Equilibria of Nitrogen, Oxygen, Argon, and Air in Molecular Sieve 5A

Pure-component equilibrium data for nitrogen, oxygen, and argon, and multicomponent equilibrium data for air in 20 × 40 mesh 5A molecular sieve were measured at 297.15, 233.15, and 203.15 K and up to pressures of 4 bar. The multicomponent data were analyzed by a statistical thermodynamic model, ideal adsorbed solution theory, an extended Langmuir-Sips equation, and an extended Langmuir equation. The multicomponent system exhibited nonideal behavior at 233.15 and 203.15 K. Isotherm parameters determined in this work may be useful in the design and evaluation of molecular sieve air separation systems.

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Introduction

Air separation by pressure swing adsorption (PSA) involves the adsorption and desorption of a multicomponent mixture (air) on fixed beds of adsorbent due to cyclic pressure variation. Certain adsorbents, such as molecular sieve 5A, have a significantly greater affinity for nitrogen in comparison to oxygen, and therefore a properly designed process is capable of yielding a product containing 95% oxygen (Lee and Stahl, 1973). In the design and modeling of such processes it is essential that the designer have means at his disposal for ascertaining the multicomponent adsorption equilibria over various pressures and temperatures. Unfortunately, the limited availability of multicomponent data and the complexities of multicomponent data collection compel one to search for practical predictive techniques. Two well-known predictive techniques, a statistical thermodynamic model (Ruthven, 1971; Ruthven et al., 1973) and ideal adsorbed solution theory (IAST; Myers and Prausnitz, 1965), are based on pure-component data and have been shown to correctly predict nitrogen-oxygen-5A adsorption equilibria at certain conditions (Ruthven, 1976; Sorial et al., 1983).

The primary goal of this work was to investigate the applicability of these techniques over a wide pressure range (up to 4 bar) and at low temperature where the mixture might be expected to act nonideally. Pure-component equilibria of nitrogen, oxygen, and argon, and multicomponent equilibria of air on molecular sieve 5A at 297.15, 233.15, and 203.15 K are presented and analyzed using statistical thermodynamic, IAST, extended Langmuir-Sips, and extended Langmuir models. Binary and ternary forms of these models have been applied to the multicomponent mixture (air) adsorption data to determine the effects of neglecting argon in a binary (N_2—O_2) analysis.

Theory

Statistical thermodynamic model

Ruthven (1971) proposed that because zeolites are crystalline structures with precise uniformity, statistical thermodynamics might be used to model their adsorption behavior. By application of techniques presented by Hill (1960), he formulated a simple theoretical adsorption isotherm for zeolites. This theory assumes that when more than one adsorbate molecule is present within a cavity the sorbate-sorbate interaction is expressed as a reduction in free cavity volume. Additionally, the potential fields within the zeolite crytalline structure are assumed to remain constant regardless of the number of sorbate molecules present. In the application of this model two parameters, the Henry's law constant K and effective molecular volume β, must be determined by analysis of pure-component isotherm data. The Henry's law constant accounts for the sorbent-sorbate interaction and is usually determined by taking the slope of the pure-component isotherm in the low-pressure regime. The effective molecular volume accounts for the sorbate-sorbate interaction and may be determined by superimposing pure-component isotherm data over theoretical isotherm curves (Ruthven, 1976). The energy of molecular interaction is expressed by a Sutherland potential (Ruthven, 1971).

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The pure-component and binary forms of the statistical thermodynamic model have been presented elsewhere (Ruthven, 1971; Ruthven et al., 1973). Here we review the ternary form of the theory. We assume a zeolite crystal with M cavities where the number of molecules necessary to entirely fill a cavity with a pure-component species A, B, or C is m_A, m_B, and m_C, respectively. According to Hill (1960) the grand partition function is,

$$G_{ABC}(\lambda_A, \lambda_B, \lambda_C, M, T) = \left[\sum_i^{m_A} \sum_j^{m_B} \sum_w^{m_C} q(i, j, w)\lambda_A^i \lambda_B^j \lambda_C^w\right]^M = Q_{ABC}^M(\lambda_A, \lambda_B, \lambda_C, T)$$

where,

$$q(i, j, w)\lambda_A^i \lambda_B^j \lambda_C^w = Z(i, j, w)\alpha_A^i \alpha_B^j \alpha_C^w$$

satisfying the restriction $i\beta_A + j\beta_B + w\beta_C \leq V$. $q(i, j, w)$ is the partition function of a single cavity of a set of equivalent cavities, and $Z(i, j, w)$ is the configuration integral for a cavity with i molecules of A, j molecules of B, and w molecules of C. The activity, α, for an ideal gas is equal to p/kT. The average concentration of A is,

$$n_A = N_A/M = \lambda_A(\partial \ln Q_{ABC}/\partial \lambda_A)_{\lambda_B, \lambda_C, T} = \frac{\sum_i^{m_A} \sum_j^{m_B} \sum_w^{m_C} iZ(i, j, w)\alpha_A^i \alpha_B^j \alpha_C^w}{\sum_i^{m_A} \sum_j^{m_B} \sum_w^{m_C} Z(i, j, w)\alpha_A^i \alpha_B^j \alpha_C^w}$$

