold system the sample tube was filled

to a pressure of less than 20 kPa. The sample gas was then injected into the flowing helium as a brief pulse. Five gases were used in this work. The reported minimum mole percent purities for helium (Alabama Oxygen), neon (Linde), argon (M&A welding), nitrogen (M&A welding) and carbon dioxide (Matheson) were 99.998, 99.998, 99.8, 99.6 and 99.8, respectively.

The primary experimental data necessary to determine the flow rate through the column included: the measured flow rate of the carrier gas, the inlet pressure, the outlet pressure, the atmospheric pressure, the flowmeter temperature, and the column temperature. The column flow rates were varied from 0.05 to 0.12 ( $\text{cm}^3/\text{s}$ ). The measured flow rate of the carrier gas,  $F_m$ , was determined with a bubble flowmeter. The outlet pressure was equal to atmospheric pressure minus the vapor pressure of the soap solution. Atmospheric pressure was determined from a mercury barometer. A Bourdon pressure gauge was used to determine the magnitude of the inlet pressure relative to atmospheric pressure. The inlet pressure was usually in the range of 200 to 250 kPa.

To determine the temperature of the chromatographic column and the flowmeter, copper-constantan thermocouples were used. The thermocouple potentials were measured relative to a water-ice reference using a Keithley 155 microvoltmeter. The output from the microvoltmeter was monitored on a strip chart recorder. The thermocouples were calibrated using a Leeds and Northrup platinum resistance thermometer (model 8163-C) and Mueller bridge. The final uncertainty in the temperature based on thermocouple measurements was better than  $\pm 0.1$  K.

Each of the twelve gas-powder systems showed an increase in  $t_s F_1$  as the temperature was decreased. However, for the neon-powder measurements,  $t_m F_1$  showed no temperature dependence. The pulse flow of neon through Nuchar S-A, Nuchar S-C, Super Sorb, and Mexican Graphite gave  $t_m F_1$  values of  $8.98 \pm 0.07$ ,  $10.02 \pm 0.09$ ,  $11.09 \pm 0.12$ , and  $11.27 \pm 0.14$  ( $\text{cm}^3$ ), respectively. Since  $B_{2s}$  for neon was found to be independent of temperature within the precision of the apparatus and since  $B_{2s}$  for neon is small over this temperature range, neon was judged to be a suitable marker gas.

Using helium as a marker gas, Boucher and Everett (1971) found that for an activated carbon at 273 K the value of  $B_{2s}$  for argon was about 60 times greater than  $B_{2s}$  for neon. Thus, the use of neon as a marker gas in the current work would be expected to cause a slight underestimate of the values of  $B_{2s}$  for the sample gases. An additional source of uncertainty in the final values of  $B_{2s}$  can be caused if deviations from Henry's law are significant over the experimental range of pressure.

## RESULTS AND DISCUSSION

The experimental values of the second gas-solid virial coefficients as a function of temperature obtained from gas-solid chromatography for the 12 gas-solid systems are reported in Table 1. For all 12 systems, as the temperature is decreased, the magnitude of the second gas-solid virial coefficient is increased. As shown by Pierotti and Thomas (1971), the heat of adsorption at zero coverage is equal to  $-R$  multiplied by the derivative of  $\ln B_{2s}$  with respect to  $1/T$ .

TABLE 1.  $B_{2s}$ -TEMPERATURE DATA

	Mexican Graphite		Nuchar S-C		Nuchar S-A		Super Sorb	
	$B_{2s}$ ( $\text{cm}^3/\text{g}$ )	$T$ (K)	$B_{2s}$ ( $\text{cm}^3/\text{g}$ )	$T$ (K)	$B_{2s}$ ( $\text{cm}^3/\text{g}$ )	$T$ (K)	$B_{2s}$ ( $\text{cm}^3/\text{g}$ )	$T$ (K)
Argon	0.044	296.8	4.13	319.1	3.52	314.4	6.31	318.2
	0.051	280.4	5.12	307.0	3.92	305.7	7.13	307.8
	0.062	265.4	5.72	298.3	4.46	296.7	9.49	288.5
			7.12	289.3	4.83	291.3	10.50	280.8
					5.14	286.7	13.07	270.0
Nitrogen					6.20	276.2		
	0.042	296.8	4.30	319.2	3.61	314.2	6.63	318.1
	0.047	286.8	5.46	307.0	3.99	305.6	7.81	307.8
	0.058	265.5	6.59	298.3	4.74	296.7	10.43	288.6
			7.68	289.4	4.94	291.3	12.05	280.8
Carbon Dioxide					5.40	286.7	14.47	270.1
					6.59	276.2		
	0.303	296.8	69.1	319.0	39.6	323.9	59.6	320.1
	0.394	287.0	84.2	313.3	47.4	316.2	73.0	311.3
	0.447	280.5	113.8	304.8	67.4	305.8	95.5	301.9
	0.624	265.5	154.9	296.2	95.2	295.4	103.8	298.4

