

## GAS-SOLID CHROMATOGRAPHY AND VIRIAL ANALYSIS FOR ARGON-5A ZEOLITE

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### ABSTRACT

A chromatographic determination of the second gas-solid virial coefficients for the argon-5A zeolite system in the temperature range 300–374 K is used in conjunction with the Lennard-Jones and Devonshire (LJD) cell model to determine the cas-cavity interaction energy, the cavity radius, and the number of cavities per gram. These energetic and structural parameters are compared with a LJD analysis based on virial coefficients determined from adsorption isotherms. This comparison shows that gas-solid chromatography (GSC) provides an alternative to the more conventional adsorption experiments and supports the validity of a virial analysis based on the LJD model.

### INTRODUCTION

Gas-solid chromatography has been used previously by Boucher and Everett (1971), Rudzinski (1972), and Rybolt and Pierotti (1984) to determine gas-solid virial coefficients. In general, GSC experiments are faster and less tedious than determining explicit adsorption isotherms. In the Henry's law region, where one is interested in studying adsorbate-adsorbent interactions without adsorbate-adsorbate interference, GSC is an especially useful alternative to determining adsorption isotherms. The purpose of this work is to provide new virial coefficient data for the argon-5A zeolite system and to compare LJD analyses of the current GSC data and previously reported adsorption data.

As reviewed by Pierotti and Thomas (1971), in the Henry's law region, the adsorption isotherm may be represented by

$$n_{\text{ad}} = B_{2s}(P_1/RT) \quad (1)$$

where  $n_{\text{ad}}$  is the moles of gas adsorbed per gram of solid,  $P_1$  is the pressure in the powder-packed column,  $R$  is the gas constant,  $T$  is the temperature, and  $B_{2s}$  is the second gas-solid virial coefficient. The second

gas-solid virial coefficient may be found from

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

where  $t$  is the residence time of the sample gas in the column,  $F_1$  is the flow rate in the powder-packed column, and  $m$  is the mass of the powder in the column (Rybolt and Pierotti 1984). As noted by Atkins and Curthoys (1978), the flow rate in the powder-packed column must be corrected for temperature and pressure variation from the inlet to the outlet of the column and thus the actual flow rate must be calculated from the measured flow rate at the gas outlet.

The 5A zeolite has been shown through X-ray crystallographic analysis to consist of a regular array of identical interconnected, approximately spherical cavities (Soto 1979). Eight sodalite units form each cavity and access to each cavity is provided by six windows or openings of mean diameter less than 0.5 nm. Because the 5A zeolite adsorbent consists of a well characterized structure, it is an ideal system to test theories that propose to model adsorption in microporous solids. The LJD theory is one such model.

Lattice summation calculations based on atom-atom and atom-ion interactions have been used to calculate thermodynamic values (Kiselev and Du 1981) and to fit adsorption data (Soto 1979). An exact lattice summation calculation requires the exact location of all cavity atoms and ions. A modified approach represents the attractive dispersion interaction as a spherical potential based on the LJD cell theory of liquids and treats only the electrostatic induction terms in an exact fashion (Soto 1981).

The basic nature of the approach discussed above is to use atomic interaction and structural parameters to find thermodynamic values. Yang (1976) and Pierotti have taken the opposite approach and used thermodynamic values in conjunction with the LJD model to extract energetic and structural parameters. Rybolt (1987) developed a modified version of this approach and ap-

plied it to monatomic gases in the 5A and 13X zeolites. In this work,  $B_{2s}$  data from several different sources including the current GSC data are used in conjunction with an LJD model to determine molecular parameters that describe the 5A-zeolite system.

#### METHODS AND MATERIALS

A gas-solid chromatographic system described previously by Rybolt and Pierotti (1984) was used to determine the flow rate and residence time of argon sample gas passing through a 20 cm column (6.35 mm o.d. copper tube) packed with 1.92 g of Linde 5A zeolite and plugged with corning pyrex wool. The powder in the column was degassed for 4 hours at 500 K by flowing helium ( $F_1 = 0.2 \text{ cm}^3/\text{s}$ ).