The expressions for the configuration integrals are,

$$\begin{aligned} Z(0, 0, 0) &= Z(0) = 1 \\ Z(1, 0, 0)p_A/kT &= Z(1, 0, 0)\alpha_A = K_A p_A \\ Z(0, 1, 0)p_B/kT &= Z(0, 1, 0)\alpha_B = K_B p_B \\ Z(0, 0, 1)p_C/kT &= Z(0, 0, 1)\alpha_C = K_C p_C \\ Z(i, j, w) &= (\mathrm{X})(\Lambda)(\Omega) \end{aligned}$$

where,

$$\begin{aligned} \mathrm{X} &= Z(1, 0, 0)^i Z(0, 1, 0)^j Z(0, 0, 1)^w / i!j!w! \\ \Lambda &= (1 - i\beta_A/V - j\beta_B/V - w\beta_C/V)^{i+j+w} \\ \Omega &= \exp\left[(1 - i\epsilon_A\beta_A - j\epsilon_B\beta_B - w\epsilon_C\beta_C)/VkT\right] \end{aligned} \tag{1}$$

The concentration of A may be found by the following expressions,

$$\Theta = \sum_i^{m_A} \sum_j^{m_B} \sum_w^{m_C} \frac{(K_A p_A)^i (K_B p_B)^j (K_C p_C)^w (\Lambda)(\Omega)}{i!j!w!}$$

$$n_A = \frac{K_A p_A + (\Theta i)}{1 + K_A p_A + K_B p_B + K_C p_C + (\Theta)} \tag{2}$$

where,

$$i + j + w \geq 2 \quad \text{and} \quad i\beta_A + j\beta_B + w\beta_C \leq V$$

Similar expressions for n_B and n_C may be obtained.

Ideal adsorbed solution theory

The ideal adsorbed solution theory (IAST) of Myers and Prausnitz (1965) suggested that the adsorbates in a multicomponent mixture in thermodynamic equilibrium form an ideal solution with constant spreading pressure. In the development of the thermodynamic equations to describe this system spreading pressure, ν, replaces pressure, and area, A, is substituted for volume. The final expressions take a form similar to Raoult's law. The isothermal Gibbs adsorption isotherm is applied (Van Ness, 1969),

$$A d\pi = \sum_i n_i d\mu_i \tag{3}$$

and when integrated for the pure-component case gives (Myers, 1984):

$$\pi_i^o A/RT = \int_{P_i^o=0}^{P_i^o} (n_i^o/P_i^o)\, dP_i^o$$

This integral is usually evaluated numerically through use of curve-fitted plots of n_i^o/P_i^o vs. P_i^o if pure-component isotherm data are available. The equations necessary for analysis of a ternary system are presented below and are a straightforward extension of the binary development found in Myers and Prausnitz (1965). They may be solved analytically to give the amount of each component adsorbed.

$$\begin{gathered} \pi_A^o = \Psi_A(P_A^o),\ \pi_B^o = \Psi_B(P_B^o),\ \pi_C^o = \Psi_C(P_C^o) \\ Py_A = P_A^o(\pi)x_A,\ Py_B = P_B^o(\pi)x_B,\ Py_C = P_C^o(\pi)x_C \\ \pi_A^o = \pi_B^o = \pi_C^o \\ x_A + x_B + x_C = 1,\ y_A + y_B + y_C = 1 \\ n_t = [x_A/n_A^o(\pi) + x_B/n_B^o(\pi) + x_C/n_C^o(\pi)]^{-1} \end{gathered}$$

Experimental

Apparatus

A diagram of the volumetric adsorption apparatus used for measuring both the pure- and multicomponent adsorption equilibria is shown in Figure 1. Volumes of the sample and charge chambers, *C1* and *C2*, were determined by water displacement and nitrogen gas expansions and are given in Table 1. Both techniques gave nearly identical results. Pressure measurements were accomplished by Statham model PA208TC-50-350 stainless steel diaphragm pressure transducers, *P1* and *P2* in Figure 1. Copper-constantan thermocouples, *T1* and *T2*, sensed the charge and sample chamber temperatures. The sample chamber was maintained at a constant temperature by a temperature-controlled chamber, *T*, composed of a two-stage refrigeration unit and internal air circulation system. During the ternary equilibrium experiments the gas phase concentrations were measured by a medical gas analyzer, *MGA*, Perkin-Elmer model MGA-1100. Other components of the experimental setup were a vacuum pump, *V*, a variable transformer, *X*, and an electrical heater, *H*.

Materials

The adsorbent employed in this work was Union Carbide 20 x 40 mesh, medical grade, molecular sieve 5A (Lot No. 9427-80-0171) described in Table 1. The dehydrated sieve was

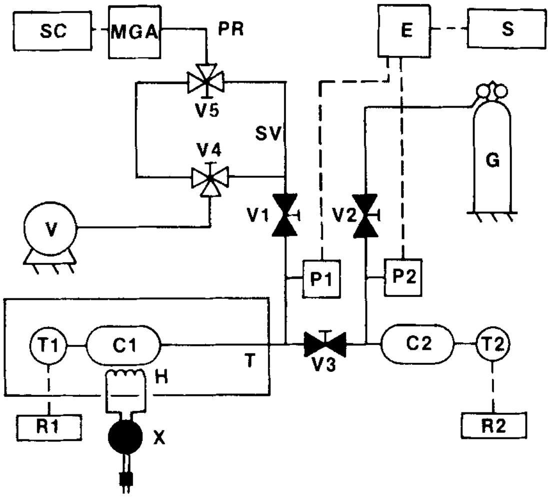

Figure 1. Experimental apparatus for pure- and multicomponent data collection.
C1. Sample chamber
C2. Charge chamber
E. Pressure transducer electronics box
G. Bottled gas
H. Heater
P1, P2. Pressure transducers
R1, R2. Digital readouts
S. Strip chart recorder
T. Temperature-controlled chamber
T1, T2. Thermocouples
V. Vacuum pump
V1, V2, V3. Manual valves
X. Variac transformer
MGA. Medical gas analyzer
SC. MGA strip chart recorder
PR. MGA gas sampling probe
SV. Sampling volume
V4, V5. Three-way valves

reported by the manufacturer to have the chemical formula $Ca_{4.5}Na_3[(AlO_2)_{12}(SiO_2)_{12}]$.

