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THESIS ABSTRACT

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NAME: George Walter Miller QUARTER/YEAR: Summer/84
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TITLE OF THESIS: Adsorption Equilibria and Performance of a Pressure Swing Adsorption Air Separation Unit

Summarize in the space below the purpose and principal conclusions of your thesis.

Current pressure swing adsorption (PSA) air separation units operating on short cycle times suffer a reduction in product oxygen concentration when subjected to lower ambient temperatures (i.e., less than -10°C). This work investigates this problem based on analysis of adsorption equilibria, column breakthrough studies, and actual PSA system data.

Pure and multicomponent data for nitrogen, oxygen, and air on molecular sieve 5A were collected at 24, -40, and -70°C up to pressures of 4.3 atmospheres absolute. Using a statistical thermodynamic model pure component data were adequately predicted over the entire temperature range (24 to -70°C). The multicomponent data were predicted at 24°C by a statistical thermodynamic model and ideal adsorbed solution theory. At the lower temperatures the gas mixture behaved nonideally.

Column breakthrough data taken at 24 and -40°C shows that the length mass transfer front during nitrogen breakthrough remains nearly constant. In contrast, the length of the mass transfer front for oxygen breakthrough increases significantly. This may indicate a difficulty in desorbing nitrogen at the low temperatures.

Actual PSA system experiments at 24 and -40°C indicate improved performance at -40°C could be obtained by lengthening the system cycle time. A six-step versus two-step per cycle comparison revealed the six-step system had slightly higher oxygen purity and recovery at 24°C and both systems had little difference in product purity and recovery at -40°C.
ADSorption Equilibrium and Performance of a Pressure Swing Adsorption Air Separation Unit

A Thesis
Presented in Partial Fulfillment of the Requirements for the Degree Master of Science
by
George Walter Miller, B.S.Ch.E.
The Ohio State University
1984
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(Nitrogen Loading vs. Total Pressure) ( Run 1) ... 243

(Oxygen Loading vs. Total Pressure) ( Run 1) ... 243
Air-5A at 24°C (Total Loading vs. Total Pressure) (Run 2) 244
SUMMARY

The pure component isotherms of nitrogen and oxygen on zeolite molecular sieve 5A were determined through use of a volumetric technique at 24, -40, and -70°C up to absolute pressures of 4.3 atmospheres. Using parameters derived from the pure component data, i.e. Henry's Law constant and the effective molecular volume, a statistical thermodynamic model correctly predicted the pure component data of Union Carbide.

The pure equilibrium apparatus was modified and multicomponent equilibrium data were collected using air and molecular sieve 5A. The pure component parameters were used with the extended statistical thermodynamic model and the IAST theory to predict the adsorption of nitrogen and oxygen from an air mixture on molecular sieve 5A. The predictions at 24°C were excellent but those at -40 and -70°C had significant deviations. Adjustment of the apparent effective molecular volumes for nitrogen and oxygen led to a good fit of the data at the lower temperatures.

Breakthrough studies using one column of the pressure swing adsorption system revealed that the nitrogen breakthrough curves at 24°C and -40°C have the same shape and length, although due to the increased adsorption capacity of the bed at -40°C its front emerges from the bed at a later time. In contrast, when comparing oxygen breakthrough curves at these temperatures the time required to reach one percent
concentration of nitrogen in the effluent is significantly longer at $-40^\circ C$. These results imply that a longer cycle time should improve performance of a pressure swing adsorption unit operating at reduced temperature, however, the significantly longer time necessary for nitrogen desorption indicates performance should be less than that attained at room temperature. Data taken from an actual pressure swing adsorption unit appear to agree with these predictions.

A bench-scale pressure swing adsorption system was constructed to determine the effect of operating at room temperature and $-40^\circ C$ on system performance. Present systems experience reduced oxygen concentration at preset flow rates and cycle times while operating at low temperatures. It was determined that lengthening the system cycle time improved performance but the percent oxygen concentrations were still less than at room temperature. Cycles of six-steps versus two steps at both room temperature and $-40^\circ C$ were tried, with the six step system showing slightly better oxygen purity and recovery at room temperature and both systems having little difference in oxygen purity and recovery at $-40^\circ C$. 
CHAPTER I

INTRODUCTION

Pressure swing adsorption (PSA) has emerged as a popular method for air separation due to economic and operational advantages. Where 95% or less oxygen concentration is required at small to moderate flow rates PSA systems can compete successfully with conventional techniques, i.e. cryogenic fractionation, due to reduced complexity and smaller energy requirements (1). The chemical industry has been aware of the advantages of PSA technology in such areas as gas purification, chemical oxidation processes, and water treatment (2,3,4,5,6,7). It has been suggested that flowrates in the range of 1 to 80 ton/day of enriched oxygen may be produced more economically by PSA (2). PSA systems have been employed by the medical profession for out-patient oxygen therapy and as a source of oxygen for field hospitals (6). In the future such systems may possibly reduce air pollutants in automobile emissions by improving the efficiency of the combustion process.

PSA systems separate air by cyclic variation of pressure in fixed beds of adsorbent which preferentially adsorb nitrogen from an entering air flow, thereby increasing the oxygen concentration in the gas phase. Following the adsorption step is a desorption step where regeneration of the beds is accomplished by pressure reduction and purging by recycling a portion of the product flow. Although the general concept of
separation has been in existence for the last two decades (28), the present impetus for its use is an economic one. The recent introduction of PSA systems operating on short cycle times has allowed these units to process large amounts of air with smaller bed sizes. Additionally, with adsorbent beds operated at ambient temperature and with the process being essentially isothermal the only energy consumed is that required for pressurizing the feed and cycling the valves.

Recently, the aviation industry and the military have placed significant emphasis on the development of an airborne oxygen generating system capable of separating air, and thus, provide an inexhaustable source of breathable oxygen for aircrew hypoxia protection (8,9,10). Presently, oxygen in either liquid or gaseous form is stored onboard the aircraft and depleted during each flight. These stored supplies are costly and place constraints on the aircraft's potential effectiveness. Obviously with conventional systems, any decision involving the basing of aircraft in a remote location must address the availability of oxygen in both the proper quantity and quality. The development of a system capable of delivering high purity oxygen for extended periods of time would result in substantial economic savings, greater flexibility in aircraft basing, and eliminate hazards associated with handling supplies of pure oxygen. An onboard oxygen generating system utilizing the principle of pressure swing adsorption is considered the prime candidate for full scale production and installation aboard military tactical aircraft.
Terrestrial and airborne versions of the system employ molecular sieve 5A as the adsorbent, a synthetic zeolite, and are potentially capable of producing a product flow with a maximum oxygen concentration of approximately 95.7% with the remainder as argon. The breathing of this gas mixture, as opposed to 100% oxygen, by aviators has been shown to present no deleterious effects (11,12).

Environmental testing of a prototype onboard oxygen generating system resulted in an interesting observation. When a system producing approximately 95% oxygen at room temperature was subjected to a reduction in ambient temperature the oxygen product concentration also dropped significantly with the most dramatic rate of degradation occurring at approximately -20°C. At -40°C the product oxygen concentration had fallen to 70%. Clearly this poses a problem because the ambient temperature within the operational envelope of some aircraft may be as low as -40°C.

This finding immediately presents two practical questions. Firstly, what mechanism is responsible for this decline in system performance at lower ambient temperatures. Secondly, what approach should be taken to nullify or minimize this reduction in oxygen concentration so that the system might return to an acceptable level of performance. An obvious first approach would involve thermal protection of the adsorbent beds, e.g. by electrical heating, to maintain a temperature above -20°C, maybe +20°C as previously suggested (10). This would certainly solve the problem for a powered aircraft which is
gradually subjected to the lower temperatures. In contrast, an
unpowered aircraft with adsorbent beds initially at a low temperature
would most certainly require additional preparation time before flight
due to the added requirement of heating the adsorbent beds to an
operational temperature. The length of time required for heating the
beds may be substantial due to the insulating characteristics of the
molecular sieve. In most cases this may not pose a significant problem,
but for a previously unpowered aircraft desiring an immediate departure,
this delay could prove to be an unacceptable constraint. Although this
problem could be solved by applying ground electrical power on a
continuous basis, the burden of providing suitable facilities and
maintaining continuous service would make this option undesirable.

Providing answers to those questions is the focus of this work.
The goals are twofold: one is to take a step toward understanding the
mechanism which causes this reduction in performance; the second is to
broaden the base of existing knowledge about PSA systems operating at
low temperature. The topics in this area include overall system
analysis, and since this is a stepwise approach into the low temperature
regime, basic research in equilibria and kinetics of the process.
Ultimately, these two mechanisms will control the theoretical and
practical limits of the PSA process. As will become readily
apparent, this work will stress equilibrium data (instead of kinetics),
and methods which will predict this data with a reasonable degree of
accuracy.
This investigation was organized into three general areas: equilibria, breakthrough data, and dual column PSA system experiments. As was previously mentioned, this work will stress the equilibrium data because accurate determination or prediction of isotherms is of fundamental importance in the design and modeling of PSA systems. Additionally, multicomponent equilibrium data are limited, and therefore, reliable techniques for predicting the behavior of the multicomponent system from the pure component data are crucial from a practical and theoretical standpoint. The multicomponent data may also lead to a better overall understanding of the interactions between the gas and solid phase.

