

## Temperature-dependent adsorption of nitrogen on porous vycor glass

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(Received 20 May 1997; revised manuscript received 10 October 1997)

Adsorption isotherms of  $N_2$  have been measured in the temperature range from 77 to 120 K in samples of porous vycor glass. From the Brunauer-Emmett-Teller theory the surface layer coverages are determined. These are found to be temperature dependent. When adsorption-isotherm coverage data are expressed as a function of the adsorption potential  $\delta\mu$ , the result is roughly temperature independent for coverages ranging from submonolayer to thin film, below capillary condensation. This characteristic curve, which represents the distribution of adsorption sites vs the adsorption potential, is compared with results from two models for the adsorbate: Dubinin's isotherm for microporous solids and its extension to rough surfaces, which places importance on the porosity of the surface, and Halsey's extension of the Frankel-Halsey-Hill isotherm, which takes into account the long-range variations of the substrate adsorption potential. The impact of this work on the interpretation of  $N_2$  adsorption data in terms of a surface area is discussed. [S0163-1829(98)02110-9]

For decades, porous materials, such as solid porous catalysts, have been characterized by interpreting gas adsorption data. Measurements are performed with nitrogen gas on a dry, out-gased sample, at the normal boiling point of nitrogen that is 77 K.<sup>1</sup> The Brunauer-Emmett-Teller (BET) model<sup>2</sup> of localized adsorption has been the method of choice for the determination of the sample surface area. This model assumes that there are a number of adsorption sites on the surface and that each one of these sites is at the base of a stack of sites extending out from the surface. It is assumed also that each pile of sites forms an independent and equivalent statistical system. Yet this model is an oversimplification, since it does not take roughness and heterogeneity effects into account. This is well known and a broad range of theories of the adsorbed film in heterogeneous and structured porous systems have been proposed<sup>3,4</sup> but, often, the range of applicability is too narrow to lead to conclusive information.<sup>5</sup> Here, we show that the temperature dependence of the adsorption can be exploited to simplify an otherwise complicated analysis of isotherms of porous vycor glass.

The investigation of the effect of confining geometries on processes taking place within them is of current interest. The commercially available porous vycor glass (PVG) is a prototype porous monolithic material that has been used in many of these studies, including superfluidity of helium<sup>6</sup> and supercooling.<sup>7</sup> PVG is also of interest as a low dielectric constant material for microelectronics.<sup>8</sup> Furthermore, PVG is utilized as a template in many emerging technologies, such as metal- and semiconductor-insulator composite<sup>9</sup> fabrication. These applications will be impacted by a more accurate determination of its surface area.

We recently reported on the temperature-dependent adsorption of  $H_2$ ,  $D_2$ , and neon on samples of PVG over a wide temperature range.<sup>10</sup> It was found that the BET adsorption description is unsuitable for these systems. Instead, a temperature-independent characteristic adsorption curve constructed from experimental data allows for the analysis of adsorption isotherms in the range from submonolayer to multilayer coverages at any temperature in a model-independent way.<sup>11</sup> The extension of the Dubinin-Kaganer

adsorption curve to heterogeneous surfaces with a pore size distribution of a fractal nature<sup>12</sup> gives the best fits to our hydrogen data over restricted ranges, but fails to provide a unified picture of the experiments. Halsey's model,<sup>13</sup> which takes into account the long-range variations of substrate adsorption potential, gives much better results for  $H_2$ . At the fundamental level it is important to understand if the adsorbates of heavier molecules such as  $N_2$  display these effects also.

The vycor sample (Corning 7930) consisted of 7 rods 3.58 mm diam. The volume was  $1.48 \text{ cm}^3 \pm 0.02 \text{ cm}^3$ . It was prepared by boiling in solutions of 30%  $H_2O_2$ , rinsing in boiling deionized water, and drying at 150 C for 2 h. After this process the sample weight was 2.14 gm. The sample was contained in a closely fitting copper adsorption cell which was immersed in a liquid  $N_2$  bath. The  $N_2$  vapor pressure was monitored and the temperature of the liquid bath calculated from tables.<sup>14</sup> Adsorption isotherms were measured volumetrically by admitting portions of gas from an adsorption volume ( $466 \text{ cm}^3 \pm 0.5 \text{ cm}^3$ ) into the experimental cell through a valve. The volume of the dead space was measured by admitting a charge of helium into the experimental cell; helium can be assumed to be negligibly adsorbed at 77.4 K. At this temperature, the dead space volume is  $0.8 \text{ cm}^3$  at STP.

