CONF-880779-1

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CONF-880779--1

DE88 013840

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For presentation at the
NATO ASI on Adsorption: Science and Technology
Vimeiro, Portugal, July 17-29, 1988

To be submitted to Separation Science and Technology

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VACUUM SORPTION PUMPING AT CRYOGENIC TEMPERATURES OF ARGON AND OXYGEN ON MOLECULAR SIEVES†

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Keywords: Adsorption, Cryosorption, Zeolite, Molecular Sieve

ABSTRACT

Cryosorption pumping is a method of evacuating enclosed volumes by adsorbing gas on a deep bed of solid sorbent (typically a zeolite) at cryogenic temperatures. Modeling the dynamic behavior of these systems for air pumping requires information on two major constituents of air, oxygen and argon, which had not been previously studied, as well as data on a nonadsorbing specie, helium. Deep beds of Davison 4A molecular sieves were subjected to a metered flow of pure gas and the pressure history of the experiment was monitored, using computer data acquisition techniques. Particle size variation is the major variable in determining the mechanism of the process. The data acquired in the current study compare favorably with previous experiments.

Previously developed models for the dynamic sorption behavior of deep beds under vacuum for two extreme conditions, micropore and macropore control were tested in this study. The sorption behavior of argon clearly fit into the category of macropore controlled sorption, indicating that these species are adsorbed primarily on the surface of the zeolite crystals, much like the theoretical and experimental results for N_2 cryosorption on the same sieves of Crabb et al.(1986). On the other hand oxygen sorption is most likely micropore controlled, and may be modeled by the method of Prazniak (1988).

INTRODUCTION

Cryosorption pumping is a method of evacuating an enclosure by adsorbing the contained gases on a refrigerated solid sorbent. It is currently used in a number of instrumentation applications and in evacuating large chambers associated with advanced

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†Research sponsored by the office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

energy applications. Investigators have typically studied the sorption behavior of air at temperatures from 77 K to 100 K, but new applications have emphasized the sorption of individual gases as well. Helium and hydrogen are of current interest in the study of fusion reactors, where large volumes of those gases must be removed from magnetic and radioactive environments. Experiments to study the cryopumping of hydrogen and helium have been carried out at temperatures as low as 4.2 K (Fisher and Watson 1976). Cryosorption pumps have also been employed to remove argon used in the sputter coating of semiconductor devices (Dennison and Gray, 1979). Such pumps can also be used to adsorb and hold hazardous gases from hazardous or gases from remote areas temporarily until a disposition can be determined (Wheeler 1974).

Typically cryosorption pumping is performed in a fixed bed of molecular sieves in which all the sorbate that enters the bed is adsorbed and no flow exits the bed. The basic components of the sorption pumping experiment are shown in a simplified manner in Fig. 1. Depending on the experiment, either liquid nitrogen or an acetone-dry ice bath is used to control the temperature of the bed. The experiment simply consists of allowing a constant flow of a gas to be admitted to a previously-evacuated and desorbed bed of molecular sieves. The pressure in the gas phase above the bed and at several locations down the bed is measured as the run progresses. The pressure range of interest is below 1 torr (133 Pa) for the vacuum applications of interest, so tests are terminated when the above-bed pressure reaches that range.

Various sorbents may be used in cryopumping applications, but zeolite molecular sieves are preferred because of their high pumping speed, physical stability, and chemical inertness. An aspect of cryosorption pumps which has not been thoroughly studied is the fundamental transport phenomena which underlie cryopumps. In a previous series of experiments Crabb and Perona (1985) began study of the individual components of air using nitrogen and carbon dioxide as their sorbed gases. The purpose of this study is to observe the sorption behavior of the two remaining major components of air, argon and O_2 in fixed beds containing the same type of 4A molecular sieves as were used by the previous experimenters and to compare the results with the Crabb and Perona (1985) model for macropore control and the model of Prazniak and Byers (1988) model for micropore control. The second objective was to observe the behavior of a non-adsorbing component, helium, in the bed.

Experimental.

In their experiments, Crabb et al.(1986) used the apparatus shown in Fig. 2 to adsorb N_2 and CO_2 on zeolite 4A molecular sieve. This apparatus was modified to streamline its performance and used in the current study. Pressurized gas flows from a cylinder through a calibrated stainless steel orifice. The gas leak rate is determined by the back pressure on the system. The leak rate for argon was 2.49 $\times 10^{-4}$ mol/s, the oxygen rate was 4.74 $\times 10^{-4}$ mol/s and the helium rate was 7.52 $\times 10^{-4}$ mole/s. A single bed was used for the experiments in the current series. The gas flows to head-space above the bed, the tubing to the pressure gauges and to the bed itself, which is a 20 cm section of 1.2 cm ID stainless steel tubing. Differential pressure cells were connected to the top and bottom of the bed with 0.63 cm OD tubing. The millivolt signal from the capacitance manometers was converted to a digital signal by an A/D conversion board (Data Translation Model 2801) interfaced to a microcomputer (IBM PC-AT) for graphical display and digital data storage. A computer code was used to convert these signals to absolute pressure and to monitor the pressure at preset time intervals throughout the run. Throughout the runs a reference pressure of about 10^{-3} torr (.133Pa) was maintained with an ion pump.