Pure component data of nitrogen and oxygen, and multicomponent equilibrium data of air were measured at temperatures of 24, -40, and -70°C up to pressures of 4.3 atmospheres absolute. Any profound changes in the equilibrium adsorption isotherms would certainly affect the performance of the separation. Air was selected as the multicomponent mixture because its isotherms should come closest to simulating the actual PSA process. The adsorbent used in this work was Union Carbide Corporation of Tarrytown, New York, molecular sieve 5A due to its superior characteristics for air separation. Data at -70°C were included so that a more complete data set over a wider range of temperature would be available for analysis. It was thought if any unusual observations were noticed at -40°C their presence would be confirmed by a more pronounced effect occurring at -70°C.
experiments were necessary because, in general, this data was not available in the literature. Considerable effort was expended in investigating techniques which could be employed to predict the experimental data within a reasonable degree of accuracy. Since multicomponent data collection is, in general, time consuming and tedious, reliable predictive models based on pure component data are of great value.

The breakthrough experiments were conducted at 24 and -40 °C, various flowrates, and pressures comparable to the actual column operating pressures, provided breakthrough curves which described the mass transfer zone within the column. Changes in the shape of the breakthrough curves and the time required to reach breakthrough would reveal any kinetic differences between operating the column at 24°C, as opposed to -40°C. In these experiments, one of the two column of the PSA apparatus was used and breakthrough curves were determined by flowing air and oxygen. Air and oxygen were chosen because these gases would better approximate the actual conditions within each PSA column, i.e. during the feed and purge steps.

A dual column, bench scale PSA apparatus was designed for laboratory use. Although built on a small scale, it is believed this system possessed similar characteristics of the larger systems. That is, trends occurring in the laboratory model should also present themselves in the larger scale models. Throughout these experiments the inlet pressure and exhaust pressure were held constant at 25 psia and
14.4 psia, respectively. Parameters varied were temperature (24 and -40 °C), cycle time, product flow rate, and purge flow rate. The purge flow rate was controlled by installation of different diameter orifices. The dependent variable of primary interest was the steady state oxygen concentration in the high pressure product. Data was collected only after the oxygen concentration in the product had reached a steady state value. The experiment was configured for both two-step and six-step cyclic operation, so that these configurations might be compared and contrasted based on product oxygen concentration, cycle time, and oxygen recovery.
CHAPTER II

BACKGROUND

This section presents a brief history behind the development of synthetic zeolites and the pressure swing adsorption process. Although zeolites have been applied widely in areas such as, catalytic cracking, isomerization, hydrocracking, etc., the ensuing discussion stresses zeolite development as it relates to air separation (13). It should become apparent that without the development of techniques for the manufacture of high quality synthetic zeolites pressure swing adsorption technology would not have evolved as a commercial separation method.

Baron Cronstedt, a Swedish mineralogist, discovered crystalline zeolites in 1756 and was the first to observe that upon heating water is evolved (13). In 1840 Damour noticed that these zeolites could be reversibly hydrated and dehydrated with no apparent change in the crystal structure whatsoever. One hundred and fifty three years after their first discovery Grandjean reported in 1909 that zeolites were capable of adsorbing organic vapors such as iodine, mercury, and ammonia (14). Weigel and Steinhoff in 1925 were the first to observe the molecular sieving properties of zeolites when they reported that chabazite adsorbed methanol, ethanol, and formic acid but excluded
acetone, ether, and benzene (15). McBain in 1926 analyzed the Weigel and Steinhoff observations and concluded that the adsorption or exclusion could be explained by a molecular size discrimination process. He proposed the name "molecular sieve" (13).

Although research on zeolites from 1926 to 1948 progressed at a slow pace, some important work was reported. In the 1930's the crystal structures of analcote and natrolite were identified by X-ray diffraction studies (16,17). Also during this period R.M. Barrer of England became intensely interested in zeolite research. His work was instrumental because it suggested future applications of zeolites. In 1938 his experiments with nitrogen and argon showed that nitrogen was more strongly adsorbed on the zeolite, chabazite (21). This he attributed to the polarity of the nitrogen caused by its quadrupole moment interacting with the ionic crystal structure of the zeolite. He is credited with proposing that zeolites could be applied to the separation of normal from isoparaffins and of polar molecules from nonpolar molecules (18,19,20). In 1956 Barrer and Sutherland (25) concluded that the permanent gases nitrogen, oxygen, and argon are selectively adsorbed based on the magnitude of their quadrupole moments (N_2>O_2>Ar), and thus the separation of nitrogen and oxygen occurred not due to any molecular sieving action but of different sorption affinity.
Although interest in zeolites grew during this period, the major obstacle confronting their commercial usage was the limited availability of zeolites. It was recognized by researchers at the time that the unique characteristics of zeolites could only be used to full advantage if the naturally occurring species could be synthesized on a large scale, but prior to 1948 attempts at synthesizing zeolites in the laboratory were unsuccessful.

While investigating new approaches to air separation R.M. Milton of the Union Carbide Corporation became interested in the natural zeolite, chabazite. His belief that a synthetic analogue to chabazite could be developed sparked a research program at Union Carbide which culminated in the development of many synthetic zeolites, some not found in nature. A technological breakthrough occurred when methods were devised to produce these synthetic varieties in large quantities (22,23). The fundamental difference between Milton's approach and earlier attempts was the use of lower crystallization temperatures. He performed his crystallizations at 25 to 150°C, in contrast, to other researchers who employed temperatures in the range of 200 to 400°C. By 1952 type A and type X zeolites had been successfully synthesized by researchers at Union Carbide. Today there are thirty-four known types of zeolitic minerals and about one hundred synthetic varieties (70).
These synthetic zeolites were formed by precipitation from a supersaturated aluminosilicate gel consisting of sodium hydroxide, sodium aluminate, and sodium silicate with excess caustic. The type of components, their concentration in the gel, and a low crystallization temperature are critical factors in the synthesis of high quality synthetic zeolite materials. If the proper conditions are maintained, crystallization will be complete in two hours. This feature made the process economically feasible. A typical synthesis may be represented by the following equations (24),

\[
\text{NaOH(aq)} + \text{NaAl(OH) (aq)} + \text{Na SiO (aq)} \xrightarrow{20\degree C} \left[ \text{Na (AlO}_2 \right] \left( \text{SiO}_2 \right) \text{ (gel)}
\]

\[
\xrightarrow{<150\degree C} \left[ \text{Na (AlO}_2 \right] \left( \text{SiO}_2 \right) \text{,NaOH,H O} \xrightarrow{<150\degree C} \text{Na [(AlO}_2 \right] \left( \text{SiO}_2 \right) \cdot w H O + \text{solution}
\]

\[
\xrightarrow{x 2 x 2 y 2} \text{(zeolite crystals)}
\]

where,

- \( w \) = number of water molecules.
- \( y/x \) = varies between 1 to 5.

After separation from the mother liquor and drying the final product of the above process is a white powder with a particle size of 1 to 5 microns. Before commercial use the powder is impregnated with 20% inert clay binder and formed into pellets to minimize attrition of the crystal structure.
First mention of an industrial process utilizing the concepts of PSA, although not for air separation, was in 1959 by C.W. Skarstrom of Esso Research and Engineering Company, Linden, New Jersey (26,27,28). The apparatus was called a heatless drier because it dried air from a moisture content of 3800 ppm to 1 ppm and exhibited nearly isothermal operation. The unit had two adsorbent beds containing either alumina or silica gel and operated in a cyclic manner by alternating the flow of wet feed air to the two beds (See Fig 2-1). While bed A received a flow of wet air and delivered a product of dry air, bed B was regenerated by venting to atmospheric pressure and purging with some product flow from bed A. The desorbed water vapor was exhausted to the atmosphere, thereby, preparing the bed for the next cycle of operation. The cycles were controlled by an electric timer. Skarstrom noted that the actual volume of the low pressure purge gas had to exceed the actual volume of the high pressure input gas if the system was to produce extremely dry air. The beds remained essentially isothermal because heat liberated during the adsorption step was reclaimed during the desorption or regeneration step.

Surprisingly, a similar system configuration with a different adsorbent finds use today in the area of air separation (See Fig 2-2). Although PSA systems for air separation have become more sophisticated as designers strive for optimization, all systems operate on the same principles as the Skarstrom's heatless drier. An excellent review of the most important patents up to 1973 has been prepared by Lee and Stahl.
Theoretical modeling of PSA systems has progressed in recent years but agreement between the predictions of theoretical models and experimental data rarely occurs unless some degree of empiricism has been incorporated into the model (35,36,37,38,39,40).
FIG 2-1. SKARSTROM’S HEATLESS ADSORPTION DRYER (27).
FIG 2-2. SCHEMATIC FLOW DIAGRAM FOR A TWO-MAN MOLECULAR SIEVE OXYGEN GENERATOR (10).
CHAPTER III

LITERATURE AND THEORY

Zeolite Structure

Smith defines a zeolite as "an aluminosilicate with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion exchange and reversible dehydration (29). The hydrated crystallographic unit cell of the type A zeolite is,

\[ \text{Me} \left[ \frac{(\text{AlO}_2^-)(\text{SiO}_2)}{12/n} \right] \cdot 27\text{H}_2\text{O} \]

where, \( n \) is the valence of the metal cation Me.