The nitrogen, oxygen, and argon gas were reported by the suppliers to be of purity 99.998, 99.99, and 99.98%, respectively. The concentrations of nitrogen, oxygen, argon, and carbon dioxide in the bottled air were measured using a medical gas analyzer, and found to be 78.1, 20.9, 0.96, and 0.03%, respectively. Water vapor content of the air was reported at $\leq 0.002\%$.

Procedure

The solid phase volume of the sample was determined by the helium displacement technique in conjunction with a statistical analysis. Helium was assumed to adsorb in negligible quantities at 297.15 K, and hence to enter the entire void volume of the zeolite crystals (α and β cages). To validate this assumption the solid phase density of pure 5A crystal was determined by the same technique. When assuming that helium enters both the α and β cages instead of only the α cages, the experimentally determined solid phase density (3.66 gm/mL) was in better agreement with the crystallographic solid phase density (3.29 gm/mL).

Table 1. Dimensions of Experimental Apparatus and Properties of Materials

Sample chamber *C1* volume	170.0 mL
Charge chamber *C2* volume	158.6 mL
Anhydrous weight of sample	32.8 g
Water wt. % of sample before initial activation	2.7%
Particle density of anhydrous molecular sieve crystals	1.57 gm/mL*
Solid phase density of anhydrous molecular sieve crystals and binder	2.97 gm/mL**
Binder wt. %	18.9%†

*Reported by supplier.
**Data from this laboratory.
†Determined in this laboratory by comparing adsorption capacity of the sample with Union Carbide pure 5A molecular sieve crystals (Lot No. 9430-8406-0073).

Preceding each run, activation of the adsorbent was performed by heating the sample to 623 K and reducing the pressure in the apparatus to less than 1 torr (0.133 kPa) for a period of at least 12 h. After cooling to the desired temperature the experiment was initiated by opening valve *V3* to permit gas to flow from the charge chamber to the sample chamber. In general, a period of 6 h was allowed in the pure-component experiments for achievement of equilibrium. Additional gas was introduced in a stepwise fashion until the maximum desired equilibrium pressure was attained. Using the appropriate PVT measurements a mass balance analysis was performed to determine the amount adsorbed at each step.

The ternary adsorption experiments involved an identical procedure except that air was injected from the charge chamber into the sample chamber. After equilibrium was attained a small gas sample was removed from the sample chamber via valve *V1* for concentration analysis. The mass of each of the three components within the sample chamber was corrected for that amount removed during the sampling process. Stepwise air injection was continued until the final equilibrium pressure was reached. This procedure maintained the total molar ratio constant within the sample chamber. Throughout the experimental work two isotherms were accomplished with each adsorbate gas at each temperature to ensure the reproducibility of the data.

Due to the static nature of the multicomponent adsorption experiments, one must ensure that the adsorbent and gas mixture have attained true equilibrium. Here this issue was addressed by a two-step procedure. First, the minimum equilibration period for the lowest temperature (203.15 K) was determined. It is at this temperature that gas phase mixing occurs at the slowest rate. Mixture isotherms were taken at increasingly longer equilibration periods. In this way one arrives at an equilibration period such that increasing the period will result in a negligible change in the experimental data. Here equilibration times >10 h were found to produce a negligible change in the data. Consequently, throughout the multicomponent work a minimum of 10 h of adsorption time was allowed for equilibration of each data point. Due to the innate homogeneity of air this time is shorter than that expected had slugs of the pure-component gases been added. Second, the mixture data were checked for thermodynamic consistency by application of the Gibbs adsorption isotherm, Eq. 3. Using this two-step approach, the validity of the multicomponent data was assured.

Results and Discussion

Pure-component adsorption

The pure-component isotherms of nitrogen, oxygen, and argon on molecular sieve 5A at temperatures of 297.15, 233.15, and 203.15 K are presented in Figure 2. A compressibility factor correction was incorporated in the calculation, although the gases behave nearly ideally at the conditions of this work.

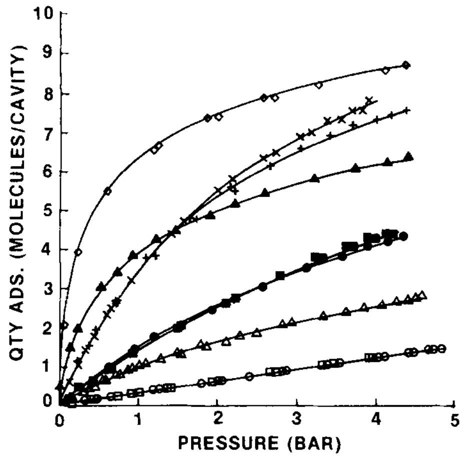

Figure 2. Pure-component equilibrium data of N_2, O_2, Ar on molecular sieve 5A.