Adsorption data are presented in Fig. 1. For clarity purposes, not all the experimental points are shown, although all points were used when analyzing the data. The isotherms are of type IV according to Brunauer's classification as they show two plateaus, and indicative of a sample with mesopores. The adsorption-desorption loop corresponds to the type of behavior associated with the presence of "ink-bottle" pores or tubular capillaries of variable cross section.

The BET isotherm<sup>2</sup> may be written as

$$\frac{n}{n_m} = \frac{x}{1-x} \frac{c}{1+(c-1)x}, \quad (1)$$

where  $n$  is the number of moles of gas adsorbed per  $\text{cm}^3$  of vycor at pressure  $P$ , and  $x$  is  $P/P_0$ , with  $P_0$  the saturation

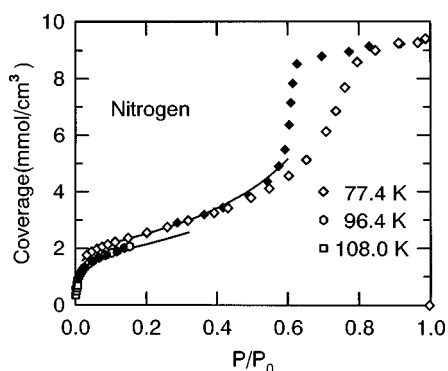


FIG. 1. Adsorption (open symbols) and desorption (full symbols) isotherms of nitrogen. The ordinate axis represents amounts adsorbed per unit volume of the sample. The temperature of the measurements is indicated.  $P_0$  is the saturation pressure at the corresponding temperature. The solid lines represent a calculation based on BET as described in the text.

pressure,  $n_m$  is the number of moles of gas per  $\text{cm}^3$  of vycor sample adsorbed in a monolayer and  $c$  is  $\exp(-(E_{\text{ads}} - E_L)/T)$ . Here  $E_{\text{ads}}$  is the molar heat of adsorption per mole at the vycor surface, and  $E_L$  is the latent heat.

Since the adsorption isotherms show hysteresis for high coverages, when reduced pressures larger than  $x=0.6$  are included we obtain negative values for  $c$ . Thus, good fits to Eq. (1) can be obtained only for low coverages. The value obtained for  $n_m$  from the BET fit is rather independent of the saturation pressure, yet larger values are obtained at lower temperatures. The BET fit to the adsorption data at various temperatures is shown in Fig. 1. The BET model fits the data rather poorly and the adsorbate density  $n_{\text{BET}}$  thus obtained is temperature dependent. Best fits are obtained for  $n_m = 2.1 \text{ mmol/cm}^3$  and  $c=138$  at 77.4 K. We obtained  $n_m = 1.78 \text{ mmol/cm}^3$  and  $c=102$  at 96.4 K. Additionally, we obtained  $n_m = 0.9 \text{ mmol/cm}^3$  and  $c=444$  at 108 K. For higher temperatures the isotherms show decreased adsorption and the BET model fits data very poorly.

Using the molecular diameter of  $\text{N}_2$  of  $0.162 \text{ nm}^2$ , a rough estimate of the pore surface area of  $207 \text{ m}^2/\text{cm}^3 \pm 10 \text{ m}^2/\text{cm}^3$  is obtained from the data at 77.4 K. From the measured porosity (filling factor) of 0.31, and assuming cylindrical pores, a pore radius of 3.1 nm is obtained. These values are consistent with the average pore radius and porosity given by the manufacturer. The pore size distribution can be obtained, from the adsorption-desorption, using the method devised by Barret, Joyner and Halender.<sup>15</sup> Analysis of PVG samples using this method gives an average pore radius of roughly 3 nm.

A convenient variable to describe saturation is  $\delta\mu = \mu_g - \mu_b$ , the difference in chemical potential per molecule between unsaturated and saturated conditions. Here  $\mu_g$  is the chemical potential per molecule of the gas at temperature  $T$  and pressure  $P$ ;  $\mu_b$  and  $P_0$  are the chemical potential per molecule and vapor pressure of the bulk phase (liquid) at temperature  $T$ , respectively.  $\delta\mu$  can be calculated from the properties of the gas through