Upon dehydration the zeolite crystal structure will maintain its well defined shape and extremely uniform pore dimensions. The effective pore diameter of zeolites vary from 3 to 10 Angstroms depending on the type of zeolite and the cation present in the structure. The one univalent cation per \( (\text{AlO}_2^-) \) tetrahedral unit is necessary to maintain electrical neutrality within the structure. These cations are easily exchanged if a different pore size is desired, for instance the \( \text{Na}^+ \) cations of molecular sieve 4A may be exchanged with \( \text{Ca}^{++} \) ions to form zeolite 5A.
The unit cell forms a cubo-octahedron building block which is constructed from twelve \( (\text{AlO}_2) \) tetrahedral units, twelve \( (\text{SiO}_2) \) tetrahedral units, and the required number of cations. These cubo-octahedrons are positioned at the corners of a 12.32 Å cubic lattice (See Fig 3-1). Entry into the spherical space, alpha or super cage (diameter = 11.3 Å, volume = 776 cubic Angstroms), within the cube is gained by passage through six eight-membered rings of oxygen atoms. In the case of zeolite 5A the effective pore diameter is 4.3 Å but molecules with critical diameters up to 5.5 Å may enter because of the constant vibration of these oxygen molecules. The cubo-octahedron units at the corners also have an internal cavity, beta cage (diameter = 6.6 Å), which can only be entered by the smallest molecules. The eight six-membered oxygen rings permitting access to the beta cage have an effective diameter of 2.2 Å. Only molecules such as water, helium, and ammonia are capable of entering this volume. Adsorption of nitrogen and oxygen only occurs in the alpha cage. The cubo-octahedron units are connected by cubes of oxygen atoms which attach to six four-membered rings. For complete descriptions of zeolite structure see Breck (7).

If an adsorbate molecule's effective diameter is larger than the zeolite pore diameter the molecule will be excluded from the intraocrystalline volume, although it may be possible for the molecule to adsorb to the outer surface of the zeolite crystals. This outer surface only represents 1% of the inner surface area therefore, any adsorption here would be extremely small. The internal surface area has been
estimated in the region of 800 to 1000 sq. meters/gm (70). Separations based on the exclusion of one or more species are referred to as molecular sieving.

Zeolites interact vigorously with molecules possessing dipole or quadrupole moments due to the ionic nature of the crystal structure. Molecules such as water, carbon dioxide, and nitrogen energetically interact with the potential fields within the zeolite. The strong interaction between the quadrupole moment of the nitrogen molecule and zeolite 5A makes air separation possible.

**Sorption in zeolites**

Upon dehydration zeolites become active adsorbents. Zeolite adsorption data is usually presented as quantity adsorbed versus pressure of the adsorbate in the gas phase at constant temperature which is referred to as an "isotherm". Adsorption and desorption isotherms for zeolites are usually identical due to the uniform structure of the crystal framework, although hysteresis may occur for some complex molecules.

Since sorption in zeolites is a pore filling process internal volume is the critical parameter and surface area has little meaning. Use of the conventional B.E.T. method for surface area determination is not applicable to zeolites. The pore filling process occurs rapidly
sorption occurs nearly instantaneously (diffusional resistance may lengthen this process) and is easily reversed returning the adsorbate molecule and the surface of the zeolite to its original state, as discussed by Young and Crowell (32), Brunauer (81), Breck (7), and Oscik (30) in detailed treatments of physical adsorption.

Physical adsorption is always exothermic as will be shown by the following thermodynamic relationship,

$$\Delta G = \Delta H - T\Delta S$$

The more ordered state of the adsorbate molecule as opposed to its gas phase counterpart requires that the change in entropy decrease. Since adsorption occurs spontaneously, the change in the Gibbs free energy must be negative and furthermore the change in enthalpy must be negative.

The magnitude of the interaction between a diffusing adsorbate molecule and the zeolite framework is directly related to the heat of adsorption. At absolute zero ($-273.15^\circ C$) (7),

$$\Delta H = I + I + I + I + I$$

where,

I = energy contribution due to dispersion,
D
I = " " " " repulsion,
R
I = " " " " polarization,
P

20
I = energy contribution due to electrostatic-dipole E-D interaction.

I = energy contribution due to electrostatic-quadrupole E-Q interaction.

\[ I = -A / r \]

\[ I = -\frac{\tau \kappa}{r} \]

\[ I = B / r \]

\[ I = \frac{\tau Q [3 \cos \phi - 1]}{4 r} \]

where,

\( \tau \) = charge

\( \omega \) = polarizability

\( \kappa \) = dipole moment

\( \phi \) = angle between the axis of the quadrupole and the line between the centers of the two molecules.

The dispersion and repulsion energies are present whenever a sorbate molecule enters the zeolite framework. However, due to their small value these energies are only noticeable when the sorbate is a nonpolar molecular, such as argon or oxygen. Furthermore, as the concentration of a nonpolar adsorbate increases, the heat of adsorption also increases slightly reflecting the rise in dispersion/repulsion interactions (34).
The electrostatic interactions between specific adsorbate molecules and the zeolite may be substantial. The largest interaction energies (20-30 kcal/gmol) occur when molecules with permanent dipole moments (i.e. water, ammonia, etc.) enter the zeolite structure. The electrostatic-quadrupole interaction for nitrogen has been estimated at 1.5 to 2.5 kcal/mol (7). The initial heat of adsorption for molecules with dipole or quadrupole moments is generally large due to the availability of energetically active sites at low coverage and decreases monotonically with increasing sorbate concentration as the less energetic sites become occupied.

The strong positive charge of the exchangeable cation can induce dipoles on unsaturated molecules. The resulting polarized molecule is then strongly adsorbed. Attempts to predict equilibrium adsorption isotherms by modeling these interactions have not been successful (41).

The isosteric heat of adsorption, $\Delta H_a$, may be evaluated by applying the Clausius-Clapeyron equation to the two-phase system of gas and adsorbate.

$$\left[ \frac{dP}{dT} \right]_c = \frac{\Delta H_a}{T(V_g - V_a)}$$

Since $V_g >> V_a$ we can neglect $V_a$ with negligible loss of accuracy. Applying the ideal gas law gives,

$$\Delta H_a = R \left[ \frac{d\ln P}{dT} \right]_c$$

22
If equilibrium isotherm data at various temperatures are available, the heat of adsorption may be evaluated. Reported values for oxygen and nitrogen adsorption on molecular sieve 5A are 3.3 and 5.0 Kcal/mole, respectively (46).

**Isotherm Models**

A. General

In general, the classical isotherm models, i.e. Langmuir, Freudlich, and Temkin (See Table 1), do not adequately represent sorption in zeolites (31,43,44,45,46,47,48). The Polanyi potential theory (61) has been extended for application to zeolitic adsorbents, although its primary value is the correlation of equilibrium data (31). Although these models may be of limited value in arriving at an empirical fit of zeolite data, the basic assumptions simply are not valid for zeolitic sorption.
Table 1. Common adsorption equations (73).

<table>
<thead>
<tr>
<th>Name</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$\theta = \frac{C_P}{1 + C_P}$</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$\theta = C_P$</td>
</tr>
<tr>
<td>Temkin</td>
<td>$P = k \exp(\theta)$</td>
</tr>
<tr>
<td>Volmer</td>
<td>$P = \frac{k \theta}{1 - \theta} \exp[\theta(1 - \theta)]$</td>
</tr>
<tr>
<td>B.E.T.</td>
<td>$\theta = \frac{c x}{(1 - x)[1 + (C - 1)x]}$</td>
</tr>
<tr>
<td>Sips</td>
<td>$\theta = \frac{(C_P)^k}{1 + (C_P)^k}$</td>
</tr>
</tbody>
</table>

Where: $k = f(T)$, $C$ and $c$ = constants.

Although the Langmuir model has limited value in empirically fitting zeolite isotherm data for non-polar molecules, the basic postulates of this model render it useless in predicting zeolite adsorption isotherms. The assumption of a energetically uniform surface with distinct adsorption sites with no sorbate-sorbate interaction cannot explain the energetic heterogeneity of the zeolite toward molecules with dipole or quadrupole moments, nor can it account for the pore filling nature of zeolites.
The equation suggested by Sips (49) which combines the Freundlich and the Langmuir isotherms is successful as an empirical equation but the constants in this equation have little physical meaning. Additionally, the Sips model, Freundlich model, and Temkin model will not reduce to Henry's Law at very low pressures which Hill (50) has shown to be an important limit for adsorption equations.

B. Statistical Thermodynamic Approach

Ruthven (52) suggested an adsorption isotherm model based on statistical thermodynamics and applicable to zeolitic adsorption. He reasoned that zeolites are well defined, uniform structures and, therefore, it should be possible to analyze the adsorption process using statistical thermodynamics and arrive at a predictive model.

A number of studies which revealed the volume filling characteristics of zeolites led to the development of the statistical thermodynamic model. Barrer (21) observed that the apparent saturation values decrease linearly with temperature (See Table 2). He speculated that the volume of the sorbed molecules increase linearly with temperature. Barrer and Sutherland (53) concluded that at high temperatures the amount sorbed was determined by the affinity of the sorbate for the zeolite but at low temperatures and pressures the amount sorbed depended on the molecular volume of the sorbate molecule and its packing density. It appeared that the intracrystalline fluid had some
of the properties of the bulk liquid (25,51). Another has speculated that adsorption in zeolites might be viewed as filling the intracrystalline volume with liquid sorbate (31). By linear interpolation between the saturated liquid molecular volume at the normal boiling point and the van der Waals molecular volume b at the critical temperature, the effective molecular volume could be estimated (31,56,57) and the saturation capacity of the zeolite could be predicted with reasonable accuracy by dividing the cavity volume V by the effective molecular volume B (55). This concept of volume filling forms the basis of the statistical thermodynamic model.

Table 2. The apparent saturation of sorption at different temperatures (21).