A modified Perkin Elmer model 154D chromatographic system with thermal conductivity detector was used for this work. The standard oven and thermistors were used to control and monitor the column temperature. A Hewlett Packard model 3370A Integrator and auxiliary chart recorder were used to determine the retention times of sample and marker gases. A gas sampling valve and auxiliary glass manifold system were used to mix and inject gases. The column flow rate was determined from the measured flow rate of the carrier gas, inlet pressure, outlet pressure, atmospheric pressure, flowmeter temperature, and column temperature using the corrected column flow rate equation (Atkins and Curthoys 1978).

Helium (Selox) was used as the carrier gas. Sulfur hexafluoride (Matheson) was used as the marker gas and argon (Matheson) was used as the sample gas. The mole purities of the gases were 99.9 percent. Unlike Ar and He, the  $\text{SF}_6$  molecule is too large to enter the cavities that form the microporous structure of the 5A zeolite and thus should serve as a suitable marker gas since its retention time in the column is not affected by cavity interactions. To correct for possible external  $\text{SF}_6$ -zeolite interactions, experiments were conducted where the carrier and marker roles of helium and sulfur hexafluoride were reversed over a temperature range from 300–374 K. The  $t_r F_1$  values, where  $t_r$  is the retention time for He as marker with  $\text{SF}_6$  as carrier, were constant over this range, whereas the  $t_r F_1$  values for  $\text{SF}_6$  as marker and He as carrier showed a slight increase as the temperature decreased. The decrease in the  $t_r F_1$  values of  $\text{SF}_6$  were adjusted in the range of 0.4 to 9 percent to a constant value of  $7.62 \text{ cm}^3$  in agreement with the he-

lium values. For standard flow rates of  $0.150 \text{ cm}^3/\text{s}$  this corresponded to retention times of about 50.8 s. The residence times of the sample gas,  $t$ , were determined from

$$t = t_s - t_m \quad (3)$$

where  $t_m$  is the adjusted retention time of the  $\text{SF}_6$  marker gas and  $t_s$  is the retention time of the argon sample gas. Based on the average of multiple runs at each temperature, GSC residence times and flow rates were determined. These values along with the corresponding second gas-solid virial coefficients are reported in Table 1.

TABLE 1. Argon-5A Zeolite Virial Coefficients From Gas-Solid Chromatography.

$T$ (K)	$F_1$ ( $\text{cm}^3/\text{s}$ )	$t$ (s)	$B_{2s}$ ( $\text{cm}^3/\text{g}$ )
300	0.152	34.6	2.74
323	0.150	25.9	2.02
333	0.154	22.5	1.80
343	0.152	21.2	1.68
374	0.146	16.8	1.28

#### THEORY AND ANALYSIS

The second gas-solid virial coefficient is dependent only on the interaction of single isolated gas molecules with the solid. In the Henry's law region, the average cavity occupancy by argon atoms is less than unity.  $B_{2s}$  may be given by a configuration integral which relates to the gas-solid interaction potential,  $u_{1s}$ , as

$$B_{2s} = \int_V [\exp(-u_{1s}/kT) - 1] dV \quad (4)$$

where  $k$  is the Boltzmann constant and  $dV$  is the volume element (Pierotti and Thomas 1971). To extract molecular parameters which characterize a particular gas-solid system it is necessary to have a structural model which can be used to represent the gas-solid interaction potential. It has been shown that the LJD cell theory of fluids can be modified to model the behavior of an adsorbate molecule inside a zeolite cavity (Stroud 1976).

Since the 5A zeolite adsorbent is a collection of identical interconnected cavities, one may write

$$B_{2s} = N_s b_{2s} \quad (5)$$

where  $N_s$  is the number of cavities per gram of zeolite and  $b_{2s}$  is the virial coefficient for a single cavity. As shown in previous work, by assuming the cavity potential is spherically symmetrical and using a Lennard-Jones 6-12 potential to represent gas-cavity atom interaction, the mean potential within a cavity can be determined (Yang 1976).