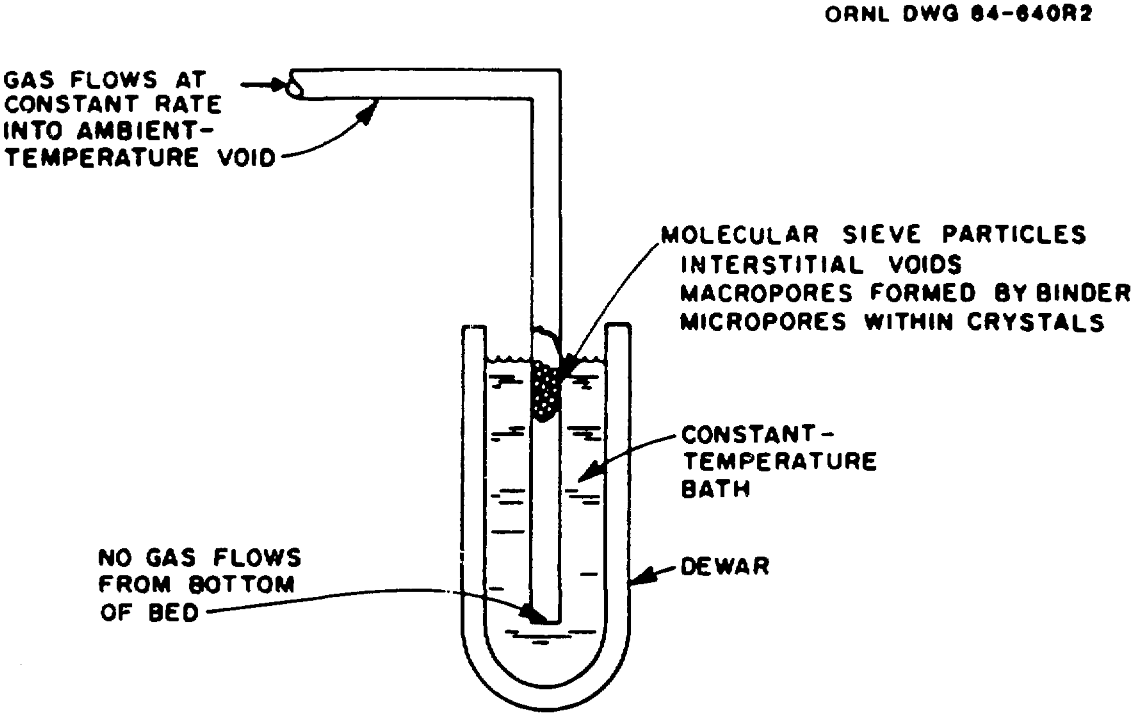

Fig. 1. Primary components of an experimental apparatus for observing the cryosorption behavior of gases.

The sorbent was from the same batch of Davison Chemical Division of W. R. Grace and Co. 4A synthetic zeolite molecular sieve as was used by Crabb et al. (1986). The material is nominally spherical, with a size range of 14 to 40 mesh, which were cut into fraction using wire mesh screens. Two series of runs were made, one with diameters ranging from 0.50 to 0.60 mm (35 to 30 mesh) and the other from 0.35 to 0.42 mm (45 to 40 mesh). In the earlier study it was determined that the mean crystal size of the zeolite is approximately 1.85 μm and that there was a considerable range around this mean.

Before a run, the bed was held at 200°C for 2 h, while it was evacuated using an external pumping system. The bed was cooled to room temperature, isolated from the external pump and then submerged in the coolant (liquid nitrogen in the current series) . After the pressure steadied to approximately 10^{-3} torr and the bed had been allowed to stand in the coolant for 2 h, the valve from the gas cylinder was opened and data acquisition began. Data were gathered from the experiment until the bed became saturated or a pressure of 1 torr was reached. Regeneration of the bed followed.

THEORETICAL BACKGROUND

The theoretical mass transport theory which describes the behavior of gases during sorption on zeolites under conditions of high vacuum was developed by Crabb et al (1986) and by Prazniak and Byers (1987). The main challenge in modeling the system surrounds nature of the mass transfer resistance of the 4A zeolite pellets which consist of cubic crystals, with a mean edge length of 1.7–2.0 mm, fixed in an inert binder. For the purposes of analysis, they were assumed to spherical with volumes equal to the cube volumes. About 10% of the sieve particle volume is occupied by the binder which includes some voids within the binder(macrovoids). The movement of molecular