TABLE 2. RESULTS OF VIRIAL ANALYSIS

Gas-Solid System	Standard Deviation of (log $Az_o$ )	$\epsilon_{1s}/k$ (K)	$Az_o$ (cm <sup>3</sup> /g)	A (m <sup>2</sup> /g)
Ar-MG	0.00473	957	0.0044	16
Ar-SC	0.00819	1,850	0.0431	152
Ar-SA	0.00242	1,469	0.0979	346
Ar-SS	0.00525	1,474	0.1812	640
N <sub>2</sub> -MG	0.00311	865	0.0057	19
N <sub>2</sub> -SC	0.00585	2,025	0.0279	94
N <sub>2</sub> -SA	0.00662	1,567	0.0761	255
N <sub>2</sub> -SS	0.00322	1,587	0.1420	477
CO <sub>2</sub> -MG	0.00988	1,977	0.0015	4
CO <sub>2</sub> -SC	0.00203	3,530	0.0057	17
CO <sub>2</sub> -SA	0.00706	3,183	0.0103	31
CO <sub>2</sub> -SS	0.00341	2,681	0.0604	179

Therefore, plots of  $\ln B_{2s}$  vs.  $1/T_1$  are expected to give a straight line if the heat of adsorption in the limit of zero coverage is constant over the range of temperatures involved. This expected linear dependence was observed. A least squares linear regression was used to fit each system. The corresponding isosteric heats and heats of adsorption were calculated by Rybolt (1981).

As discussed by Steele (1967) the relation between the second gas-solid virial coefficient and the gas-solid interaction potential is expressed in terms of a configuration integral. If the solid is considered to have a uniform surface, this integral may be written as

$$B_{2s} = A \int [\exp(-u_{1s}/kT) - 1] dz. \quad (6)$$

A Lennard-Jones (3,9) potential,

$$u_{1s} = (3\sqrt{3}/2)\epsilon_{1s}[(z_0/z)^9 - (z_0/z)^3] \quad (7)$$

is frequently used to represent the adsorbate-adsorbent interaction. Upon substitution of a Lennard-Jones (3,9) potential for  $u_{1s}$  in Eq. 6, the resultant integral is equal to  $B_{2s}/Az_o$ . Since  $Az_o$  should not vary measurably with temperature,  $B_{2s}$ -temperature data can be used to find the value of  $\epsilon_{1s}$  which causes the minimum variation of  $Az_o$  for a given gas solid system.

For each of the 12 gas-solid systems, an iterative procedure was used to find the value of  $\epsilon_{1s}/k$  which gave the minimum value of the standard deviation of (log  $Az_o$ ). Evaluation of the integral was carried out by a numerical integration procedure utilizing Georgia Tech's Control Data Corp. Cyber 70, model 74-28 computer. The function of interest was divided into segments and each part was integrated using CDC's supplied subroutine, LEGEND. This subroutine uses a 16 point Legendre-Gauss quadrature formula. Values of the minimum standard deviation of (log  $Az_o$ ), and the associated  $\epsilon_{1s}/k$  and  $Az_o$  are given for each of the 12 gas-solid systems in Table 2.

Estimates of  $z_o$ , the hard sphere distance of closest approach, were taken from Levy (1976) for the gas-graphite systems. The values of  $z_o$  for graphite with Ar, N<sub>2</sub>, and CO<sub>2</sub> were 0.283, 0.298, and 0.337 (nm), respectively. As shown in Table 2, these values of  $z_o$  were used in conjunction with the values of  $Az_o$  to estimate the surface area associated with each gas-solid system. The virial surface areas are found to be much less than the BET areas of 26, 903, 1661, and 3169 (m<sup>2</sup>/g) for MG, SC, SA, and SS powders, respectively. The observed discrepancies between the virial and BET areas increase as the gas is changed from Ar to N<sub>2</sub> to CO<sub>2</sub>. As discussed by Brunauer (1970) part of the difference is due to the enhanced adsorption in the micropores and capillaries of fine-pored adsorbents during a BET analysis. In the Henry's law region of adsorption, used in the virial analysis, the coverage is low enough so that condensation within pores does not occur. However, at the higher coverages used in a BET analysis gas may be adsorbed on

walls and condensed in pores. This pore condensation causes the BET area to over estimate the "true surface area" for solids with small pores. Several additional factors responsible for an under estimate of the surface area in an approximate virial analysis are discussed below.