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Gas</th>
<th>Temp. (K)</th>
<th>Apparent Saturation (cc NTP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>chabazite</td>
<td>N2</td>
<td>89.2</td>
<td>164.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>194.5</td>
<td>75.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>194.5</td>
<td>75.2</td>
</tr>
<tr>
<td></td>
<td>N2</td>
<td>83.0</td>
<td>170.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>193.0</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>193.0</td>
<td>90.0</td>
</tr>
<tr>
<td>analcite</td>
<td>N2</td>
<td>79.5</td>
<td>30.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>194.5</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>194.5</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>H2</td>
<td>62.2</td>
<td>33.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>78.5</td>
<td>27.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90.0</td>
<td>23.7</td>
</tr>
</tbody>
</table>

+ Data of Rabinowitsch and Wood (54).
The derivation of the pure component isotherm equation based on the statistical thermodynamic model is presented below. More detail is given by Hill (50) and Ruthven (52).

Each zeolite cavity is assumed to be a totally independent site for adsorption, i.e. interaction with neighboring cavities are neglected. Consider a macroscopic system of M equivalent, independent, distinguishable cavities which contain s sorbate molecules where the number of sorbate molecules/cavity range from zero to m. Let the partition function below represent the cavity with s sorbate molecules adsorbed.

\[ q(s) = \sum_j j \exp(-\epsilon(s)/kT) \]

Let N be the total number of sorbate molecules in the system and \( a \) be the number of cavities with s molecules, then the canonical ensemble partition function for the system is,

\[
C(N,M,T) = \frac{M!}{\prod_{s=0}^{m} a_s!} q(0)^{a_0} q(1)^{a_1} \cdots q(m)^{a_m}
\]

where, \( a = a_s, a_{s-1}, \ldots, a_0 \) satisfying the restrictions:

\[
\sum_{s=0}^{m} a_s = M \quad \text{and} \quad \sum_{s=0}^{m} s a_s = N
\]

The grand partition function \( G \) is:
Where the grand partition function may be represented as a product of a subsystem of grand partition functions,

\[ G(\lambda, M, T) = Q(\lambda, T) \]

where,

\[ Q = q(0) + q(1)\lambda + \cdots + q(m)\lambda \]

\[ n = \sum_{s=0}^{m} q(s)\lambda \quad \text{or,} \]

\[ G(\lambda, M; T) = \left[ \sum_{s=0}^{M} q(s)\lambda \right]^{M} = Q \]

Finding the average number of molecules in the macroscopic system,

\[ n = \bar{N} = \lambda \left[ \frac{\partial \ln G}{\partial \lambda} \right]_{M,T} = M \lambda \left[ \frac{\partial \ln Q}{\partial \lambda} \right]_{T} \]

Then the average number of molecules/cavity \( c \) is:
\[ c - n = \frac{\lambda}{\text{M}} \left[ \frac{\partial \ln Q}{\partial \lambda} \right] = \frac{\sum_{s=0}^{m} \frac{\text{sq}(s) \lambda}{\text{S}}}{\sum_{s=0}^{m} \frac{\text{q}(s) \lambda^3}{\text{S}}} \]

Since \( Z(s) \) is the configuration integral then,

\[ c - n = \frac{m}{\text{M}} \sum_{s=0}^{m} \frac{sZ(s)a}{z} = \frac{Z(s)a + 2Z(s)a}{2} + \ldots + \frac{mZ(s)a}{m} \]

where the configuration integral \( Z \) is:

\[ Z = \frac{1}{s!} \int_{s}^{V} \exp[ - \frac{U(r \ldots r)}{kT} ] \, dr \ldots \, dr \]

and \( r \) = position vector, \( V \) = volume of the cavity, \( k \) = Boltzmann's constant, \( T \) = absolute temperature, \( U \) = potential energy for the subsystem, \( a \) = activity of the sorbate = \( p/kT \) for an ideal gas.
To evaluate the configuration integrals in terms of measurable quantities is very difficult therefore, the adsorbed molecules are treated as a van der Waals gas (52), and the following assumptions are applied:

1. The form of the potential field within the cavity is independent of the number of molecules in the cavity.

2. When two or more molecules are in the cavity, they move randomly and independently, and the molecular interaction is simply expressed as a reduction in free volume.

3. The energy of interaction between sorbate molecules may be represented by the Sutherland potential as in the derivation of the van der Waals equation (50):

\[ U(r) = \begin{cases} 6 & r < \sigma \\ -\xi \left( \frac{\sigma}{r} \right) & r \geq \sigma \end{cases} \]

This potential assumes rigid spheres of diameter \( \sigma \) which attract each other according to an inverse power law. This model is simple and fairly accurate (74). These approximations give the following configuration integral,

\[
Z = Z \left( 1 - \frac{sB}{V} \right)^s \exp\left( \frac{sB \xi}{V kT} \right)
\]

\( \frac{1}{s!} \)

where, \( 2 \leq s < \frac{V}{B} \)

\( \xi \) and \( \sigma \) are molecular constants from the Sutherland potential function.
(in the absence of available Sutherland constants Lennard-Jones constants are generally used). The resulting equation for the adsorption of a pure component gas has been shown by Ruthven (52) to be:

\[
\begin{align*}
Kp + (Kp) (1-2B/V) \exp(2B\xi/VkT) + \ldots + (Kp) (1-mB/V) \exp(mB\xi/VkT) \\
\frac{\prod \left( Kp \right) (1-mB/V) \exp(mB\xi/VkT)}{(m-1)!}
\end{align*}
\]

\[
\frac{c = \frac{2}{2!} \frac{2}{m!} \frac{m}{m!} \frac{1}{1} \frac{1}{1}}{1 + Kp + 1(Kp) (1-2B/V) \exp(2B\xi/VkT) + \ldots + (Kp) (1-mB/V) \exp(mB\xi/VkT)}
\]

Where \( K \) is the Henry's Law constant and,

\[
Kp = Z \frac{a}{1} = Z \frac{p}{kT}
\]

\( m < \frac{V}{B} \)

The configuration integral may be simplified to give,\

\[
Z = Z \frac{s}{1} (1 - sB/V)
\]

\[
\frac{s}{s!}
\]
The resulting isotherm equation then is,

\[
\frac{\frac{2}{K_p + \left( K_p \right) \left( 1 - \frac{2B}{V} \right) + \cdots + \left( K_p \right) \left( 1 - \frac{mB}{V} \right)}{(m-1)!}}{1 + \left( K_p \right) \left( 1 - \frac{2B}{V} \right) + \cdots + \left( K_p \right) \left( 1 - \frac{mB}{V} \right)}
\]

The \((1 - \frac{mB}{V})\) term corrects for the reduction in cavity volume which implies the integer \(m \leq \frac{V}{B}\) since the correcting term must not be negative. Restricting \(m\) to integer values is a weakness in the model since experimental data generally do not conform to this assumption. In the model the Henry's Law constant \(K\) accounts for the sorbent-sorbate interaction and \(B\), the effective molecular volume, accounts for the sorbate-sorbate interactions. At low pressures this equation reduces to the familiar Henry's Law equation. Although \(K\) may be calculated theoretically for simple systems (52), generally its value is determined from experimental isotherm data at low pressures. A problem arises in selecting a value for \(B\), the effective volume of the molecule, since the molar volume of the sorbate varies with temperature. The use of \(b\), the van der Waals oovolume, suggested in earlier work (52) has limited value. The value for \(B\) may be estimated by linear interpolation between van der Waals \(b\) at the critical temperature and the molar volume of the saturated liquid at the boiling point (56,45). More recently Ruthven (46) suggested superimposing a plot of the theoretical isotherm curves with vary values of \(V/B\) over the actual isotherm data plotted on
the same coordinates. K values may be predicted over a range of temperature from a vant Hoff plot where the K values derived from the data have been fit to a straight line and represented by the equation,

$$K = K_0 \exp \left( \frac{q_0}{RT} \right)$$

Although the assumptions may seem crude, this model has been widely and successfully applied for zeolite adsorption (31,45,46,52,58,75). The model is not without limitations, however. For systems approaching saturation ($\theta > 0.9$) this model may give unsatisfactory results (46). The model may also be inappropriate for adsorption of monotomic molecules and small polar molecules which tend to collect at the localized sites (31).

The statistical thermodynamic model can be extended to predict multicomponent mixture equilibria. Presented below is the derivation of the model equations for a binary mixture. For greater detail refer to Hill (50) and Ruthven (45). Proceeding with the same assumptions given for the pure component model, the grand partition function for the two component (A+B) mixture may be given as,

$$G = \left[ \sum_{i} \sum_{j} q(i,j) \sum_{A} \sum_{B} \frac{1}{\lambda^A \lambda^B} \right] = Q_{AB}$$

where $q(i,j)$ is the partition function for a cavity containing $i$ molecules of $A$ and $j$ molecules of $B$. This summation must include all values of $i$ and $j$ which satisfy,

$$i_B + j_B < V_{A}$$

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Since \( q(i,j) \lambda \lambda = Z(i,j) a a \) then,

\[
\begin{align*}
& c = n = \lambda \left[ \frac{\partial \ln Q}{\partial \lambda} \right]_{A} \lambda = \lambda, T \quad \sum_{i} \sum_{j} Z(i,j) a a \\
& M \quad i, j \quad A \quad B \quad A \quad B \quad A \quad B
\end{align*}
\]

and,

\[
\begin{align*}
& c = n = \lambda \left[ \frac{\partial \ln Q}{\partial \lambda} \right]_{B} \lambda = \lambda, T \quad \sum_{i} \sum_{j} Z(i,j) a a \\
& M \quad i, j \quad B \quad B \quad B \quad B \quad A \quad A \quad A \quad B
\end{align*}
\]