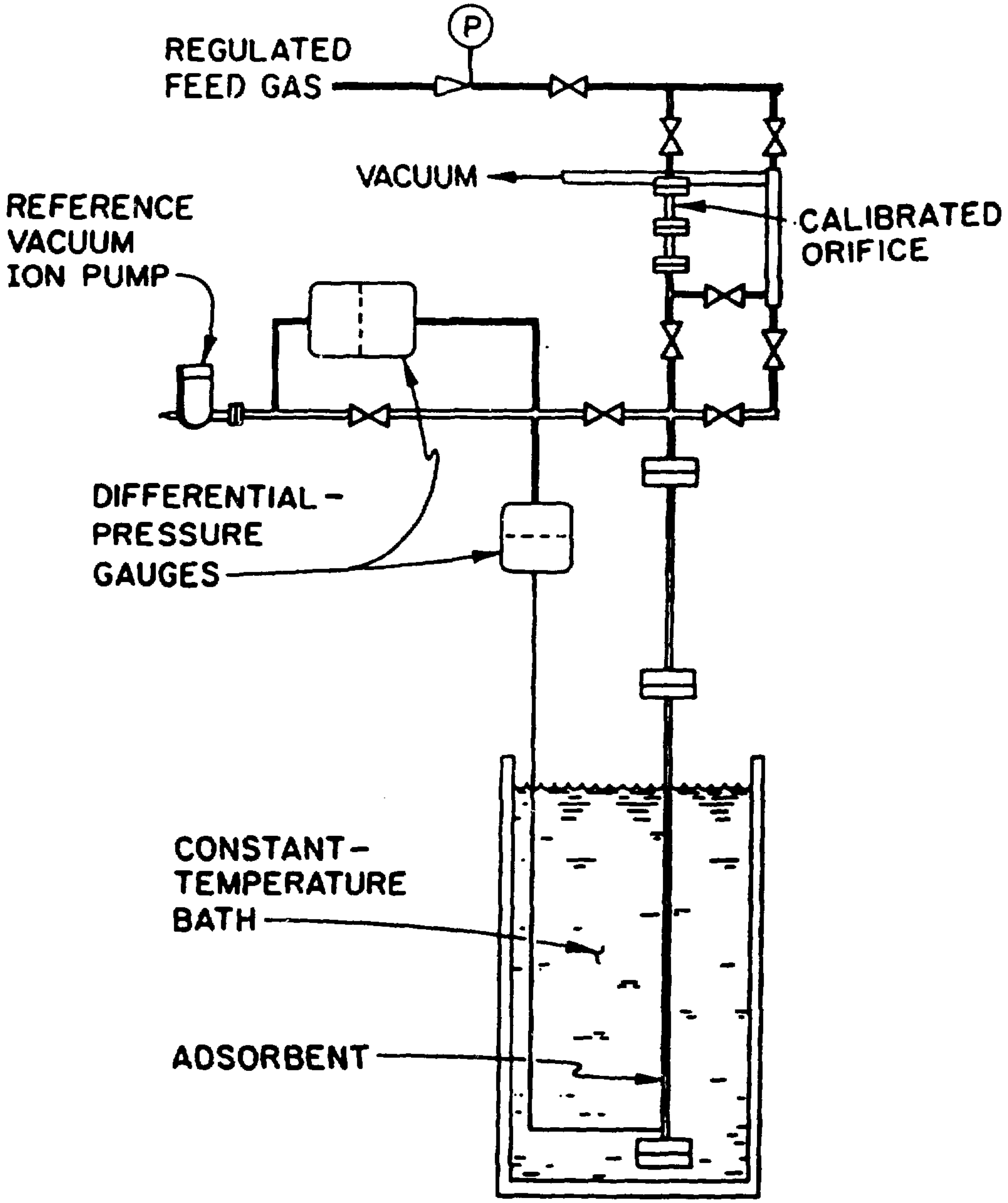

Fig. 2 Sorption Pumping Apparatus

species within the crystals presumably occurs in the intracrystal voids (microvoids). The remaining volume consists of interstitial voids between the molecular sieve particles which is usually referred to simply as the void fraction (ϵ). If the major transport resistance occurs within the macrovoids, as might be the case when crystal surface adsorption occurs, a macropore model is used, and the characteristic size is the diameter of the molecular sieve particle. On the other hand, if the major resistance to transport is within the crystals, a micropore model is called for, and the characteristic size is the zeolite crystal equivalent diameter. The characteristic lengths in these two limits are an order-of-magnitude different.

The model presented here assumes micropore control, creating a situation where the macropores are considered as part of the interstices. The unsteady-state mass balance on a differential section of bed is a typical one for granular bed applications.

$$\epsilon \frac{\partial c}{\partial t} + \epsilon \frac{\partial (vc)}{\partial z} + \rho_b \frac{\partial \bar{q}}{\partial t} = 0, \tag{1}$$

The accumulation of sorbate within the volume in the fluid phase, $\epsilon(\partial c/\partial t)$, is related to the accumulation of material in the unit volume due to the changing flux of gas molecules through the interstices and macrovoids, $\epsilon[\partial(vc)/\partial z]$, and the mean accumulation of sorbate in the solid phase, $\rho_b(\partial \bar{q}/\partial t)$. The unsteady-state diffusion equation for a sphere in one dimension represents transient diffusion in the solid phase,

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D_z \frac{\partial q}{\partial r} \right], \tag{2}$$

where D_z is the effective zeolitic diffusivity.

Boundary conditions at the top of the bed ($z = 0$) is given as a fluid-phase balance. This flux is be expressed in terms of the flow into the system and the accumulation of gas in the head space,

$$\epsilon A D_p \left. \frac{\partial c}{\partial z} \right|_{z=0} = \frac{Q}{RT_a} - V \left. \frac{\partial c}{\partial t} \right|_{hs} . \tag{3}$$

The feed, Q, is constant. Although $V\partial c/\partial t|_{hs}$, the accumulation in the head space, is not known explicitly, it can be related to the accumulation at the top of the bed. The zero-flux condition at the bottom of the bed ($z = l$) is expressed as

$$\left.\frac{\partial c}{\partial z}\right|_{z=L} = 0 \tag{4}$$

Turning to the solid phase, a symmetry condition is implicit in the model, while solid-gas equilibrium is assumed at the zeolite crystal surfaces. Because of the low pressure range concentration can be related to pressure by the ideal gas law. The Langmuir isotherm,

$$\frac{q(R)}{q_m} = \frac{kp}{1+kp}, \tag{5}$$

was used by Crabb and Perona (1985) to represent the adsorption of CO_2 and N_2 on zeolite 4A molecular sieve, will be applied in the current study for O_2 and argon. Experimental isotherm data were available for pressures as low as 1 torr, but extrapolations were necessary to include the pressure range of the experiments.

The second term in Eq. (1), representing the flux of gas molecules through a cross-section of the bed can be represented using a form of Fick's law with an effective pore diffusivity, D_p:

$$\frac{\partial(vc)}{\partial z} = D_p \frac{\partial^2 c}{\partial z^2} \tag{6}$$

The pore diffusion is has three significant contributions in the vacuum sorption case, D_K, the Knudsen diffusion, D_m, the molecular diffusion and, D_{Pois}, the Poiseuille Diffusion. Ruthven (1984) gives the following equation for estimating the pore diffusivity from the component diffusivities described above:

$$D_p = \left[\frac{1}{D_K} + \frac{1}{D_m}\right]^{-1} + \quad D_{\text{Pois}} \; . \tag{7}$$

At low pressures and small pore radii, collisions of molecules with the walls of pores are the primary resistance to flow, and Knudsen diffusion is dominant. At higher pressures when collisions between molecules become the primary resistance to flow, molecular diffusion and Poiseuille flow are dominant. In the transition region, contributions from all three mechanisms may be computed using Eq. (7).