	297.15 K	233.15 K	203.15 K
Nitrogen	△	▲	◇
Oxygen	○	●	+
Argon	□	■	×

Details of the calculation and tabulation of the data may be found elsewhere (Miller, 1984). The oxygen and argon data were correlated by a Langmuir equation while the nitrogen data were correlated using a Sips equation (Sips, 1948):

$$n_{\mathrm{O\,or\,Ar}} = \frac{aP}{1 + bP}; \quad n_{\mathrm{N}} = \frac{aP^d}{1 + bP^d}$$

The constants in these equations are given in Table 2. The amount adsorbed, n, has units of molecules/cavity, and pressure, P, has units of bar. In subsequent calculations these equations were used to represent the data. Interestingly, the argon and oxygen isotherms are nearly identical at 297.15 and 233.15 K, but at 203.15 K and pressures above 2 bar higher argon sorption was observed.

Heat of adsorption

The isosteric heat of adsorption for the pure gases was determined by application of the Clausius-Clapeyron equation with the assumptions that the ideal gas law applies and the volume of the adsorbed phase is negligible when compared to the gas phase volume. The final equation is,

$$\Delta H_{ads} = R[d \ln P/d(1/T)]_n$$

Table 2. Constants for the Pure-Component Langmuir and Sips Equations.

Gas	Temp., K	a	b	d
O_2	297.15	0.350	0.034	—
	233.15	1.735	0.172	—
	203.15	4.911	0.420	—
Ar	297.15	0.334	0.018	—
	233.15	1.585	0.123	—
	203.15	4.618	0.344	—
N_2	297.15	1.117	0.120	0.826
	233.15	6.278	0.617	0.653
	203.15	13.021	1.053	0.549

The results of this analysis are shown in Figure 3. The high isosteric heat at low coverage for nitrogen is expected due to the strong quadrupole moment of the nitrogen molecule interacting with the cations of the zeolite framework. For both oxygen and argon, the isosteric heat of adsorption is nearly independent of the coverage, suggesting that adsorption occurs on an energetically homogeneous surface. Heat of sorption of Ar decreases with sorbate concentration, which may explain the difference between oxygen and argon sorption at higher coverage. The initial isosteric heat of adsorption for oxygen determined by this work was 3.37 kcal/mol, which is in close agreement with that reported by Ruthven (1976) of 3.30 kcal/mol.

Prediction of pure-component isotherms

The statistical thermodynamic model was studied to determine its usefulness in predicting pure-component isotherms. Equation 2, simplified to the pure-component form, may be used as a predictive tool if values for K and β can be determined. K values for pure oxygen and argon were found by taking the derivative of the Langmuir equation at $P = 0$. β values for oxygen and argon were determined by matching the experimental isotherms to theoretical curves of n vs. KP (Ruthven, 1976). Approximate K and β values for pure nitrogen were determined by first superimposing the data on theoretical curves of n vs. KP. More exact values were then found by curve-fitting the data to the pure-component form of the statistical thermodynamic equation. K values were fitted to a linearized form of the vant Hoff equation [$K = K_o \exp(q_o/RT)$] by a least-squares technique. The results of this analysis are shown in Tables 3 and 4. Inclusion of Eq. 1 in the model had a negligible effect on the results. The effective molecular volume for oxygen and argon remained constant over the entire temperature range. In contrast, the effective molecular volume for nitrogen varied linearly with temperature. β for nitrogen may be estimated by the following equation,

$$\beta_{N_2} = 125.6 - 14.24 \times 10^3(1/T)$$

with T in Kelvins over the range 203 to 297 K.

With β and K defined for any temperature within the range of

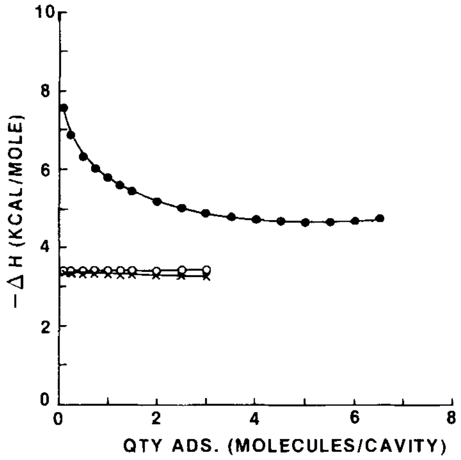

Figure 3. Isosteric heat of adsorption in molecular sieve 5A.

● nitrogen; ○ oxygen; × argon

Table 3. Parameters K_o and q_o for vant Hoff Equation*

System	K_o molecules/ cavity · bar	q_o kcal/mol
O_2-5A	1.16×10^{-3}	3.37
Ar-5A	1.14×10^{-3}	3.35
N_2-5A	1.57×10^{-3}	4.04

*$K = K_o \exp (q_o/RT)$

the original data, pure-component data at other temperatures may be predicted by employing the pure-component form of the statistical thermodynamic model. In Figure 4 data found in Ruthven (1976) were extrapolated to a pressure of 5 bar based on parameters given in that work, and are presented with predictions based on parameters derived from this work. In all cases good agreement is observed between the data and the predictions over the unextrapolated pressure range.