The detailed treatment of applying the LJD cell model to this problem is presented elsewhere (Rybolt 1987), but the results may be summarized as follows. The second gas-solid virial coefficient is expressed in terms of four basic parameters:  $a$ , the cavity radius,  $N_s$ , the number of cavities per gram,  $r^*$ , the gas-solid equilibrium molecular separation, and  $E^*$ , the adsorbate-cavity interaction energy.  $B_{2s}$  is given as

$$B_{2s} = c \cdot g(T, V^*, E^*) \quad (6)$$

where  $c$  is a constant given as

$$c = 2\pi a^3 N_s \quad (7)$$

and  $g(T, V^*, E^*)$  is an integral function given by

$$g(T, V^*, E^*) = \exp\{-[E^*/T][V^{*-4} - 2V^{*-2}]\} \\ \times \int_0^1 \exp\{-[E^*/T][V^{*-4}L(y) - 2V^{*-2}M(y)]\} y^{1/2} dy \quad (8)$$

where

$$V^* = (a/r^*)^3 \quad (9)$$

$$y = (r/a)^2 \quad (10)$$

$$L(y) = (1 + 12y + 25.2y^2 + 12y^3 + y^4)(1 - y)^{-10} - 1 \quad (11)$$

$$M(y) = (1 + y)(1 - y)^{-4} - 1 \quad (12)$$

and  $r$  is the radial position within the cavity,  $V^*$  is a reduced cavity volume, and  $y$  is a reduced cavity radial position. Note that this transformation of variables allows the integral, Eq. (8), to be evaluated from 0 to 1 in  $y$  instead of from 0 to  $a$  in  $r$ . In this integral representation of the LJD model, the adsorbate molecule is free to move around within the fixed spherical cavity of the adsorbate. The potential field felt by the adsorbate depends on the distance  $r$  ( $y$  in reduced variables) from the center of the cavity.

The functional dependence of  $B_{2s}$  on temperature is described by Eq. (8). Note that this theoretical description for  $B_{2s}$  is specific to the structural model chosen.

In this case, the model is of interconnected spherical cavities. A flat surface or cylindrical pore model would lead to a different integral expression with different parameters to describe the adsorbent structure.

Determining the parameter values of  $a$ ,  $N_s$ , and  $E^*$  which best fit the experimental virial coefficients is based on the following procedure. If a unique value of  $V^*$  is chosen then a unique selection of  $E^*$  can be made using Eqs. (6), (7), and (8). Since  $c$  is a constant that involves only the structural parameters  $a$  and  $N_s$  then it should not vary with temperature. Thus the best  $V^*$  and  $E^*$  pair would be one in which  $B_{2s}/g$  is equal to  $c$ , a constant which does not vary as the temperature  $T$  is changed. The minimum value of the standard deviation of  $\log c$  is used as the criterion for goodness of fit of selected  $V^* - E^*$  values. The standard deviation of  $\log c$  rather than that of  $c$  is used so that only the scatter and not the magnitude of the numbers will affect the standard deviation. In the case of the chromatographic data, five temperature values are available in the range 300 to 374 K. Experimental values of  $B_{2s}$  are divided by calculated values of the integral  $g$  for a given  $V^*$  and  $E^*$  pair at each associated temperature  $T$ . An iterative procedure, in which the value of  $E^*$  is cycled until the minimum value of the standard deviation of  $\log c$  is found, is used to find the best fit  $E^*$  for a given  $V^*$  value. A Macintosh Plus computer using Microsoft Fortran was used for this analysis. The integral in Eq. (8) is evaluated using a numerical integration subroutine QUANC8 which is based on a quadrature adaptive Newton-Cotes eight panel method (Forsythe 1977).

For any selected value of  $V^*$  there is clear choice of  $E^*$ . However, it is not possible to use this same criterion of minimizing the standard deviation of  $\log c$  to make a unique selection among  $V^*$  and  $E^*$  pairs. For any  $V^*$ , an  $E^*$  value can be found which gives a good fit of the data even if the  $V^*$  and  $E^*$  values are physically unreasonable. In general, as  $V^*$  becomes smaller then the best fit  $E^*$  becomes smaller also. Fortunately, there is another criterion which places a restriction on acceptable  $V^*$  and  $E^*$  pairs. The interaction energy,  $w(r^*)/k$ , at equilibrium separation between the adsorbate and cavity wall,  $r^*$ , may be calculated from

$$w(r^*)/k = E^* \{ (1/20)V^{*-11/3} [(1 - V^{*-1/3})^{-10} \\ - (1 + V^{*-1/3})^{-10}] \\ - (1/4)V^{*-5/3} [(1 - V^{*-1/3})^{-4} \\ - (1 + V^{*-1/3})^{-4}] \} \quad (13)$$

or from

$$|w(r^*)/k| = \frac{d(\ln B_{2s})}{d(1/T)} \quad (14)$$

(Rybolt 1987). Since Eq. (14) can be used to calculate  $w(r^*)/k$  directly from experimental data then this provides a restriction to be placed on allowed pairs  $V^*$  and  $E^*$ .