In the solid phase, the diffusivity of the sorbate within the crystals is also considered to be dependent on the concentration of the diffusing species. Garg and Ruthven (1973a) suggest that the Darken equation, which leads to the following relationship

$$D_z = \frac{D_0}{\left(1 - \frac{q}{q_m}\right)} . \tag{8}$$

where D_z is the concentration-dependent solid phase diffusion coefficient and D_0 is the corrected diffusivity which is a constant. Incorporating the concentration-dependent diffusivity, the diffusion equation for the sorbent particle can be rewritten as

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D_z(q) \frac{\partial q}{\partial r} \right] . \tag{9}$$

Returning to Eq. (1), it will not be possible to express the average accumulation of the sorbate in the solid phase, $\rho_b(\partial\bar{q}/\partial t)$, as a simple function of the pressure. However, it can be expressed in terms of the other dependent variable, the point solid loading, q. The concentration profile can be integrated to obtain $\bar{q}$, and $\partial\bar{q}/\partial t$ can be computed by difference, but it is numerically complex to do so. Instead, $\partial\bar{q}/\partial t$ can be calculated in terms of the sorbate flux at the surface of the crystal. Because the net flux in a crystal is assumed to be inward, a crystal acts as a mass sink, and the flux of sorbate across the crystal surface is equivalent to the instantaneous mean accumulation in the crystal. The accumulation can be calculated from the concentration gradient at the crystal surface and the packing characteristics of the sorbent:

$$\frac{\partial \bar{q}}{\partial t} = D_z(q)\phi_z \left.\frac{\partial q}{\partial r}\right|_{r=R} , \tag{10}$$

where ϕ_z is the crystal surface area per unit crystal volume, or $3/R$.

Incorporation of Eqs. (9) and (10) into the model Eqs., (1) and (2) yields the fluid balances in terms of the gas pressure and the solid loading.

$$\left.\frac{\partial p}{\partial t}\right|_z = \frac{RT}{\epsilon}\left\{\frac{\epsilon D_p(p)}{RT}\frac{\partial^2 p}{\partial z^2} - \rho_b\left[D_z(q)\phi_z \left.\frac{\partial q}{\partial r}\right|_{r=R}\right]\right\} , \tag{11}$$

This balance with the previously-stated boundary conditions represents a nonlinear system of equations, which must be solved numerically for realistic experimental situations. Prazniak and Byers (1987) have applied orthogonal collocation methods to the solution. Four constant must be evaluated either by independent experiment or by some other means, such as theoretical computation or fitting parameters. Two of the parameters k and q_m are respectively the linear constant and the capacity factor in the Langmuir equilibrium equation. Equilibrium data, when available, will yield these numbers. The single variable associated with the fluid phase transport reduced to r_p, the mean pore radius of the macrovoid volume. Measurement is relatively simple here, but since it involves averaging and assuming a spherical shape, where the particles are actually cubic, the validity of the number is in question. Finally the solid diffusion value D_O may be measured, but so few measurements actually exist, so that this variable actually is a fitted parameter.

RESULTS AND DISCUSSION

The objectives of this study was to round out the results on the components of air which was begun by Crabb and Perona (1985) by reporting data on the cryosorption of O_2 and argon on 4A molecular sieves. It was anticipated that argon would possibly behave somewhat like N_2, while the O_2 results might be somewhat similar to those of CO_2. In addition data on the sorption of He were take in an attempt to monitor a nonadsorbing case. An added objective in all cases was the taking of very short time data, to follow the very great increase in pressures which occurred in the first few minutes of any run. The results are reported for each of the chemical species independently.

Helium Experiments.

Like most of the experiments in the series, pure helium experiments were made with beds of 10.5 cm depth containing different particle sizes (38.4 and 46.0 μm). A He back pressure of 0.73 MPa gave a constant flow rate of 7.52×10^{-4} torr L/s into the sorption system. The results of all experiments were virtually identical to the one shown in Fig. 3 for a 46.0 μm bed. The data indicate a linear increase in pressure with time over the 5- min experiment. The pressure drop over the length of the bed was negligible except for the first half minute.

Since helium is not sorbed to any significant extent in these molecular sieves, only flow parameters can contribute to any pressure drop in the bed. It would appear from the linear character of the head-space pressure that the equalization of pressure is faster than the instrumentation used in these experiments. With zero sorption the model given in Eq. 11 reduces to

$$\frac{\partial p}{\partial t} - D_p \frac{\partial^2 p}{\partial z^2} = 0 \qquad (12)$$