Multicomponent adsorption

Mixed-gas adsorption on molecular sieve 5A from a ternary mixture of N_2-O_2-Ar at constant total molar ratio of 0.7813:0.2091:0.0096 and at temperatures of 297.15, 233.15, and 203.15 K are shown in Figures 5–8, and are tabulated in Table 5. The isothermal adsorbed mole fractions were found to vary only slightly ($\leq 2\%$) with substantial changes in total pressure and gas phase composition. Larger variation in the adsorbed mole fractions did occur with changes in temperature. The predictions of both the binary and ternary forms of the statistical thermodynamic and IAST models are shown in these figures. The ternary models with argon included had a negligible effect on the predicted amounts of nitrogen and oxygen adsorbed. The low concentrations of carbon dioxide and water in the bottled air were assumed to have a negligible effect on the experimental results, and hence were excluded from the models. The pure-component values for K and β were used in both the binary and ternary analysis. At 297.15 K agreement between the predicted N_2 and O_2 sorption for both models and the data was excellent. At 233.15 and 203.15 K both models deviate from the data. Oxygen and argon adsorption at 233.15 and 203.15 K was predicted more accurately by the statistical thermodynamic model, as can be seen in Figures 6–8.

Table 4. K Values and Effective Molecular Volumes Based on Pure-Component Isotherms

System	Temp., K	K molecules/ cavity · bar*	V/β	β Å^3
O_2-5A	297.15	0.350	22	35.2
	233.15	1.735	22	35.2
	203.15	4.911	22	35.2
Ar-5A	297.15	0.334	26	29.8
	233.15	1.585	26	29.8
	203.15	4.618	26	29.8
N_2-5A	297.15	1.40	10	77.6
	233.15	10.96	12	64.6
	203.15	32.50	14	55.4

*One molecule/cavity is equivalent to 0.566 mmol/g of anhydrous molecular sieve crystals or 0.452 mmol/g of anhydrous molecular sieve crystals with 20% inert binder by weight.

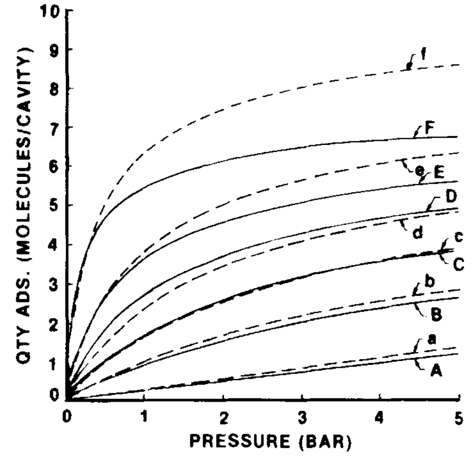

Figure 4. Pure component equilibrium data on molecular sieve 5A.

— Extrapolation of data of Ruthven (1976) using parameters given there.

---- Prediction of statistical thermodynamic model using parameters derived in this work.

A, a = Oxygen at 298 K; B, b = nitrogen at 298 K; C, c = nitrogen at 273 K; D, d = nitrogen at 255 K; E, e = nitrogen at 232 K; F, f = nitrogen at 205.5 K.

The parameter β was found to have a profound effect on the results of the statistical thermodynamic model. At 233.15 K an increase in the value of β_{N_2} from the pure-component value of 64.6 to 70.5 Å^3 with a simultaneous decrease in the value for β_{O_2} from 35.2 to 29.8 Å^3, permitted an accurate prediction of the ternary data, Figure 9. Also, at 203.15 K an increase in the value of β_{N_2} from the pure-component value of 55.4 to 59.7 Å^3

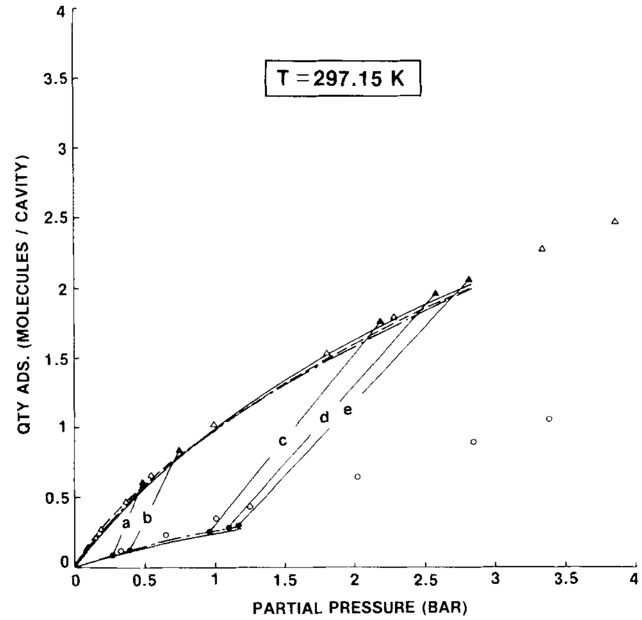

Figure 5. Prediction of mixed gas adsorption.

Mixed gas data points connected by lines *a–e*, tabulated in Table 5.