The expressions for the configuration integrals are,

\[
egin{align*}
Z(0,0) &= Z(0) = 1 \\
Z(1,0) &= Z(1,0) a = K p \\
Z(0,1) &= Z(0,1) a = K p \\
Z(i,j) &= Z(1,0) Z(0,1) \left( 1 - iB /V - jB /V \right) \\
& \quad i, j
\end{align*}
\]

Neglecting the sorbate-sorbate interaction term the final equations are,

\[
egin{align*}
K p + \sum_{i} \sum_{j} i(K p) (K p) (1 - iB /V - jB /V) \\
& \quad i, j \quad A \quad A \quad B \quad B \quad A \quad A \quad B \quad B
\end{align*}
\]

\[
\begin{align*}
& c = 1 + K p + K p + \sum_{i} \sum_{j} (K p) (K p) (1 - iB /V - jB /V) \\
& \quad i, j \quad A \quad A \quad B \quad B \quad A \quad A \quad B \quad B
\end{align*}
\]

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\[
\begin{align*}
K_p + \sum \sum_j^{i+j} (K_p)^i (K_p)^j (1 - iB/V - jB/V) \\
\frac{1}{1 + j} \\
\frac{c}{B} \\
\frac{1 + K_p + K_p + \sum \sum_j^{i+j} (K_p)^i (K_p)^j (1 - iB/V - jB/V)}{A A B B A A B B} \\
\frac{1}{1 + j!}
\end{align*}
\]

where the summations are carried out over all values i and j
satisfying both restrictions:

\[
i + j \geq 2 \quad \text{and} \quad iB + jB \leq V
\]

\[
K, K, B, B \text{ are determined from the pure component isotherm data}
\]
Since all parameters are known \(c, c\) may be calculated explicitly to give the mixed gas equilibria from the pure component data. This binary model has been applied successfully to a number of systems (45,46). Recently, the binary model gave an excellent representation of the oxygen-nitrogen equilibrium data of Sorial, Granville, and Daly (71) over the temperature range \(278.15^\circ \text{K} \text{ to } 303.15^\circ \text{K}\) and at total pressures of 1.7 and 4.4 bar. Furthermore, this method has been used to analyze the equilibrium data gathered in this work, as discussed in Chapter V.

C. The Ideal Adsorbed Solution Theory

The ideal adsorbed solution theory (IAST) of Myers and Prausnitz (60) represents zeolitic adsorption in certain systems (59). Ideal behavior implies that the components in a multicomponent mixture adsorb
as if they were present as pure components at their partial pressure in
the mixture. Ruthven (45) has shown that when \( B \approx B \) and either,

\[
\xi \sim \xi \quad \text{or} \quad B \frac{\xi}{\sqrt{V_{T,B}}} \frac{1}{A A B B} \ll 1
\]

the statistical thermodynamic model predicts that ideal behavior should
be observed even at high sorbate concentrations. In addition, ideal
behavior will also occur if the sorbate concentration is less than about
one molecule/cavity, even if the effective molecular volumes differ
widely. Conversely, when these characteristics do not occur the system
will tend toward nonideality.

IAST proposes that Raoult's Law, which has been used extensively
for vapor-liquid equilibria of ideal mixtures, may be adapted for use in
predicting mixed gas adsorption. Both equations are shown below for
comparison,

\[
\begin{align*}
T &= \text{constant} \\
\text{sat} & \quad P_y = P(T) x \quad (\text{vapor-liquid equilibria}) \\
\text{sat} & \quad P_y = P(\Pi) x \quad (\text{mixed gas adsorption}) \\
\end{align*}
\]

where,

\( \Pi = \text{spreading pressure} \)

\( P(T) = \text{vapor pressure of component } i \text{ at temperature } T. \)
The adsorbates are assumed to have equal spreading pressures.

The thermodynamic equations which describe the mixed gas adsorption system require the following assumptions (60):

1. The adsorbent is assumed to be thermodynamically inert. This implies that the change in thermodynamic properties, such as enthalpy, internal energy, etc., are small compared to the changes of these same properties for the adsorbing gas.

2. The ideal gas law applies.

3. The adsorbent has a temperature invariant area for adsorption which is the same for all adsorbates.

4. Gibbs definition for adsorption applies (72), that is, \( n_e \), the surface excess amount of sorbed gas, is the excess number of moles of \( i \) present in the system above that number present in a reference system where no adsorption occurs at the same equilibrium pressure (30). The volumetric technique gives the experimental isotherms in terms of the surface excess (60).

The development of the IAST equations shown below may be found in Myers and Prausnitz (60). In writing the thermodynamic equations for the adsorbed phase, we substitute the spreading pressure, \( \Pi \), for
pressure, $P$, and substitute area, $A$, for the volume, $V$.

\[ dU = TdS - \Pi dA + \sum \mu \, dn \]

\[ dG = -SdT + A \, d\Pi + \sum \mu \, dn \]

Hence, the work term is ($-\Pi dA$), and since $\Pi$ is positive for physical adsorption, the adsorbed phase does work on the adsorbent.

The Gibbs adsorption isotherm (72) is,

\[ -A \, d\Pi + \sum n \, d\mu = 0 \quad \text{(constant T)} \]

which upon integration gives,

\[ \Pi(P) = \frac{RT}{A} \int_{t=0}^{\circ} n(t) \, d\ln(t) \]

where $t$ is a dummy variable. This integral is evaluated graphically by plotting $n/P$ versus $P$ and finding the area under the curve. The evaluation of this integral requires the pure component isotherm data at the proper temperature, i.e. $n = F(P)$. This step results with,

\[ \Pi = F(P) \]

We may then write:

\[ \Pi(P) = F(P) \]

\[ P_y = P \, y \]

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\[ P_y = P_x \]

Assuming constant \( \Pi \),

\[ \Pi = \Pi \]

\[ 1 = x + x \]

\[ 1 = y + y \]

There are nine unknowns and seven equations, so that, we must define two variables in order to analytically determine the remaining seven. The total adsorbed is subsequently found by,

\[ n = \frac{1}{t \left( x + x \right)} \]

\[ \left( \frac{x}{1} + \frac{x}{2} \right) + \left( \frac{o}{n} + \frac{o}{n} \right) \]

where \( n \) and \( n \) are the amounts of pure component 1 and component 2 adsorbed at \( \Pi \) and \( T \).

The advantages of the IAST are its elimination of a specific isotherm model and its simple computational method but this theory does have some drawbacks. Pure component data must be available at the desired temperature over a wide pressure range. Without a model, use of the theory outside the range of the available data is questionable. Assumption of equal areas of adsorption for all adsorbates may not be
valid for zeolites where the area will depend on the effective molecular volume of the sorbate (60). The assumption that the adsorbent is thermodynamically inert may not be completely valid for zeolites. These drawbacks are not drastic, however, for permanent gases in zeolite 5A. Results of data analysis by this method are given in Chapter V.

**Diffusion**

A. Background

Important factors which influence the rate of diffusion in zeolite systems are: temperature, the rate at which diffusing molecules can reach the surface of the crystals (here we assume a system of zeolite pellets), the size of the molecules with respect to the size of the zeolite pores, the strength of the interactions between zeolite and the molecules, and adsorbate concentration. The resistances to zeolitic diffusion can be categorized as: external fluid film, macropore or intercrystalline, and micropore or intracrystalline (31). The macropore and micropore resistances are generally considered the most important.

The external fluid film resistance which occurs at the boundary of the zeolite pellet has been well studied. This resistance is generally of little importance in zeolite systems because the bulk fluid velocity is usually sufficient to minimize this effect (31). On the other hand, the macropore resistance, which involves the passage of the molecules
through the elaborate pore system of the clay binder, may occur by the mechanism of Knudsen or by molecular diffusion, and has been shown (at least in some systems) to influence the overall rate of diffusion. Variation of the pellet size will reveal whether macropore resistance is significant. In many systems the rate of crystal surface diffusion is rapid, therefore, the assumption of local equilibrium at the crystal surface is valid (31). The relative magnitudes of external or bulk diffusion, macropore diffusion, and micropore diffusion are $10^{-1}$, $10^{-3}$, $10^{-11}$, and $10^{-2}$ cm/sec, respectively (7).

Intracrystalline diffusion in most cases is the rate limiting step in the diffusion process due to the combined effects of the molecular dimensioned channels and the strong potential fields emanating from the crystal framework. Investigations of activation energies and diffusion coefficients for the adsorption of gases suggest the diffusing molecule encounters periodic potential fields within the zeolite (7). As a result, attempts at predicting equilibrium isotherms, heats of adsorption, and diffusivities through the use of idealized models of the potential fields have been unsuccessful (41).

A number of investigations have attempted to determine whether the diffusion rate controlling step in zeolites occurs in the macropore or the micropores. Kondis and Dranoff (63) studied the diffusion of ethane in synthetic type A zeolite. Both pelleted and powdered zeolite gave identical diffusion rates and equilibrium data. Since the powdered form had no binder (hence no macropore system) it was concluded that
intracrystalline diffusion was the controlling mechanism. In another experiment using erionite, a natural zeolite, both 1/8" pellet and 20X35 mesh granules gave rates of diffusion of the same order of magnitude, therefore, intracrystalline diffusion was reported as the controlling mechanism (76). In a third study, the rate of diffusion was compared using synthetic zeolite NaA pellets with an inert binder and pure crystals. The equilibrium data were corrected due to the presence of the binder. The results of the work indicated both had identical rates of diffusion and equilibrium data, i.e. the binder did not affect the rate of diffusion (77). In a fourth experiment, the rates of diffusion through pellets of NaA and CaA were measured using ethane. The calculated micropore and macropore diffusivities revealed that for NaA micropore diffusion was the limiting rate mechanism, but for CaA both macropore and micropore diffusion appeared to be important (7). Obviously, intracrystalline diffusion plays a significant role in most zeolite systems.