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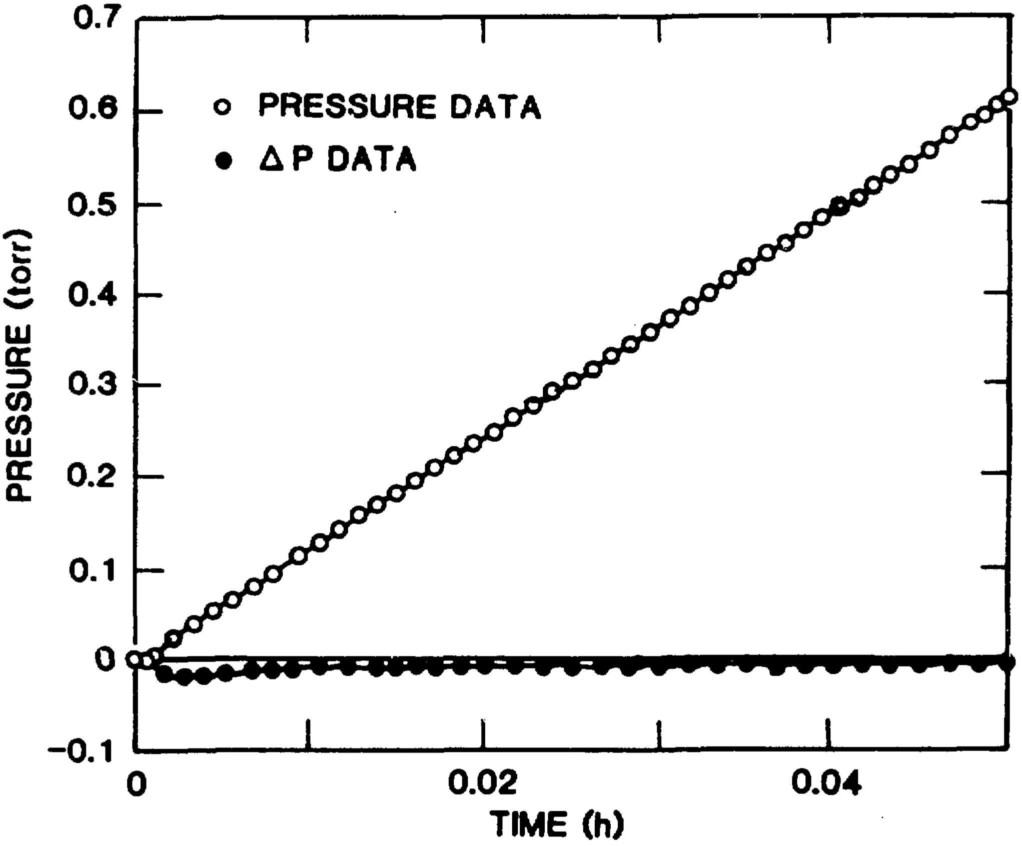

Fig. 3. Sorption of helium into a bed of 38.5 μm Davison 4A molecular sieves, 10.5 cm deep.

with the initial and boundary conditions as follow

$$p(z,0) = 0$$

$$\left.\frac{\partial p}{\partial z}\right|_{z=L} = 0$$

$$\text{and} \quad \left.\frac{\epsilon D_p}{RT}\frac{\partial p}{\partial z}\right|_{z=0} = F$$

where F is the constant mass flux into the top of the bed.

A solution is presented by Carslaw and Jaeger (1959) as follows:

$$p = \frac{Ft}{\rho c L} + \frac{FLRT_b}{\epsilon D_p}\left[\frac{3z^2 - L^2}{6L^2} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}e^{-D_p n^2 \pi^2 t/L^2}\cos\frac{n\pi z}{L}\right] \tag{13}$$

The first term in Eq . 13 is the linear increase in pressure with time for flow into a closed vessel. The remainder is a correction for transient behavior in position and time. Based on the assumptions of Crabb and Perona (1985), D_p for helium at 77K is approximately 150 cm^2/s. Since the second term in Eq. 13 is negligible for $D_p t/L^2 > 0.3$, virtual equilibration occurs in 0.22 seconds. This is a much shorter time than is possible to monitor with the current experiment. We would probably require a much longer bed, say 10m in depth. The experiments do show that the transport resistance within the bulk void volume if the experiments using the sorbing gases (O_2 and A) is negligible compared to the resistance within the zeolite pellets.

Argon and Oxygen Experiments.

Sorption data were taken with beds of pellets of two different average pellet diameters, 0.385 mm and 0.55 mm. The model of Prazniak and Byers was applied to these data. Micropore control of the transport is implicit in this model. Previous application of this model to CO_2 and N_2 data of Crabb and Perona yielded good agreement in the case of CO_2, where both the headspace pressure and the pressure drop histories were well modeled. On the other hand, accurate results were not found for the very low diffusivities which appear to be required for N_2.

Sorption curves for argon and oxygen are given in Fig. 4-7. Parameter values for k, q_m, r_p and D_0 which characterize the process based on the Prazniak and Byers model are listed in Table 1.

The values were obtained by exploring the range of reasonable parameters for each sorption experiment. It should be noted that there exist no equilibrium sorption data for these gases on Davison 4A molecular sieves in the temperature range of interest. Therefore equilibrium parameters were included in the list of fitted parameters. The process of modeling vacuum sorption of these gases would be aided immeasurably by the existence of equilibrium data. There is some evidence that in the low pressure region the Langmuir isotherm does not give as good a fit to the data as does the Freundlich isotherm (Byers, Watson, and Sisson; 1988). It was found that the theoretical prediction is most sensitive to r_p and q_m. Therefore it is of interesting to find the shape of the equilibrium curves in this region.

For argon, the parameter values which yield a good fit for the 0.385 mm particles predict much longer sorption times than the data indicates for the 0.55 mm particles (Fig. 4 and 5). The strong dependence of the data on particle diameter indicate that the assumption of micropore control is not valid. This result is not unexpected in light of the fact that argon is more lightly sorbed than N_2, whose behavior appears to be macropore controlled (Crabb and Perona 1986).

The oxygen data yielded a similar result (Fig. 6 and 7), which is somewhat unexpected, since the data indicate sorption which is quite similar in magnitude to CO_2. There are a number of possible explanations. The most obvious is that oxygen is different and has a significant contribution from macropores. This possibility is under