$$\delta\mu = -T \ln(\rho_0/\rho) + 2(B/R)(P - P_0), \quad (2)$$

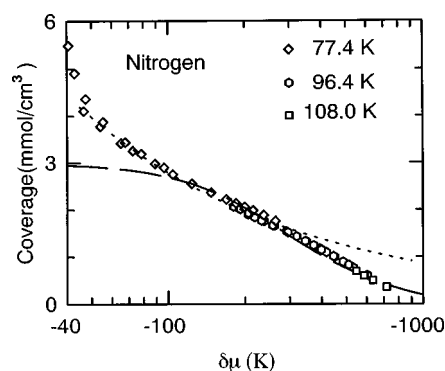


FIG. 2. Temperature-independent adsorption curve of  $\text{N}_2$  at low coverages. The dotted line is a fit based on the FHH equation as described in the text. The dotted-dashed line represents a fit based on a fractal distribution of micropores, Eqs. (4), with  $x_{\text{min}} = 0.2 \text{ nm}$ ,  $x_{\text{max}} = 1.7 \text{ nm}$ ,  $d=2.3$ , and  $m = 1.38 \times 10^{-5} \text{ K}^{-2}$ .

where  $R$  is the gas constant and  $B$  is the virial coefficient. For the gas densities at temperature  $T$  and pressure  $P$ ,  $\rho$ , and at temperature  $T_0$  and pressure  $P_0$ ,  $\rho_0$ , we use the virial equation of state.<sup>16</sup> It is well known that when adsorption isotherm data are presented as a function of the adsorption potential  $\delta\mu$ , the result is roughly temperature independent. This is shown in Fig. 2. This does not apply to coverages and temperatures at which hysteresis sets in, that is, in the region of capillary condensation. We note that the departure of Eq. (2) from the ideal gas result,  $T \ln(P/P_0)$ , is less than 6 K and therefore only matters in the region of capillary condensation. A temperature-independent curve is also obtained for hydrogen adsorption on PVG.<sup>10</sup>

At *prima facie* the temperature dependence of the surface layer coverages may be an artifact related to the varying chemical potential range utilized for the various temperatures. However, as shown in Fig. 1, the fits of the BET equation to the experimental data are not very satisfactory. At 77.4 K, best fit is obtained for  $E_{\text{ads}} - E_L = 350 \text{ K}$  since the adsorption strength parameter  $c$  is equal to 92. An essential feature of the BET isotherm is a temperature-independent inflection, occurring for  $\delta\mu \sim E_{\text{ads}} - E_L$  and  $n = n_{\text{BET}}/2$ , which identifies the formation of a monolayer. The feature in the experimental data in Fig. 2 at around 350 K is rather broad, indicating that  $E_{\text{ads}}$  and  $n_{\text{BET}}$  are not well defined for  $\text{N}_2$  on porous vycor glass.

Fig. 2 shows the best fit to the data of the Frankel-Halsey-Hill (FHH) equation at intermediate coverages:<sup>3</sup>

$$n(\delta\mu) = n_{\text{FHH}}(-\delta\mu)^{-\nu}, \quad (3)$$

where  $n_{\text{FHH}}$  is the coverage strength. From this fit, the values  $n_{\text{FHH}} = 29.2 \text{ mmol/cm}^3$  and  $\nu = 0.51 \pm 0.05$  are obtained. This value of  $\nu$  is anomalous because one expects  $\nu = \frac{1}{3}$  for a purely dispersive potential. At very high adsorption potentials  $\delta\mu$ , the decrease of the adsorption data is more pronounced. The plots of  $n$  vs  $\delta\mu$  show a slight temperature dependence for large adsorption potentials. Coverages at 77.4 K are larger than those at 96 K for the same adsorption potential around  $\delta\mu = -200 \text{ K}$ . Also, coverages at 96.4 K are larger than those at 108 K at the same chemical potential around  $-600 \text{ K}$ . A similar, slight temperature dependence is also exhibited by hydrogen and neon.<sup>10</sup> This could be due to

a number of reasons. It is easiest to argue a lack of equilibrium between the adsorbate and pressure gauge. Yet, we have repeated the experiment a number of times and obtained the same results. Figure 2 shows that  $n$  vs  $\delta\mu$  exhibits a slight temperature dependence. As indicated by Bering, Dubinin, and Serpiensky,<sup>17</sup> the temperature dependence of the characteristic adsorption curve is due to the positive value of the adsorbate entropy. The entropy of adsorption is also discussed in the context of Halsey's isotherm in Ref. 13.