Zeolite diffusivities display a dramatic exponential sensitivity toward temperature indicative of an activated rate process (31). At very low temperature CO2, N2, and Ar adsorption on zeolite 4A is hindered because these molecules do not possess sufficient activation energy to pass through the narrow openings. Breck (7) reports that the rate of adsorption of argon and nitrogen on zeolite A powder decreases rapidly with temperature. Nitrogen will require a large activation energy for diffusion because of its strong quadrupole interaction with
the zeolite (78).

Ruthven's (31) study of the diffusion of monotomic and diatomic gases in type A zeolite shows an interesting concentration dependence. In zeolite 5A the diffusivity dramatically drops in the Henry's Law region from an initially high value to a minimum value at about one third of the saturation concentration, and as concentration increases the diffusivity dramatically rises (31). This behavior is indicative of a collisional diffusion mechanism where the mean free path of the diffusing molecule is determined by the intermolecular collisions. This suggests that, when the molecules are sufficiently small relative to the windows, they pass freely from cavity to cavity and the collisional mechanism controls diffusion.

It has been pointed out that the true driving force for diffusion in zeolites is the gradient of the chemical potential rather than the concentration gradient (31). Therefore, since most early studies were based on the concentration gradient their results, particularly at high concentrations of adsorbate are questionable. The proper equation for the Fickian diffusivity \( D \) is,

\[
D = D \left( \frac{d \ln p}{d \ln c} \right)_0
\]

where,

\[
D = \frac{D}{c}
\]

\[
D = D \exp\left( - \frac{E}{RT} \right)
\]
D is the diffusivity at zero concentration.

The term \( \frac{d \ln p}{d \ln c} \) would be equal to one at low concentration and at high concentrations becomes significant. For diffusion data of oxygen, nitrogen, and argon on zeolite 5A (See Table 3).

Table 3. Diffusion data for O\(_2\), N\(_2\), and Ar on zeolite 5A (62).

<table>
<thead>
<tr>
<th>System</th>
<th>E (Kcal)</th>
<th>( D \times 10^7 )</th>
<th>( \text{A} \times 10^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar-5A</td>
<td>(&lt;1.0)</td>
<td>0.01</td>
<td>3.4 molecules/cm/cavity sec</td>
</tr>
<tr>
<td>O(_2)-5A</td>
<td>1.0</td>
<td>0.026</td>
<td></td>
</tr>
<tr>
<td>N(_2)-5A</td>
<td>1.5</td>
<td>0.052</td>
<td></td>
</tr>
</tbody>
</table>

In studies concerning the diffusion of water in zeolites the size of the water molecules (2.8 Å) eliminates any consideration that molecular size affects the diffusion process. Instead, the strong dipole moment of the water molecule interacts with the zeolite cations such that the molecules will actually cluster at the sites (7).
B. Experimental Methods

A number of techniques are available for the experimental measurement of diffusivities such as volumetric, gravimetric, and chromatographic (31). The simplest method is to measure transient adsorption/desorption curves. For a system of spherical particles subjected to a step change in concentration,

\[
\frac{m}{\infty} = \frac{2A}{v} \left( \frac{D \cdot t}{\pi} \right)^{0.5} \quad (m/m < 0.25)
\]

\[
\mathbf{w} = 1 - \frac{6}{5} \sum_{n=1}^{\infty} \frac{1}{\pi^n} \exp \left( -\frac{n^2}{\pi^2} \right) \frac{2^n}{2^n} D \cdot \frac{t}{r}
\]

and \( A/v = 3/r \).

Listed below are some of the problem areas associated with obtaining reliable diffusivity data.

1. Intraparticle diffusion must be the rate limiting process.

2. Pressure (during step changes of concentration) must remain nearly constant.

3. Isothermal conditions must be maintained.

4. Differential measurements should be taken due to possible temperature effects over large intervals.

5. Zeolite must be activated thoroughly before use because water in the bed will greatly affect the results.

6. Crystals should not possess structural defects.
Rate experiments performed using breakthrough studies of packed column filled with adsorbent should give, in principle, the same zeolitic diffusivities as those obtained from the gravimetric method, but this method is generally not reliable (64). Breakthrough curves obtained from this technique are simply concentration profiles representing the mass transfer front at the effluent end of the column when a step change in concentration is applied to the bed inlet. The shape and time required for breakthrough of the front provides valuable information about the mass transfer resistance and operational parameters of the column. The length of the front will vary depending on the inlet flowrate, temperature, pressure, particle size, and the effects of coadsorbables. Under isothermal conditions the shape of the front is partially dependent on the adsorption rate. If the adsorption process is rapid, the front would appear almost vertical for a favorable isotherm in the absence of dispersion effects.

**Separation Factor**

The binary mixture separation factor is defined as,

$$
\alpha_{(x,y,z)} = \frac{\frac{X}{Y}}{\frac{A}{G}} = \frac{X}{Y} \cdot \frac{A}{G}
$$

where,

- $X$ = mole fraction of component $X$ in the adsorbed phase.
- $A$ =
X = mole fraction of component X in the gaseous phase.
G

Y = " " " Y " " adsorbed ".
A

Y = " k " " gaseous " .
G

x = more strongly adsorbed component.

y = less " " " .

z = adsorbent.

For a binary mixture is a measure of the adsorption selectivity of the adsorbent toward adsorbates X and Y. If the value of $\alpha >> 1$, the adsorbent preferentially adsorbs component X, thus separation of components X and Y is possible. If $\alpha \sim 1$ the separation of components X and Y will be difficult or impossible.

Since the value of $\alpha$ is based on equilibrium data an $\alpha > 1$ is a necessary but not a sufficient criteria in determining the feasibility of a separation process. An extremely slow rate may render the separation infeasible. Predictions of $\alpha$ from pure component data have been unsuccessful. Therefore, $\alpha$ should be ascertained experimentally.

Sorial, Granville, and Daly (71) report $\alpha$(N2,02,5A) is relatively insensitive to temperature and pressure changes. Ruthven (46) has drawn some general conclusions about the relationship of the effective molecular volumes of the sorbates, separation factor, and system operating parameters. Where the component with the smaller effective molecular volume is adsorbed
more strongly increases with increasing pressure, and conversely, where the component with the larger effective molecular volume is more strongly adsorbed (as in the case of the N₂-O₂ system) decreases with increasing pressure.

Domine and Hay report the following separation factors for the nitrogen-oxygen binary mixture at 20°C (See Table 16).

Table 16. Separation factors reported by Domine and Hay (67).

<table>
<thead>
<tr>
<th></th>
<th>5A</th>
<th>13X</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N₂,O₂)</td>
<td>2.75</td>
<td>2.36</td>
</tr>
<tr>
<td>(O₂,Ar)</td>
<td>1.08</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Description of a PSA Process

Pressure swing adsorption (or as a two column version of the process is sometimes called, heatless adsorption) is capable of separating gas mixtures due to preferential adsorption of one or more of the components in the gas mixture. The process is operated on short cycles, whereby the high pressure feed is introduced to the columns of adsorbent in an alternating fashion, consequently, the less strongly adsorbed component or components concentrate in the product flow and the more strongly adsorbed components are collected in the exhaust/waste stream. For a nitrogen-oxygen separation regeneration of the beds is
accomplished by pressure reduction, and a combination of displacement and purge stripping with the low pressure oxygen enriched purge flow. Critical parameters in the operation of the system are cycle time and purge/feed ratio.

We restrict our discussion to a two column system capable of operation at two- or six-steps per cycle (See Fig 3-2 and 3-3). The six-step system will be discussed first because the two-step system is a simplification of this system. Nitrogen-oxygen separation is considered with an adsorbent of molecular sieve 5A. The exhaust pressure $P_L$ is assumed to be atmospheric pressure. Argon is neglected in the discussion, although in an actual air separation process it usually emerges in the product or enriched oxygen flow. A simplified schematic diagram of the flows associated with a 6-step and a 2-step system is shown (See Fig 3-4).

6-Step Cycle:

(1) Feed air at high pressure $P_H$ enters column A through valve 3 while product oxygen-enriched flow exits through valve 5. Column B depressurizes from $P_H$ to $P_L$ by exhausting waste gas (slightly nitrogen-enriched air) through valve 1.

(2) Feed air and product flows continue as in step 1, valve 7 opens diverting a portion of the product flow through an orifice and countercurrently down column B finally exhausting through valve 1. Henceforth, this product flow which passes
through the columns countercurrently will be referred to as low pressure purge flow. The orifice may have a fixed diameter or in more sophisticated systems will be replaced by a variable flow control valve.

(3) Feed air and product flows continue as in step 1 but valve 1 closes and column B begins repressurization with a portion of the product flow from column A. Column A and B reverse roles:

(4) Feed air at high pressure enters column B through valve 2 while product leaves through valve 6. Column A depressurizes through valve 4.

(5) Feed air and product flows continue as in step 4 and valve 7 opens to begin purging column A.

(6) Feed air and product flow continue as in step 4 but valve 4 closes as column A begins to repressurize with a portion of the low pressure purge flow from column B. This completes one cycle of operation.

2-Step Cycle.

(1) Feed air at high pressure repressurizes column A, product flow exits column A, and purge flow from column A passes through column B discharging at valve 1. Column B depressurizes to $P_L$ and is countercurrently purged by flow from column A.

(2) Feed air at high pressure repressurizes column B, product
flow leaves column B, and purge flow from column B passes countercurrently through column A leaving through valve 4. Column A depressurizes to P and is purged by flow from column B. This completes one cycle of operation.