To make an unambiguous selection of  $V^*$ , Eq. (13) is used to calculate  $w(r^*)/k$  for each  $V^* - E^*$  pair.

A plot of these  $w(r^*)/k$  values versus  $V^*$  generates a curve that goes through a maximum. On each side of the maximum there is one value of  $V^*$  which gives a  $w(r^*)/k$  which agrees with the one calculated from Eq. (14). The higher of these two values of  $V^*$  has been found to give the best fit of the data and so the higher  $V^*$  is always selected.

The procedure described above is used to find the  $w(r^*)/k$ ,  $V^*$ , and  $E^*$  which give the most consistent prediction of the available experimental data based on the theoretical equations and judged by determining the minimum value of the standard deviation of  $\log c$ . Also found from this analysis is the average value of the constant  $c$ ,  $\langle c \rangle$ . Eqs. (7) and (9) are used in conjunction with the best estimate of  $r^*$  to find values of  $a$  and  $N_s$ . Soto (1979) used the distance of closest approach between an argon atom and zeolite solid based on an oxygen-oxygen surface diameter of 0.276 nm and an Ar gas diameter of 0.335 nm. This gives an Ar-zeolite hard sphere separation of 0.306 nm and an equilibrium separation of 0.343 nm based on the relation between these two values for a Lennard-Jones 6-12 potential (Pierotti and Thomas 1971).

## RESULTS AND DISCUSSION

In Table 1 the  $B_{2s}$  values determined from gas-solid chromatography show the expected increase as the temperature is lowered. This trend indicates that, as expected, the gas-solid interaction increases with decreasing temperature.

To ascertain the validity of these data in the 300-374 K range it is necessary to compare them to other virial coefficients for the same argon-5A zeolite. Second gas-solid virial coefficients were obtained from Henry's law constants compiled by Yang and Pierotti (private communication).  $B_{2s}$  values were calculated from these

Henry's law constants and included 4 points in the 273-348 K range (Barrer 1956), 4 points in the 195-298 K range (Springer 1964), and 9 points in the 203-268 K range (Derrah and Ruthven 1975).

Figure 1 shows a plot of  $\ln B_{2s}$  versus  $1/T$  for each of these 4 sets of data. The GSC data seem to be in good agreement with adsorption isotherm data of Derrah (1975) and Springer (1964) while the data compiled for Barrer seem somewhat high. The solid line represents the best line (based on linear regression analysis) through the current GSC, Derrah, and Springer data.

The slope is 1381 K, intercept is  $-3.519$ , and the correlation coefficient is 0.997.

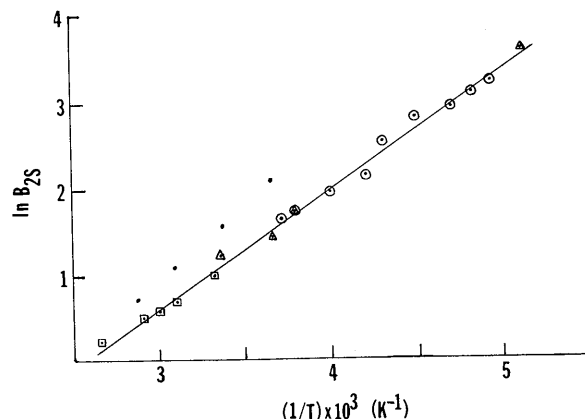


Figure 1. Plot of  $\ln B_{2s}$  versus  $1/T$  for Argon-5A Zeolite: this work - squares; Barrer - free points; Derrah - circles; Springer - triangles. Line represents linear fit of combined data: Derrah, Springer, and this work.

To compare further these virial coefficients, each of the four sets of data was analyzed individually and two combinations of the data sets, one with and one without the GSC data, were also analyzed. Tables 2 and 3 show the results. Eq. (14) was used in conjunction with the data shown in Fig. 1 to find the  $w(r^*)/k$  values shown in Table 2. The GSC slope is somewhat less than that of the Derrah and Springer data, but the Barrer slope is much higher. The best  $E^*$  and  $V^*$  values were found by using the fitting procedure outlined in the previous section which gives  $V^*$  and  $E^*$  pairs leading to the minimum of the standard deviation of  $\log c$  and also gives a  $w(r^*)/k$  value from Eq. (13) that agrees with the one calculated from the slope of  $\ln B_{2s}$  versus  $1/T$ .