It has been proposed that the isotherm equation by Dubinin<sup>17</sup> for porous materials is a good starting point. This isotherm is confined to the monolayer and submonolayer regions. It assumes a gaussian distribution of adsorption sites on the surface, and is expressed as  $n = n_K \exp[-(\delta\mu/V_K)^2]$ , with  $V_K$  a characteristic adsorption potential. Kaganer<sup>18</sup> discussed this equation and interpreted  $n_K$  as the number of molecules in a monolayer. Note that the formation of a monolayer, as identified from a sharp bend in the characteristic adsorption isotherm, occurs for  $\delta\mu = V_K$  in this model. The Dubinin isotherm is useful to describe adsorption on heterogeneous surfaces such as flat (nonporous) glass. The characteristic curves of nitrogen on pyrex glass measured by Hobson and Armstrong<sup>19</sup> are remarkably well represented by Dubinin's isotherm, for coverages in the monolayer and submonolayer region. Best fit is obtained in that case for  $V_K = -880 \pm 10$  K. This isotherm fits the characteristic curve of Fig. 2, only over a very limited range of coverages. Best fit is obtained for  $V_K = -542 \pm 10$  K and  $n_K = 2.0$  mmol/cm<sup>3</sup>. Note that the characteristic adsorption energies for N<sub>2</sub> on PVG are less than for pyrex glass. An opposite effect is observed for H<sub>2</sub>. The low coverage region will be examined further below. The broad feature indicates a wide distribution of characteristic adsorption potentials.

The effect of a distribution of pore sizes on the adsorption was recently considered theoretically by Jaroniec, Lu, Madey, and Avnir.<sup>12</sup> They considered the vycor surface as a fractal. They find that the adsorption isotherm can be expressed as

$$n(\delta\mu) = n_J \int_{x_{\min}}^{x_{\max}} J(x) \exp[-mx^2(\delta\mu)^2] dx, \quad (4)$$

where  $n_J$  is the number of moles of gas adsorbed per cm<sup>3</sup> of vycor.  $J(x) = J_0 x^{2-d}$  is the normalized micropore size distribution function,<sup>20</sup> with  $x$  the half width of the slitlike micropores, and  $d$  the fractal dimension.  $x_{\max}$  and  $x_{\min}$  denote the maximum and minimum values of  $x$ , respectively.  $m$  is a parameter related to the fractal distribution.

The fractal form of the FHH equation [Eq. (3)] can be obtained from Eq. (4) for  $x_{\min} = 0$  and  $x_{\max} = \infty$ , with  $\nu = 3 - d$ :  $n(\delta\mu) = n_{\text{FHH}}(-\delta\mu)^{-(3-d)}$ . Following the interpretation offered by Jaroniec, Lu, Madey and Avnir,<sup>12</sup> and using  $\nu = 0.51$  as obtained from a fit to the intermediate coverage data, we obtain  $d = 2.49 \pm 0.05$ . Recent small-angle neutron scatterings experiments give  $d = 2.4$  for dry samples.<sup>21,22</sup> Analysis of the small-angle x-ray scattering is more involved,<sup>23</sup> a value of  $d = 2.40 \pm 0.10$  is obtained with this technique. This is very promising, however, a very wide pore size distribution, of roughly between 1 and 100 nm, is required to fit the intermediate coverages where the FHH works well. Instead, in order to fit the low coverages, a very

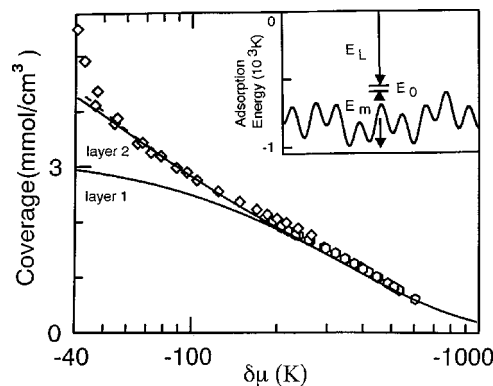


FIG. 3. Characteristic adsorption curve of nitrogen on PVG.  $\delta\mu$  is the chemical potential difference between the adsorbed state and the bulk at the same temperature. The dotted line represents Halsey's isotherm, Eq. (5), with  $n_H = 2.95$  mmol/cm<sup>3</sup>,  $E_0 = 40$  K, and  $E_m = 350$  K. The adsorption in the first and the first two layers are shown also. Inset: A schematic view of the adsorption potential as a function of position.

narrow distribution is needed. We have fitted the isotherm in Eqs. (4) to our adsorption data at low coverages. A best fit is obtained for a restricted range of pore sizes from  $x_{\min} = 0.2$  nm to  $x_{\max} = 1.7$  nm. This is shown in Fig. 2. Thus, we were not able to obtain a single pore size distribution that adequately fits both low and intermediate coverages. This leads us to disfavor the fractal form of the adsorption isotherm by Jaroniec *et al.*, in spite of the agreement between the value of  $d$ , the surface fractal dimension, obtained from the modified FHH behavior and previous determinations.