Brief Review of the Equilibrium Theory for Modeling PSA Processes

Shendalman and Mitchell (35) modeled a heatless adsorption process for separating a trace contaminant (1.09% CO2) which is preferentially adsorbed from a nonadsorbable carrier stream of helium. This specific feed gas was chosen to minimize the effect of coadsorbables and to ensure the concentration of CO2 at the feed pressure had nearly linear isotherms. The theoretical approach was based on the theory of parametric pumping developed by Pigford et al. (79).

The model was applied to a four-step/cycle process (See Fig 3-5). During step 1 feed passes through column A producing a product flow and simultaneously a portion of this product flow is passed countercurrently through column B for purging accumulated adsorbate. In step 2 column A is depressurized and column B is repressurized to the inlet feed pressure. In step 3 and 4 the columns reverse roles. In step 3 high pressure feed enters column B and a product flow leaves while a portion of the product flow is diverted to column A for purging. In step 4 column A is repressurized to the feed pressure and column B enters blowdown or depressurization. It should be noted that during steps 2
and 4 the product flow from the columns ceases.

Two major assumptions were incorporated into the model equations. Firstly, equilibrium is always assumed to exist between the adsorbate and adsorbent. Secondly, a linear isotherm is assumed for the adsorption of CO2 at its concentration and pressure in the feed gas. Other assumptions believed to be of less importance were:

(a) A non-adsorbing carrier gas, present in large excess.
(b) Isothermal process.
(c) One dimensional flow with no axial dispersion.
(d) Negligible pressure drop through the bed. This implies a linear velocity gradient in the bed.
(e) Ideal gas law applies.

A one dimensional component mass balance gives,

\[ \varepsilon \left( \frac{\partial c}{\partial t} + \frac{\partial (v c)}{\partial z} \right) + (1 - \varepsilon) \frac{\partial n}{\partial t} = 0 \]

\( \varepsilon \) = void fraction.
\( c \) = molar density in the gas phase.
\( n \) = molar density in the adsorbed phase.
\( t \) = time.
\( z \) = position.
\( v \) = interstitial velocity.
\( y \) = mole fraction of adsorbate in gas the gas phase.
\( P \) = total pressure.
\( k \) = partition coefficient.

For an ideal isothermal compressible flow the equation of continuity is,

\[
\frac{\partial P}{\partial t} + \frac{\partial vP}{\partial z} = 0
\]

Let \( n = k^2 \) and combine,

\[
P[\varepsilon + (1-\varepsilon)k] \frac{\partial y}{\partial t} + \varepsilon pv \frac{\partial y}{\partial z} + (1-\varepsilon) ky \frac{\partial P}{\partial t} = 0
\]

This hyperbolic partial differential equation is solved by the method of Lagrange-Charpit or method of characteristics to yield a pair of ordinary differential equations,

\[
\frac{dt}{P[\varepsilon + k(1-\varepsilon)]} = \frac{dz}{\varepsilon pv} = -\frac{dy}{(1-\varepsilon) ky} \frac{\partial P}{\partial t}
\]

The equations will then reveal the concentrations within the process with respect to time and position and afford an opportunity to investigate the effects of the individual parameters.

It was shown that only if the purge/feed ratio, \( R = \frac{L_L}{L_H} > \left( \frac{P_H}{P_L} \right) \frac{\varepsilon}{[\varepsilon + k(1-\varepsilon)]} \) and no breakthrough of feed into the product occurs then the process will give perfect cleanup of the feed.

\( L_L \) = hypothetical penetration distance of a concentration front in a low pressure bed.

\( L_H \) = hypothetical penetration distance of a concentration front in a high pressure bed.
front in a high pressure bed.

If \( R < \left( \frac{P_H}{P_L} \right) \varepsilon / \left[ \varepsilon + k(1-\varepsilon) \right] \) the process has inadequate purge flow and is not capable of perfect cleanup. The experimental data indicated an \( R_{crit} \) (i.e. the minimum value of \( R \) which gives low concentrations of \( CO_2 \) in the product) existed and was approximately equal to 1.2. The theory suggests that the \( CO_2 \) level in the product is independent of \( R \) once the \( R_{crit} \) is reached.

The experimental data and the predictions from the model gave poor agreement. Possible reasons for the discrepancies were non-linear isotherm, rate processes, and dispersion. The model did give qualitative agreement and led to improved understanding of the process.

In a later study Mitchell and Shendalman (36) extended their mathematical model for a trace contaminent which is preferentially adsorbed in an non-adsorbable carrier to include a mass transfer resistance. In these experiments the configuration of the process remained unchanged. The previous assumptions of equilibrium between the adsorbate and the adsorbent was replaced by a single mass transfer coefficient. The controlling step was assumed to be in the pores of the adsorbent pellet. The final mass balance equation was,

\[
\frac{\varepsilon P v}{R T} \frac{\partial v}{\partial z} + \frac{\varepsilon p}{R T} \frac{\partial y}{\partial t} = -(1-\varepsilon) k A \left( \frac{k p y}{R T} - n \right)
\]

\[
\frac{\partial n}{\partial t} = k A \left( \frac{k p y}{R T} - n \right)
\]

\( k = \) mass transfer coefficient.
A = mass transfer area.

p

The following characteristic trajectories were obtained using

the method of characteristics,

\[-(1-\varepsilon)k A \left(\frac{K_p y}{RT} - n\right)\]

\[
dy/dz = \frac{CP_v/RT}{-(\text{gas phase})} (gas phase)\]

\[
dz/dt = v \quad (gas phase)\]

\[
dn/dt = k A \left(\frac{K_p y}{RT} - n\right) \quad (adsorbate)\]

\[
dz/dt = 0 \quad (adsorbate)\]

Two approaches are undertaken in the analysis to identify the bounds of the process. In the first we assume equilibrium between the gas and sorbate occurs during steps 1 and 3 of the process. In the second we assume the pressure changes are so rapid that no mass transfer occurs between the gas and the solid. The values for $K$ and $k_p A_p$ were determined by a breakthrough curve run at 4 atm. pressure. The mass transfer coefficient was assumed to be constant throughout the process. Comparison with experimental data was poor since the observed data fell between the two approaches taken but closer to the equilibrium approach. Qualitative agreement was achieved since the approaches did bracket the data.
Chan, Hill, and Wong (80) extended the equilibrium model to include separations of two components both adsorbable but one is a preferentially adsorbed trace contaminant. The assumptions were:

(1) Equilibrium exists between the gas and solid at all times.
(2) Isothermal operation.
(3) Pressure drop through each bed is small.
(4) Negligible dispersion axially and radially.
(5) Linear isotherms assumed.
(6) Ideal gas law applies.

After a brief examination of the performance characteristics of the process they concluded that gas mixtures with large separation factors required less purge flow for complete removal of the trace contaminant than did mixtures with small separation factors. Additionally, when the gas mixture to be separated has a large separation factor the system performance may be improved by increasing the pressure ratio, \( P_H / P_L \). Increasing the pressure ratio in a system with small separation factor will not improve performance. Experimental results were not presented to support their theoretical conclusions.

Knaebel and Hill (82) further extended the equilibrium theory to include separation of a binary feed of arbitrary composition. The assumptions of their work were:

(1) Linear, uncoupled isotherms
(2) Isothermal operation
(3) Ideal gas law assumed

(4) Diffusional resistance and dispersion neglected.

It was concluded that when $\beta$ is small (i.e. small concentration of the heavy component in the feed) the purge requirement is minimal, perfect cleanup occurs over all pressure ratios, recoveries increase with increasing pressure ratio, and pressurization with product gives higher recoveries than pressurization with feed.

$$\beta = \frac{\beta_A}{\beta_B}$$

$$\beta = \frac{\varepsilon}{\varepsilon + (1 - \varepsilon) \frac{k}{k}}$$

$k$ is the equilibrium distribution coefficient for species $i$.

Conversely, when $\beta$ is large (i.e. large concentration of the heavy component in the feed) higher pressure ratios are required and recoveries are small.
FIG 3-1. STRUCTURAL MODEL OF MOLECULAR SIEVE 5A.
FIG 3-2. SIMPLIFIED SCHEMATIC DIAGRAM OF A DUAL COLUMN PSA AIR SEPARATION UNIT.
FIG 3-3. VALVE POSITIONS DURING ONE CYCLE FOR THE SYSTEM SHOWN IN FIG 3-2.
FIG 3-4. COMPARISON OF SIX-STEP AND TWO-STEP CYCLE.
FIG 3-5. SHENDALMAN AND MITCHELL FOUR-STEP CYCLE.
EXPERIMENTAL

A. Materials

The adsorbent employed in this work was Union Carbide Corp., 20X40 mesh ("0.0102" to "0.0201" diameter), medical grade, molecular sieve 5A (Lot No. 9427800171) (See Fig 4-1 to 4-5). This sieve is reported by the manufacturer to be 80% anhydrous crystals and 20% inert clay binder. The chemical formula for the anhydrous crystal is,

\[
\text{Ca} \quad \text{Na} \quad \left[ (\text{Al}_1\text{O}_2) (\text{Si}_2\text{O}_7) \right] \\
4.5 \quad 3 \quad 2.12 \quad 2.12
\]

Theoretically, the sieve is 75% exchanged with Ca.
The gases used in this work are listed in Table 4.