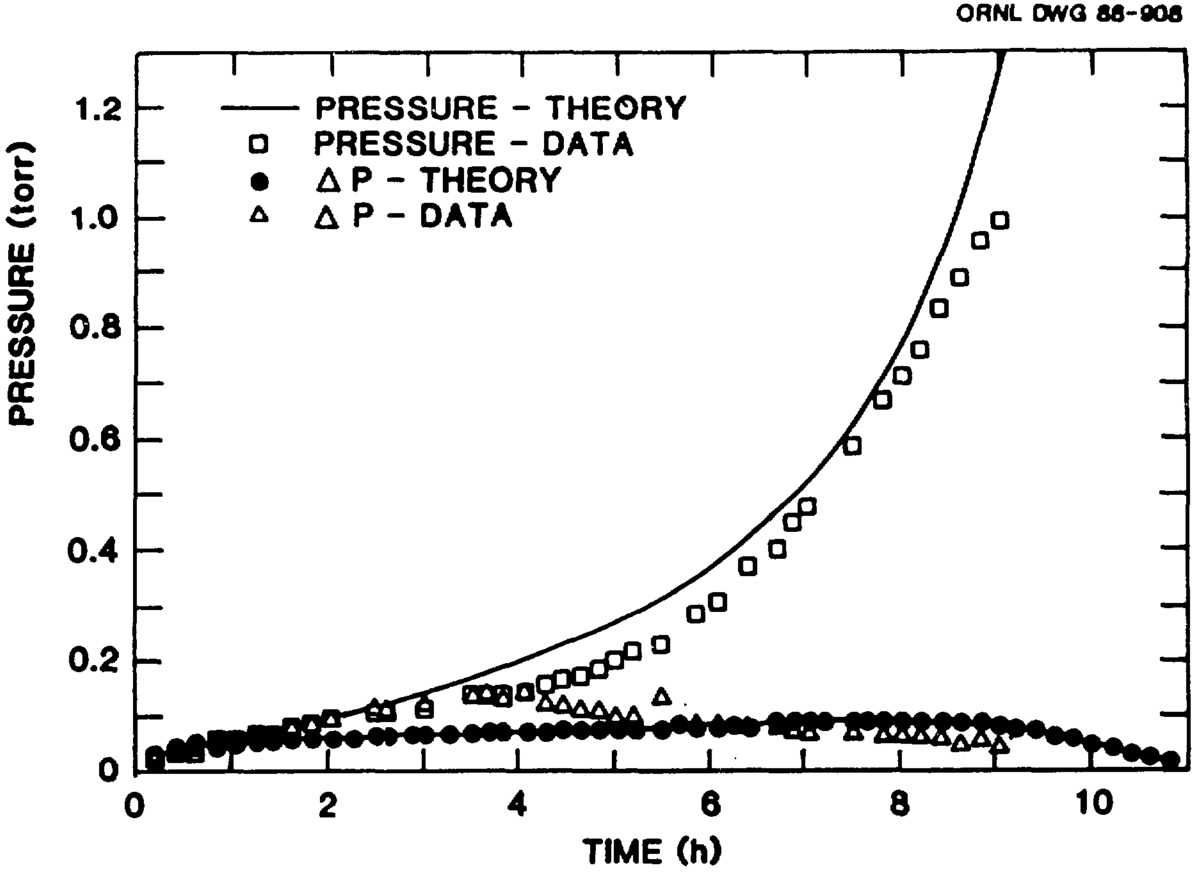

Fig. 4. Sorption of argon on Davison 4A molecular sieve spheres (0.385 mm mean diameter).

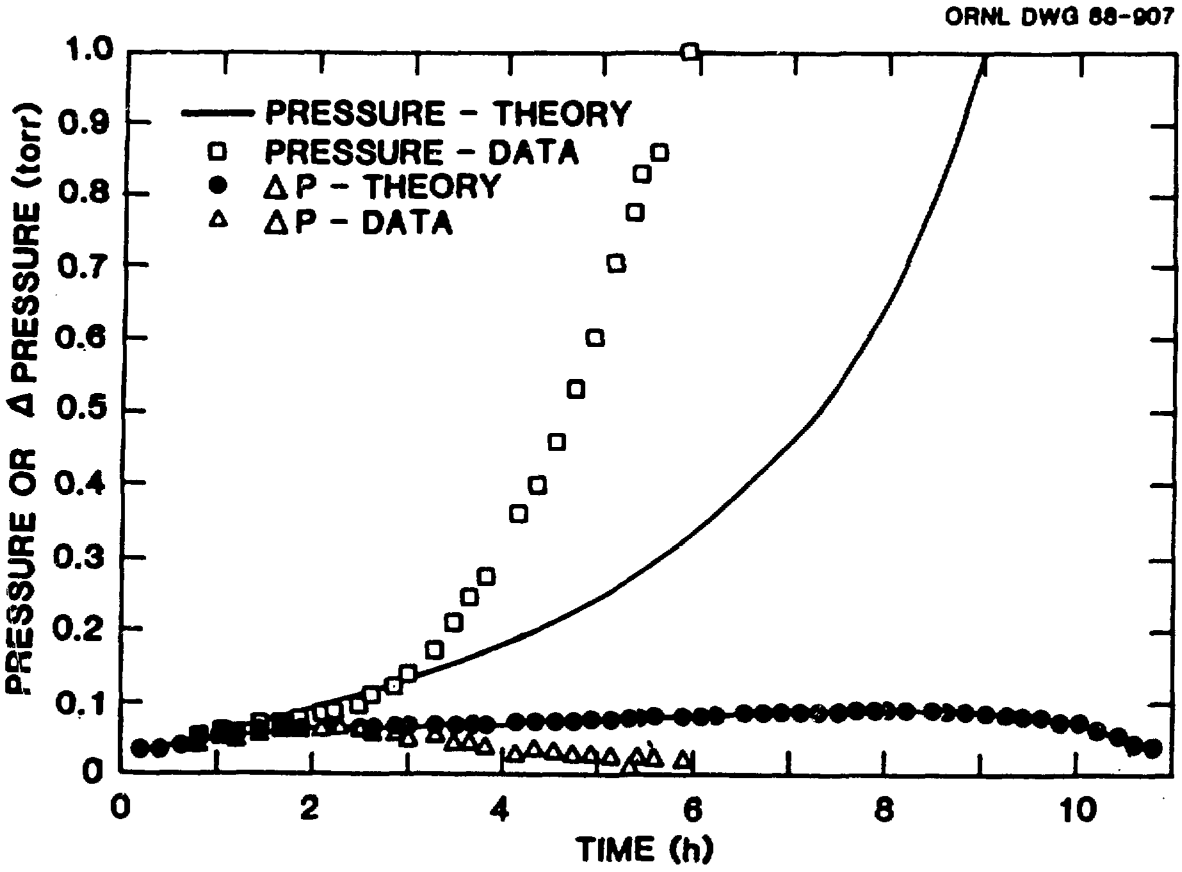

Fig. 5. Sorption of argon on Davison 4A molecular sieve spheres (0.55 mm mean diameter).