Using  $B_{2s}$ -temperature data for an argon-graphite system, Rybolt and Pierotti (1979) found that a Lennard-Jones (3,17) potential provided the best fit of the experimental data and gave a 30% larger estimate of the graphite surface area than obtained with a (3,9) potential. The use of a steeper repulsive potential would increase the surface areas found for Ar-MG, Ar-SC, Ar-SA, and Ar-SS. For porous carbons a better virial analysis would include more complicated gas-solid interaction potentials which would model the three dimensional pore structure. Larger surface areas will be found when the three dimensional pore structure is included in the virial analysis. Yang (1979) has used the Lennard-Jones and Devonshire cell model to determine cavity properties of a Linde 5A zeolite from argon-zeolite virial coefficients. An exact treatment for nitrogen and carbon dioxide is even more complicated because a spherical potential is valid only for a monatomic adsorbate. The use of a spherical potential causes a severe underestimate of the surface area because of hindered rotation of the adsorbed N<sub>2</sub> and CO<sub>2</sub> molecules. A more exact virial analysis, such as the work by Levy (1976), would include the dependence of the polarizability and hard sphere internuclear separation as a function of the angle of the axis of the molecule normal to the surface plane. In future studies it should be possible to use virial coefficients determined from gas-solid chromatography in conjunction with more sophisticated modeling techniques to specify the structure of a variety of porous substances.

## NOTATION

A	= specific surface area of solid
$B_{is}$	= $i$ th gas-solid virial coefficient
$F_1$	= flow rate in powder-packed column
$F_m$	= measured flow rate
$f$	= fugacity
$k$	= Boltzman constant
$L$	= length of packed column
$m$	= mass of powder in column
$n_a$	= moles of adsorbed gas in powder packed column
$n_{ad}$	= moles of gas adsorbed per gram of solid
$n_g$	= moles of sample gas in the vapor phase (unadsorbed)
$P_a$	= atmospheric pressure
$P_1$	= pressure in powder-packed column
$P_i$	= inlet pressure on upstream side of column
$P_o$	= outlet pressure in flowmeter
$R$	= gas constant
$T$	= temperature
$T_1$	= temperature of powder-packed column
$T_f$	= temperature of flowmeter
$t$	= residence time of sample gas in column, $t = t_s - t_m$
$t_m$	= retention time of marker gas, neon
$t_s$	= retention time of sample gas
$u_{1s}$	= gas-solid interaction potential
$V_g$	= interstitial volume in column
$v$	= velocity of gas through column
$z$	= gas-solid internuclear separation
$z_o$	= gas-surface distance of closest approach
$\epsilon_{1s}$	= maximum depth of gas-solid interaction potential

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## Influence of Particle Size on the Pressure Fluctuations and Slugging in a Fluidized Bed

K. SVOBODA, J. ČERMÁK,  
M. HARTMAN, J. DRAHOŠ,  
and K. SELUCKÝ

Institute of Chemical Process Fundamentals  
Czechoslovak Academy of Sciences  
165 02 Prague, Czechoslovakia

In aggregative fluidization the pressure fluctuations are closely interrelated with the behavior of solids and gas in the bed. These random fluctuations of pressure can be measured by a sensitive pressure transducer, recorded and subjected to the statistical analysis.

Kang et al. (1967), Winter (1968), and Lirag (1971) appear to be early investigators who attempted to relate the statistical properties of pressure fluctuation signals to phenomena occurring in the fluidized bed. An effort was also taken to define an index of the quality of fluidization from the statistical characteristics of pressure fluctuations. The practical regime of aggregative fluidization is bounded by the beginning of bubbling at a low fluid velocity and by the onset of slugging at a high fluid velocity. For any fluidized-bed reactor there is an optimum bubbling rate providing the required mixing without excessive loss in contacting efficiency. The fluctuations of pressure drop across a fluidized bed are known to increase with an increase in the intensity of bubbling. Thus knowledge of two fundamental properties of pressure fluctuations, i.e., the frequency spectrum and pressure drop amplitudes, is a useful tool for the rational diagnosis of behavior of a fluidized-bed reactor.

The nature of pressure fluctuations in a fluidized bed is a complex function of particle properties, bed geometry, flow conditions, pressure and temperature. An effect of bed size, gas flow rate and particle properties on the pressure oscillation in slugging beds was studied by Broadhurst and Becker (1976). The authors presented dimensionless correlations for estimation of the major frequency

and the peak in the frequency spectrum for group B of Geldart's classification of solids (1973). Sadasivan et al. (1980)-developed empirical equations relating the characteristic frequency and maximum pressure drop fluctuations to solid properties, gas flow rate, and height of the static bed.

Aside from the influence of the operating conditions on the major frequency and amplitude of the pressure fluctuations, Fan et al. (1981) also explored the causes of the fluctuations. The authors concluded that the formation and motion of bubbles appear to be the major causes of pressure fluctuations in a fluidized bed. In our recent study (Svoboda et al., 1982) we have investigated an effect of temperature on the pressure fluctuations in the bed of different materials. We have found that the pressure fluctuations are smaller and more rapid at elevated temperatures than those at ambient temperature.

Our experience shows that no systematic investigation of the influence of particle size on the fluctuation characteristics has been conducted. Particularly, experimental data covering a wide range of gas velocities for group D of the Geldart's classification are lacking.

In this work the effect of particle size and relative gas velocity on the dominant frequency and mean pressure amplitude is investigated. Attempts have also been made to determine the onset of slugging from the power frequency spectrum, to correlate the dominant frequency of slugging with particle size and to explore the effect of excess gas velocity ( $U_f - U_{mf}$ ) on the mean pressure amplitude for particles of different size.