△ pure N_2 data; ○ pure O_2 data; ▲ ternary N_2 data; ● ternary O_2 data

— Binary and ternary statistical thermodynamic model

---- Binary and ternary IAST

—·— Ternary Langmuir-Sips equation

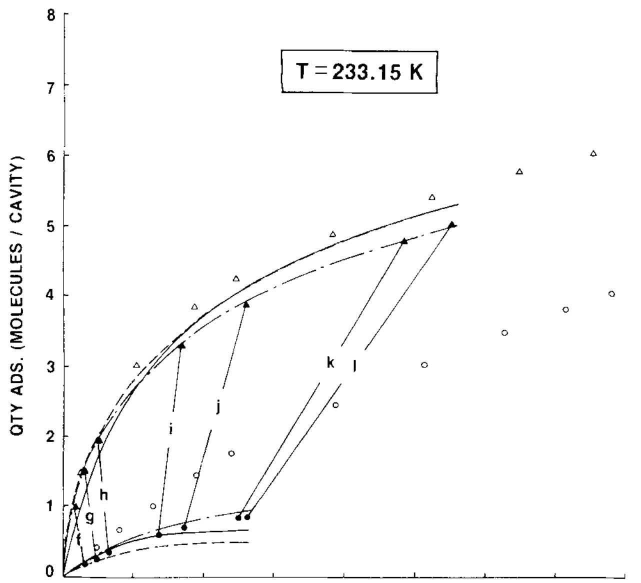

Figure 6. Prediction of mixed gas adsorption.
Mixed gas data points connected by lines *f–l*, tabulated in Table 5.
△ pure N_2 data; ○ pure O_2 data; ▲ ternary N_2 data; ● ternary O_2 data
— Binary and ternary statistical thermodynamic model
---- Binary and ternary IAST
—·— Ternary Langmuir-Sips equation

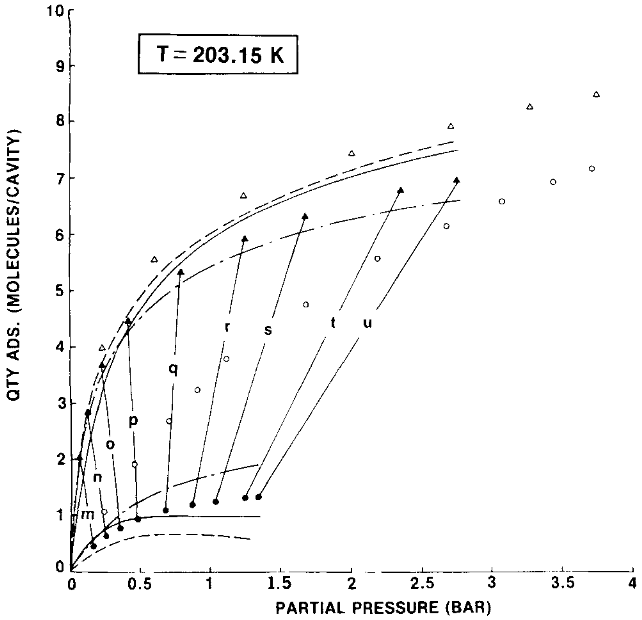

Figure 7. Prediction of mixed gas adsorption.
Mixed gas data points connected by lines *m–u*, tabulated in Table 5.
△ pure N_2 data; ○ pure O_2 data; ▲ ternary N_2 data; ● ternary O_2 data
— Binary and ternary statistical thermodynamic model
---- Binary and ternary IAST
—·— Ternary Langmuir-Sips equation

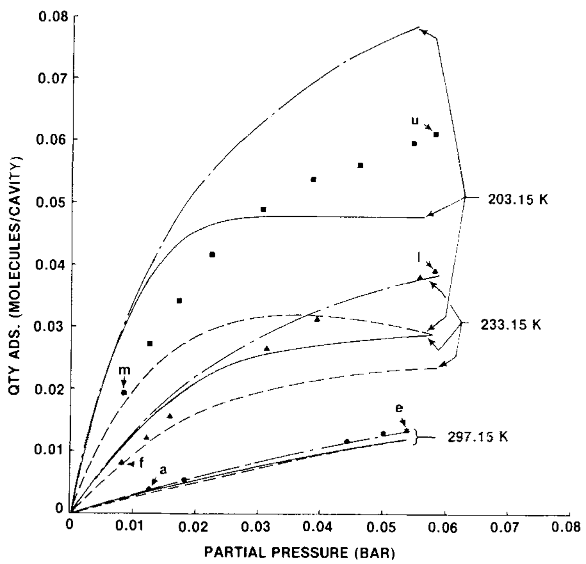

Figure 8. Prediction of ternary argon adsorption.
a-e, f-l, m-u: data points tabulated in Table 5.
Ternary argon data at: ● 297.15 K; ▲ 233.15 K; ■ 203.15 K
— Ternary statistical thermodynamic model
---- Ternary IAST
—·— Ternary Langmuir-Sips equation

and a decrease in the value of β_{O_2} from 35.2 to 27.7 Å^3 gave an accurate prediction of the experimental data. At 203.15 K it would appear that a slight adjustment in K would also be necessary if one desires to fit the data in the low-pressure regime.

Prediction of the multicomponent data was also attempted by an extended Langmuir-Sips equation. The nitrogen form of this

Table 5. Gas Mixture Adsorption Data for Nitrogen, Oxygen, and Argon in Molecular Sieve 5A.