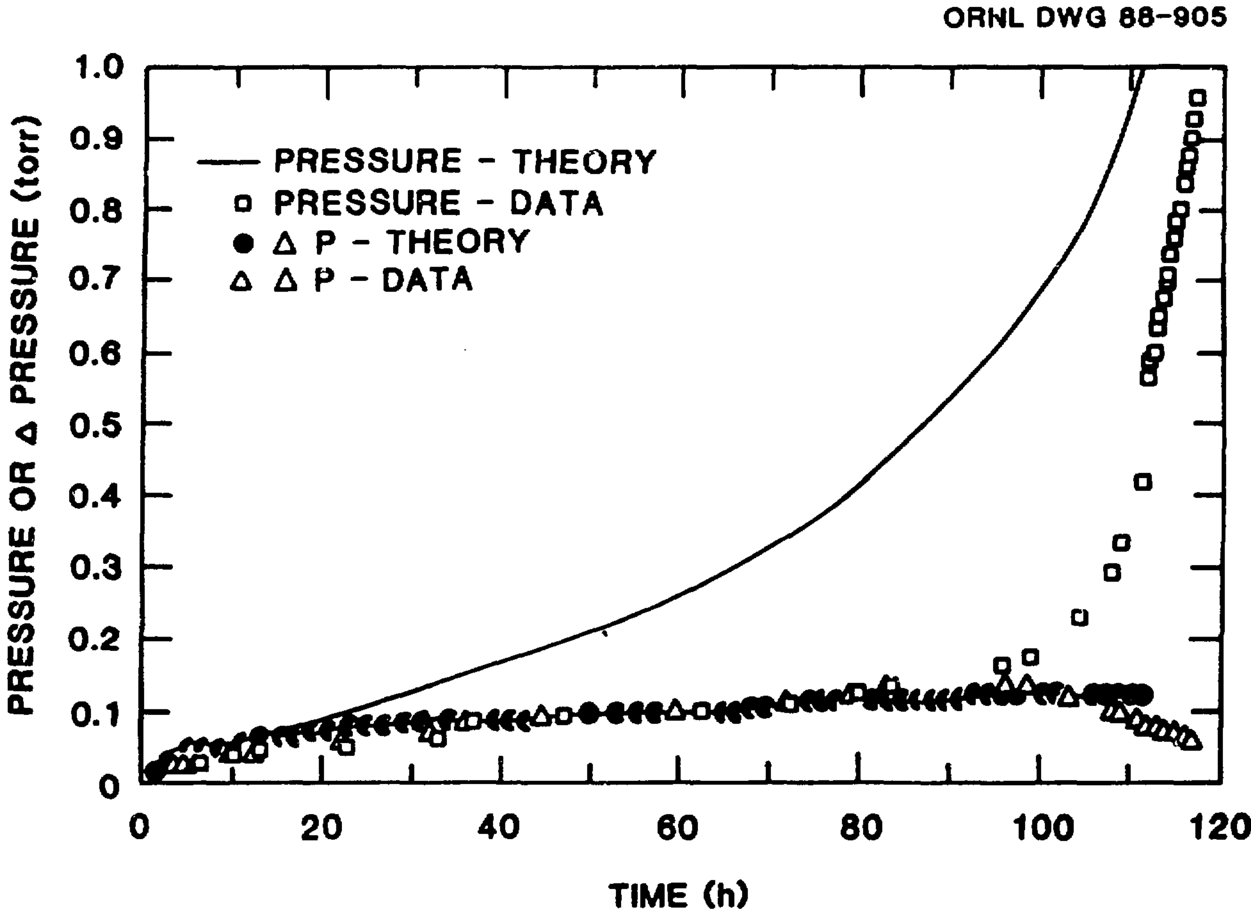

Fig. 6. Sorption of oxygen on Davison 4A molecular sieve spheres (0.385 mm mean diameter).