We have also fitted the experimental data to Halsey's isotherm for heterogeneous surfaces.<sup>13</sup> This isotherm is based on the assumptions that the adsorbate-solid interaction is due to dispersion interactions and that the distribution of energies over a site in each layer has an exponential form. The adsorbate density can be expressed as  $n = n_H(\theta_1 + \dots + \theta_r + \dots)$ , where  $n_H$  is the number of sites per unit volume of sample and  $\theta_r$  is the occupation probability of the  $r$ th layer:

$$\theta_r = \exp\{[\delta\mu + (E_0/r^3)]/(E_m/r^3)\}. \quad (5)$$

Here  $E_m$  is the modulation and  $E_0$  is the absolute value of the energy distribution minimum. The  $r^3$  factor takes into account the dependence of the adsorption potential on the layer distance to the surface. For positive exponents  $\theta_r$  is taken to be one. The resulting characteristic curve is temperature independent. At intermediate coverages Halsey's isotherm behaves like a FHH isotherm, Eq. (5), with  $\nu = 0.37$ , independently of the  $E_m$  value. As shown in Fig. 4, comparison with the experimental data reveals good agreement for intermediate coverages. From a best fit of Eq. (5) to the experimental data the values of  $E_0 = 40$  K,  $E_m = 350$  K, and  $n_H = 2.95$  mmol/cm<sup>3</sup> are obtained. Taking the molecular area of N<sub>2</sub> to be 0.162 nm<sup>2</sup>, an estimate of the pore surface area of 288 m<sup>2</sup>/cm<sup>3</sup>  $\pm$  10 m<sup>2</sup>/cm<sup>3</sup> is obtained. This is roughly 40% larger than that estimated from the BET method. The origin of this discrepancy lies in the long-range variations of the adsorption potential that favors the formation of islands of adsorbate in the sites of minimum adsorption potential. Figure 3 shows the adsorbate density for layers 1 and 2, separately. According to Halsey's model, the second layer starts filling before the first layer has been completed filled. This

highlights the importance of the heterogeneity of the PVG. Presumably, the potential variations are due to compositional and morphological heterogeneities and therefore the spatial scale  $\xi$ , which is much larger than the  $N_2$  molecular diameter and of the order of magnitude of the pore diameter, that is  $\sim 6$  nm. The inset of Fig. 3 shows a sketch of the surface adsorption potential according to our model.  $E_L$ , the latent heat per molecule, is taken to be  $-600$  K.<sup>16</sup> The inset illustrates a very important point: small to moderate heterogeneities of the adsorption energy can result in large variations of the potential difference between the adsorbed and the liquid state. In summary, Halsey's model fits the data over a wide range of coverages and temperatures since it incorporates both the adsorbate chemical potential heterogeneity and its dependence upon distance in a balanced way.

A comparison between our  $N_2$  adsorption isotherm for PVG at 77.4 K and that for porous silica Si-60 by Drake, Yacullo, Levitz, and Klafter<sup>5</sup> shows many similarities in the low coverage, intermediate, and capillary condensation regimes. However, the interpretation of the data is very different. Most striking is the adherence to the BET model in Ref. 5. Measurements of the temperature dependence of  $N_2$  ad-

sorption on Si-60 can perhaps resolve this discrepancy.

In conclusion, the temperature dependence of the adsorption of  $N_2$  allow us to test the theoretical models of heterogeneous adsorption. Extension of the Dubinin-Kaganer characteristic adsorption curve to heterogeneous surfaces with a pore size distribution of a fractal nature gives the best fit to our data over a limited coverage ranges but fails to provide a unified picture of the experiments. Halsey's model for heterogeneous adsorption gives remarkably good results considering that it has only two adjustable parameters. In this model, the fluctuations of the adsorption potential are not distributed randomly across the interface but grouped together in patches so as to give rise to long-range variations of the adsorption potential. Our best estimate of the surface area of our sample of PVG is based on Halsey's method and is  $288 \text{ m}^2/\text{cm}^3$ . We find that BET is unsuitable for our system and underestimates the surface area by 40%.

This work was supported by NSF through Grant Nos. DMR-926079 and DMR-9632819. Acknowledgment is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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