TABLE 2. Energetic and Fitting Parameters from Virial Analysis.

Data Reference	$w(r^*)/k$ (K)	$E^*$ (K)	$V^*$	standard deviation of log $c$
(1) This Work	1145	12981	8.43	0.00745
(2) Barrer	1734	17968	8.08	0.00312
(3) Derrah	1356	13957	8.05	0.03866
(4) Springer	1381	14205	8.05	0.03555
(1 - 3 - 4)	1381	14459	8.12	0.03371
(2 - 3 - 4)	1213	12900	8.18	0.07275

The reduced volume,  $V^*$ , values do not vary much, and thus the  $E^*$  values are approximately proportional to the  $w(r^*)/k$  values. Note that the combined data set that includes the GSC data gives a smaller standard deviation value and hence better fit than the combined set that excludes the GSC data but includes the Barrer data.

TABLE 3. Structural Parameters from Virial Analysis.

Data Reference	$\langle c \rangle$ ( $\text{cm}^3/\text{g}$ )	$r^*$ (nm)	$a$ (nm)	$N_s \times 10^{-20}$ (cavities/g)
(1) This Work	0.4828	0.343	0.698	2.26
(2) Barrer	0.1475	0.343	0.688	0.72
(3) Derrah	0.3483	0.343	0.687	1.71
(4) Springer	0.3183	0.343	0.687	1.56
(1 - 3 - 4)	0.2943	0.343	0.689	1.43
(2 - 3 - 4)	0.6189	0.343	0.691	2.98

From Table 3 it is obvious that the values of  $\langle c \rangle$  and  $N_s$  are fairly sensitive to variation from one set of  $B_{2s}$  to another. The same value of  $r^*$  of 0.343 nm was used for each of the six data sets and since  $V^*$  is reasonably constant, the cavity diameter,  $a$ , calculated from Eq. (9), does not vary by much. The values determined from this analysis of 0.69 to 0.70 nm agree very well with the X-ray crystallographic average of 0.709 nm (radial distances vary from 0.704 to 0.723) for the 80 oxygen atoms that form the interior of the 5A zeolite. The other structural parameter  $N_s$  varies from one set to another and because  $a$  is relatively constant then  $N_s$  is approximately proportional to  $\langle c \rangle$  through Eq. (7).

The GSC data give a value of  $N_s$  that is slightly higher than the data of Derrah and Springer, but when the three sets are combined, the final value of  $N_s$  is slightly lower,  $1.43 \times 10^{20}$  cavities/g. The known value is  $3.59 \times 10^{20}$  cavities/g based on X-ray crystallographic studies. The combined data virial analysis gives a value that is only 40% of the true value. The structural model used does not make any attempt to account for the interior cavity wall surface that is missing due to the presence of the cavity windows. This lost surface area is approximately 50% in the 5A zeolite and if this factor were included in Eq. (7) when  $N_s$  is calculated from  $\langle c \rangle$  then the calculated  $N_s$  values would roughly double. Thus the exclusion of cavity windows in the LJD model is responsible for most of the apparent discrepancy between calculated and actual values of  $N_s$  for the 5A zeolite. We can see from this consideration that the combined set which includes the GSC data gives a much better agreement with experimental values than the combined set which includes Barrer's data instead.

The isolated GSC data also give a reasonable fit of the data with a value of  $N_s$  approximately 60% of the true value. Derrah's and Springer's data give values about 50% of the true value. Considering the approximations in the sphericalization of the cavity potential and the procedure of grouping the electrostatic induction and dispersion forces together, the derived structural parameters compare well with the expected values. These results support the use of a virial coefficient treatment as a model for adsorbate-adsorbent interactions in the Henry's law region.

The fitting procedure used in a LJD virial analysis is sensitive to the available experimental values of  $B_{2s}$ ; therefore it is desirable to have sufficient data over a broad temperature range. Because of the relative ease and speed of gas-solid chromatography relative to conventional adsorption isotherm techniques, the methods outlined in this paper can make a positive contribution toward obtaining such data and using it to model behavior of adsorbates in microporous solids.

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