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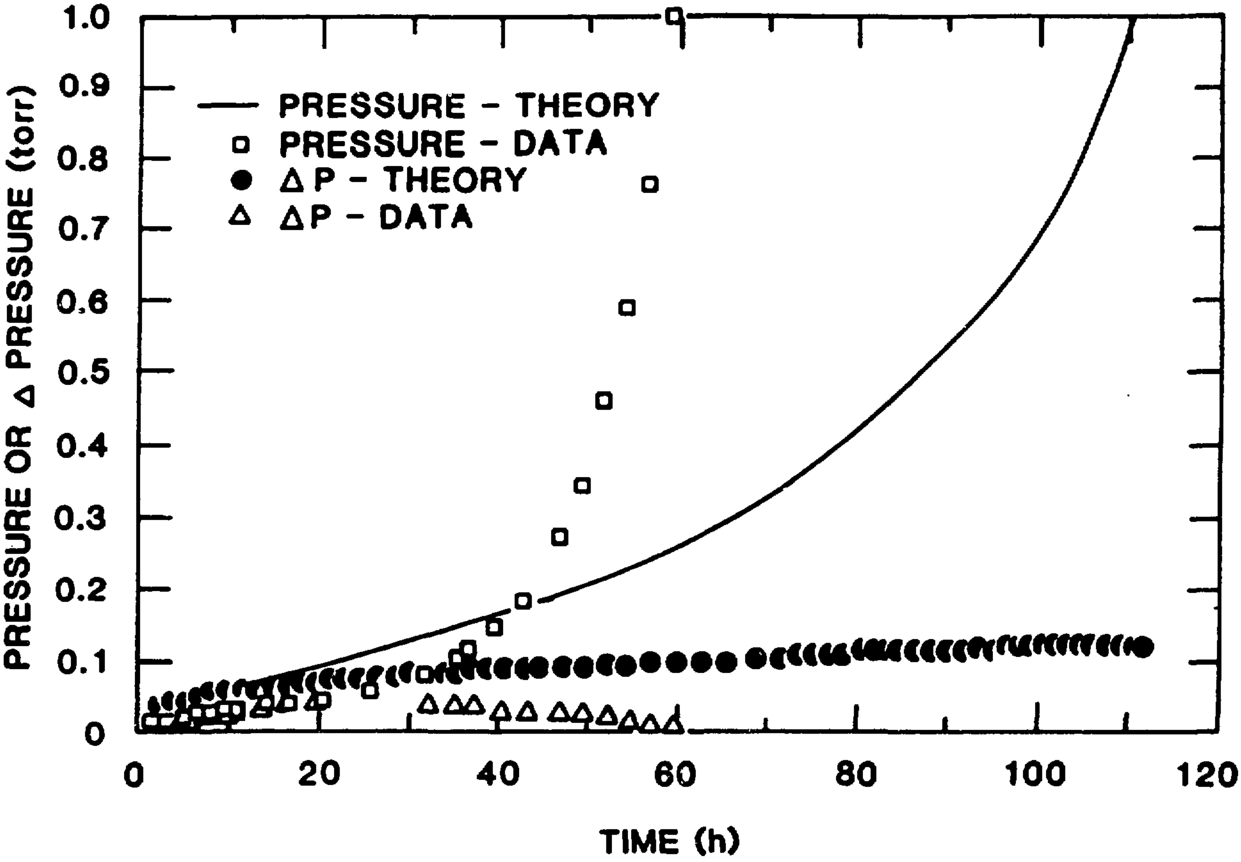

Fig. 7. Sorption of oxygen on Davison 4A molecular sieve spheres (0.55 mm mean diameter).

Table 1

Model Parameter for the Micropore Theory

Parameter	Existing Runs	Current Runs
	CO_2 Runs	*O_2 Runs*
k	4.0 torr^{-1}	4.0 torr^{-1}
q_m	0.0040 mol/g	0.0035 mol/g
r_p	0.0064 cm	0.0025 cm
D_0	1×10^{-13} cm^2/s	1×10^{-13} cm^2/s
	N_2 Runs	*Argon Runs*
k	20.0 torr^{-1}	4.0 torr^{-1}
q_m	0.00019 mol/g	0.00012 mol/g
r_p	0.0064 cm	0.0020 cm
D_0	1×10^{-11} cm^2/s	1×10^{-11} cm^2/s

consideration. Secondly the shape of the equilibrium curve may well be different from our Langmuir isotherm assumption. Finally, the behavior of oxygen is often different from other gases, for instance in its magnetic properties, and we may be observing a manifestation of this difference (Breck 1974).

In terms of application to vacuum sorption pumping of air, the data indicate that the sorption will probably control the process as it is manifested in the head- space pressure. Oxygen and CO_2 would be preferentially sorbed, while argon exists in air to a much lessor extent than N_2. Because of its high concentration and low saturation solid phase concentration on 4A molecular sieves, N_2 would be the only gas left in a space above a vacuum sorption apparatus in relatively short order. Thus this sieve would be a questionable choice for this service. These assertions are based on the assumption that there is no interaction between the sorbing species in the sorption on the solid. Testing of this assumption would require more experimentation with multicomponent vacuum sorption and equilibrium sorption. A multicomponent extension of the Prazniak and Byers model is readily accomplished.

NOTATION

A	Cross-sectional area of bed, cm^2
c	Concentration of gas, mol/cm^3
D	General diffusivity of sorbate in sorbent particle [Eq. (46)], cm^2/s
D_0	Corrected diffusivity, cm^2/s
D_K	Knudsen diffusivity, cm^2/s
D_M	Molecular diffusivity, cm^2/s
D_p	Pore diffusivity for bed, cm^2/s
D_{Pois}	Poiseuille diffusivity, cm^2/s
D_z	Zeolitic diffusivity, cm^2/s
k	Langmuir equilibrium constant, torr^{-1}
L	Length of bed, cm
M	Molecular weight of sorbate, mol/g
n	Number of moles in ideal gas equation
p	Column pressure, torr
$\hat{p}$	Column pressure ratio, p/p_r
p_r	Reference pressure, torr
Δp_{max}	Maximum pressure drop, torr
q	Point solid loading in sorbent particle, mol sorbed gas /g molecular sieve
$\bar{q}$	Average solid loading in sorbent particle, mol sorbed gas /g molecular sieve
$\hat{q}$	Solid loading, q/q_m
q_m	Langmuir saturation constant, mol/g molecular sieve
Q	Flow into headspace, torr·L/s
r	Radial position in sorbent particle, cm
$\hat{r}$	Radial distance ratio, r/R
r_p	Mean pore radius, cm
R	Sorbent particle radius, cm, or
R	Gas constant, torr L/mol K
t	Time, s
T_a	Ambient temperature, K
T	Bed and sorbate temperature, K
v	Gas velocity through bed, cm/s
V	Volume, cm^3
z	Axial distance along bed, cm
$\hat{z}$	Axial distance, z/L

Greek Letters

ϵ	Fraction of bed available to gas, cm^3 void/cm^3 bed

θ_G	Fraction of bed available to gas, cm^3 void/cm^3 bed
ρ_b	Bulk density of molecular sieve, g/cm^3 bed
ϕ_Z	Sorbent fraction of bed volume, cm^3 sorbent /cm^3 bed
μ	Gas viscosity, g·cm/s

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