Data Point	p_N	p_O	p_{Ar}	n_N	n_O	n_{Ar}
			297.15 K			
a	0.491	0.277	0.0125	0.603	0.094	0.0042
b	0.759	0.399	0.0180	0.829	0.129	0.0057
c	2.190	0.972	0.0439	1.758	0.269	0.0119
d	2.581	1.107	0.0497	1.953	0.295	0.0132
e	2.832	1.183	0.0533	2.070	0.308	0.0137
			233.15 K			
f	0.092	0.165	0.0082	0.993	0.189	0.0081
g	0.170	0.252	0.0122	1.487	0.281	0.0121
h	0.261	0.333	0.0159	1.916	0.357	0.0155
i	0.859	0.689	0.0314	3.297	0.600	0.0266
j	1.314	0.874	0.0394	3.873	0.704	0.0314
k	2.428	1.260	0.0558	4.777	0.840	0.0381
l	2.773	1.326	0.0582	5.011	0.855	0.0392
			203.15 K			
m	0.055	0.164	0.0084	2.009	0.444	0.0193
n	0.119	0.253	0.0125	2.874	0.625	0.0273
o	0.220	0.353	0.0171	3.652	0.780	0.0342
p	0.415	0.480	0.0224	4.465	0.941	0.0416
q	0.791	0.674	0.0307	5.320	1.097	0.0489
r	1.243	0.863	0.0386	5.916	1.198	0.0538
s	1.666	1.025	0.0460	6.298	1.251	0.0561
t	2.354	1.232	0.0546	6.762	1.321	0.0597
u	2.752	1.334	0.0580	6.946	1.334	0.0612

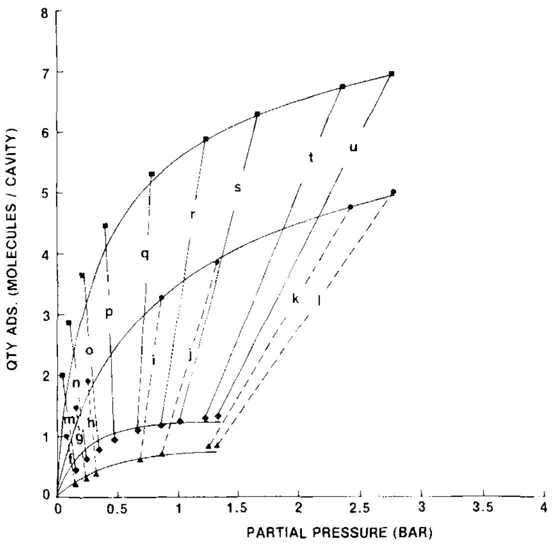

Figure 9. Prediction of N_2 and O_2 mixed gas adsorption using adjusted effective molecular volumes.

Mixed gas data points connected by lines *f–u*, tabulated in Table 5.
Ternary O_2 adsorption data at: ▲ 233.15 K; ◆ 203.15 K
Ternary N_2 adsorption data at: ● 233.15 K; ■ 203.15 K
— Binary statistical thermodynamic model with adjusted effective molecular volumes:
233.15 K $\beta_{O_2} = 29.8$; $\beta_{N_2} = 70.5$ Å^3
203.15 K $\beta_{O_2} = 27.7$; $\beta_{N_2} = 59.7$ Å^3

equation is:

$$n_N = \frac{a_N P_N^d}{1 + b_{Ar}P_{Ar} + b_O P_O + b_N P_N^d}$$

Similar equations for oxygen and argon may be obtained. The constants in this equation are given in Table 2. This predictive equation gave excellent results at 297.15 and 233.15 K, but at 203.15 K some deviation between the prediction and the data was observed; see Figures 5–8. When pure-component data are available this equation would be a valuable tool for the prediction of N_2-O_2-Ar-5A sorption.

Finally, prediction of the mixture data was also attempted by an extended Langmuir equation of the form:

$$n_N = \frac{r_N P_N}{1 + b_{Ar}P_{Ar} + b_O P_O + s_N P_N}$$

Here the form of the equation for calculation of the amount of nitrogen adsorbed is shown. The best-fitting Langmuir constants, r_N and s_N, for the pure-component nitrogen data were determined by a regression analysis technique identical to that used for the pure oxygen and argon data. Prediction of the nitrogen mixture data at 297.15, 233.15, and 203.15 K using the extended Langmuir equation resulted in errors of 2, 6, and 8%, respectively. For oxygen and argon the errors were significantly higher ($\geq$20%).

Thermodynamic consistency

The thermodynamic consistency of the mixture data was tested by a method similar to that described in Myers (1984). If the data satisfy the Gibbs adsorption isotherm, Eq. 3, one may be confident that the data are correct. At equilibrium the fugacities in the gas and adsorbed phases are equal. Hence,

$$Py_i\phi_i = P_i^o(\pi)\phi_i^o\gamma_i x_i \qquad (4)$$

may be written for each component. The gas phase fugacity coefficients may be assumed equal to unity at the conditions of this work. From the integrated form of Eq. 3 the spreading pressure of the mixture was determined:

$$\pi A/RT = \int_0^{p_N} (n_N/p_N)\,dp_N + \int_0^{p_O} (n_O/p_O)\,dp_O + \int_0^{p_{Ar}} (n_{Ar}/p_{Ar})\,dp_{Ar}$$

Activity coefficients were then calculated using Eq. 4 and the experimental data. The excess Gibbs free energy was calculated:

$$\Delta g^e/RT = \sum_i x_i \ln \gamma_i$$

The excess reciprocal loading was determined for each data point:

$$(1/n)^e = (1/n) - (1/n)^{id}$$

where,

$$(1/n)^{id} = \sum_i (x_i/n_i^o)$$

The results of these calculations are shown in Table 6. It can be

Table 6. Results of the Thermodynamic Consistency Test

Data Point*	$\pi A/RT$ molecule/ cavity	γ_N	γ_O	γ_{Ar}	$\Delta g^e/RT$ molecule/ cavity	$(1/n)^e$ (molecule/ cavity)$^{-1}$
			297.15 K			
a	0.778	1.066	0.896	0.876	0.0394	−0.144
b	1.133	1.027	0.874	0.870	0.0041	−0.058
c	2.632	0.981	0.860	0.887	−0.0368	−0.013
d	2.974	0.977	0.860	0.880	−0.0408	−0.011
e	3.182	0.974	0.859	0.894	−0.0427	−0.009
			233.15 K			
f	1.190	2.585	1.425	1.531	0.852	−0.430
g	2.048	1.948	1.217	1.280	0.590	−0.191
h	2.879	1.693	1.115	1.152	0.458	−0.112
i	6.401	1.357	0.872	0.884	0.235	−0.022
j	8.106	1.326	0.791	0.807	0.200	−0.014
k	11.06	1.297	0.702	0.731	0.165	−0.009
l	11.76	1.294	0.676	0.701	0.160	−0.009
			203.15 K			
m	2.498	3.600	1.613	1.811	1.131	−0.295
n	4.668	2.210	1.218	1.331	0.683	−0.108
o	6.939	1.784	1.047	1.134	0.482	−0.054
p	9.835	1.574	0.886	0.936	0.350	−0.027
q	13.43	1.460	0.772	0.811	0.266	−0.014
r	16.30	1.427	0.700	0.737	0.232	−0.008
s	18.32	1.413	0.657	0.712	0.215	−0.006
t	20.82	1.413	0.582	0.643	0.196	−0.005
u	22.00	1.412	0.546	0.597	0.187	−0.004

*Points correspond to those in Table 5.

shown from Eq. 3 that

$$(1/n)^e = \frac{\partial(\Delta g^e/RT)}{\partial(\pi A/RT)} \qquad (5)$$

The slope of the excess Gibbs free energy vs. the spreading pressure was determined for each data point. The fact that these slopes agree closely with the values obtained for the reciprocal excess loading (differences of $<10\%$) indicates a high degree of thermodynamic consistency. The slight differences between these values might be attributed to the inaccuracies associated with evaluating the integrals for the mixture spreading pressure.

Conclusions

At high pressure (>4 bar) and low temperature (203.15 K) the pure-component isotherms indicate that the separation of argon and oxygen may be possible, based solely on equilibrium data. Of course, one must investigate whether the system kinetics would favor such a separation.

At 297.15 K the predictions of the binary and ternary statistical thermodynamic model and the ideal absorbed solution theory (IAST) model are nearly identical and are in excellent agreement with the experimental data. At 233.15 and 203.15 K the predictions of both models deviate from the experimental data considerably, although the statistical thermodynamic model gives better results than the IAST. Slight adjustment of the parameter β in the statistical thermodynamic model resulted in an excellent representation of the ternary nitrogen and oxygen data, which suggests that development of a method for determining β of components in mixtures may lead to improved predictions of multicomponent sorption. Additionally, pure-component isotherms within the temperature range 203–297 K may be estimated using the statistical thermodynamic model and parameters determined in this work.

In general, the extended Langmuir equation gave rather poor predictions of the mixed-gas adsorption. In contrast, the extended Langmuir-Sips equation gave excellent predictions, and therefore should be a valuable tool for prediction of N_2-O_2-Ar adsorption in molecular sieve 5A if pure-component data are available. In this regard, one could estimate the pure-component isotherms through use of the statistical thermodynamic model.

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Notation

A = specific area of adsorbent
a, b, d, r, s = constants in the Langmuir and Sips equations
G = grand partition function
Δg^e = excess Gibbs free energy function
H = isosteric heat of adsorption, kcal/mol
i, j, w = integers
K = Henry's law constant, molecules/cavity · bar
K_o, q_o = parameters of the vant Hoff equation
k = Boltzmann constant
m = saturation limit V/β, molecules/cavity
N = number of molecules
n = amount adsorbed, molecules/cavity
$n_i^o(\pi)$ = amount adsorbed of pure component i at spreading pressure of mixture
P = total pressure, bar
p = partial pressure, bar
$P_i^o(\pi)$ = equilibrium pressure of pure component i at spreading pressure of mixture
$q(i, j, w)$ = partition function of a single cavity with i molecules of A, j molecules of B, w molecules of C
R = universal gas constant
T = temperature, K
V = cavity volume for 5A molecular sieve, 776 Å^3
x = mole fraction in adsorbed phase
y = mole fraction in gas phase
Z = configuration integral for a cavity

Greek letters

α = activity for an ideal gas, p/kT
β = effective molecular volume, Å^3
γ = activity coefficient
ϵ = molecular constant of attraction in Sutherland potential function
π = spreading pressure of adsorbed phase
λ = exp (μ/kT)
μ = chemical potential
ϕ = gas phase fugacity coefficient
Ψ = function

Superscripts

e = excess function
o = standard state
id = ideal value

Subscripts

A, B, C = components A, B, C
Ar, N, O = argon, nitrogen, oxygen
i = component i
t = total

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