Table 4. Specifications of gases used in the equilibrium studies.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Purity</th>
<th>Supplier</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>99.998%</td>
<td>Burdett Gas Products Co.</td>
<td>Water pump</td>
</tr>
<tr>
<td>Oxygen</td>
<td>99.99%</td>
<td>Matheson Gas Products</td>
<td>Ultra-high purity</td>
</tr>
<tr>
<td>Air</td>
<td>20.9% O2</td>
<td>Liquid Air Corp.</td>
<td>Compressed Air</td>
</tr>
<tr>
<td>Air</td>
<td>78.0% N2</td>
<td>Lot. No.1678/682C</td>
<td>Breathing quality</td>
</tr>
<tr>
<td>Air</td>
<td>0.96% Ar</td>
<td></td>
<td>(oil free)</td>
</tr>
<tr>
<td>Air</td>
<td>&lt;30ppm H2O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Air purity determined using a Perkin-Elmer MGA-1100 medical gas analyzer and a dew point meter.

B. Pure Component Equilibrium Apparatus

A volumetric type pure component equilibrium apparatus was constructed for measuring the isotherms of nitrogen and oxygen at 24, -40, and -70°C and up to pressures of approximately 4.3 atmospheres absolute (See Fig. 4-6 and 4-7). The unit was designed to satisfy five primary goals: accurate data collection; simple, reliable operation; economical construction; easy conversion to a multicomponent equilibrium apparatus; and convenient installation into the temperature controlled chamber. All the stated goals were attained. The apparatus had a length of approximately three feet, a width of one foot, a depth
of 6", and weighed about 10 pounds.

The range of pressures and temperatures of operation prompted use of stainless steel construction. The sample chambers (C1 and C2) and their associated piping were mated through the use of stainless steel compression fittings with a design range which encompassed the range of operation. The sample chamber volumes (C1 and C2) were nominally 150 ml each and the outside diameter of the stainless steel tubing was largely 1/4" except for a short section of 3/8" tubing located at the inlet to the sample chamber (C1). The valves (V1-4) had stainless steel bodies and Kel-F seats for leakproof operation at both positive and negative pressures, and were manually operated.

System pressure measurements were accomplished through the use of Statham model PA208TC-50-350 stainless steel diaphragm pressure transducers (P1 and P2). The units outputted a low voltage DC signal which was sent to the electronics box (E) for signal conditioning, conversion to units of Torr or psia, and readout display. A high level conditioned DC signal was, simultaneously, sent to the strip chart recorder (S). The charge chamber temperature and sample temperature measurements were sensed by copper-constantan thermocouples and were displayed on readouts (R1 and R2) in units of °C.

Other units of the system were the rotary vacuum pump (V), temperature controlled chamber (T), variable transformer (X), and an electric tape heater (H).
The pressure transducers (P1 and P2) and the electronics box (E) were calibrated as a system over the range 0-75 psia with a calibrated high accuracy Wallace-Tiernan pressure gauges (Model FA129 and 61A-1A-0150). The transducer signals were linear from 0 to 75 psia and nonlinear above 75 psia.

The determination of the volume of the sample and charge chamber and their associated piping was accomplished by a water displacement method and these results were checked using several gas expansions. The volume to be measured was evacuated to \(-1\) Torr and then distilled water at room temperature was permitted to fill the volume. The weight of the water was determined by the difference method and its volume was calculated based on the reported densities of water (65) (See Table 5 and 6).

### Table 5. Sample chamber volume determination using water displacement.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Dry Weight (gm)</th>
<th>Wet Weight (gm)</th>
<th>Water Weight (gm)</th>
<th>Water Temp. (°C)</th>
<th>Water Density (gm/ml)</th>
<th>Calc. Chamber Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1396.0</td>
<td>1565.4</td>
<td>169.4</td>
<td>28</td>
<td>0.996264</td>
<td>170.0</td>
</tr>
<tr>
<td>2</td>
<td>1395.7</td>
<td>1565.2</td>
<td>169.5</td>
<td>26</td>
<td>0.996814</td>
<td>170.0</td>
</tr>
<tr>
<td>3</td>
<td>1395.8</td>
<td>1564.9</td>
<td>169.1</td>
<td>27</td>
<td>0.996744</td>
<td>169.7</td>
</tr>
<tr>
<td>4</td>
<td>1395.9</td>
<td>1565.4</td>
<td>169.5</td>
<td>26</td>
<td>0.996814</td>
<td>170.0</td>
</tr>
<tr>
<td>5</td>
<td>1396.0</td>
<td>1565.3</td>
<td>169.3</td>
<td>26</td>
<td>0.996814</td>
<td>169.8</td>
</tr>
</tbody>
</table>

Sample chamber volume = 170.0 ml
Table 6. Charge chamber volume determination using water displacement.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Dry Weight (gm)</th>
<th>Wet Weight (gm)</th>
<th>Water Weight (gm)</th>
<th>Water Temp. (°C)</th>
<th>Water Density (gm/ml)</th>
<th>Calc. Chamber Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1206.8</td>
<td>1364.8</td>
<td>158.0</td>
<td>26</td>
<td>0.996814</td>
<td>158.5</td>
</tr>
<tr>
<td>2</td>
<td>1206.8</td>
<td>1364.6</td>
<td>157.8</td>
<td>&quot;</td>
<td>&quot;</td>
<td>158.3</td>
</tr>
<tr>
<td>3</td>
<td>1206.9</td>
<td>1364.7</td>
<td>157.8</td>
<td>&quot;</td>
<td>&quot;</td>
<td>158.3</td>
</tr>
<tr>
<td>4</td>
<td>1207.3</td>
<td>1365.4</td>
<td>158.1</td>
<td>&quot;</td>
<td>&quot;</td>
<td>158.6</td>
</tr>
<tr>
<td>5</td>
<td>1207.5</td>
<td>1365.6</td>
<td>158.1</td>
<td>&quot;</td>
<td>&quot;</td>
<td>158.6</td>
</tr>
</tbody>
</table>

Charge chamber volume = 158.6 ml

Several gas expansions were performed as a check of the results obtained using the water displacement method. The gas expansions were from the charge chamber (C2) into the sample chamber (C1) via valve (V3). The charge chamber volume was assumed to be 156.8 ml as previously determined from the water displacement experiment. The results of these experiments are shown below (See Table 7).
Table 7. Results from nitrogen and helium expansions into the sample chamber.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Gas</th>
<th>Initial Charge Chamber Pressure (atm)</th>
<th>Initial Sample Volume Chamber Pressure (atm)</th>
<th>Initial Volume of Gas (ml)</th>
<th>Initial Temp (°C)</th>
<th>Final Pressure (atm)</th>
<th>Final Volume of Sample Chamber (ml)</th>
<th>Calc. Volume of Sample Chamber (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N2</td>
<td>2.041</td>
<td>0</td>
<td>158.6</td>
<td>25</td>
<td>0.986</td>
<td>169.5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>He</td>
<td>2.041</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.980</td>
<td>171.8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>1.000</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.482</td>
<td>170.7</td>
<td></td>
</tr>
</tbody>
</table>

These results are in good agreement with the previous water displacement experiments, therefore, we conclude:

Volume of the Sample Chamber = 170.0 ml

" " " Charge " = 158.6 "

The anhydrous weight of the molecular sieve sample was determined by regenerating the sample at <1 Torr pressure and 350°C for a minimum of 12 hours. This regeneration procedure became standard practice and was accomplished before each equilibrium run. It was noted that when the heating tape temperature reached approximately 300 °C the sample began "boiling" violently, apparently releasing the residual water of hydration. The results of the initial regeneration are shown below,

Gross volume of sample = 50 ml

Weight of sample before regeneration = 33.7 gm
Weight of sample after regeneration = 32.8 gm
" lost during regeneration = 0.9 gm or

0.027 gm

gm anhydrous wt.

This residual weight (mostly water) is close to the specification of ~2% residual water stated by the manufacturer. The anhydrous weight of the molecular sieve sample will be taken as 32.8 gm. It should be noted that this same sample was employed in all the equilibrium experiments.

To calculate the amount adsorbed the true dead space of the sample chamber must be ascertained. We define the true dead space as the volume of the sample chamber minus the volume of the solid crystal.

This dead space volume was obtained by a helium displacement technique. It is assumed that helium will fill the entire void volume of the zeolite but adsorb in negligible quantities at room temperature. The advantage of this technique is that the pressure of the pressure of the helium can be related directly to the true dead volume. The experimental approach taken was to expand helium into the sample chamber a sufficient number of times, so that, through application of statistical analysis we might arrive at a reasonable value for the true dead space volume. The data from twenty expansions are presented (See Table 8). Helium is assumed to be an ideal gas over the range of pressure in which the experiment was conducted (66).
Table 8. Determination of the true dead space of the sample chamber.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Initial Pressure (Torr)</th>
<th>Final Pressure (Torr)</th>
<th>Calc. Sample Volume (ml)</th>
<th>Calc. True Dead Space Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1500</td>
<td>750</td>
<td>11.4</td>
<td>158.6</td>
</tr>
<tr>
<td>2</td>
<td>2000</td>
<td>1008</td>
<td>13.92</td>
<td>156.08</td>
</tr>
<tr>
<td>3</td>
<td>2500</td>
<td>1246</td>
<td>10.38</td>
<td>159.62</td>
</tr>
<tr>
<td>4</td>
<td>3000</td>
<td>1495</td>
<td>10.34</td>
<td>159.66</td>
</tr>
<tr>
<td>5</td>
<td>3500</td>
<td>1743</td>
<td>10.13</td>
<td>159.87</td>
</tr>
<tr>
<td>6</td>
<td>1500</td>
<td>750</td>
<td>11.40</td>
<td>158.6</td>
</tr>
<tr>
<td>7</td>
<td>2000</td>
<td>998</td>
<td>10.76</td>
<td>159.24</td>
</tr>
<tr>
<td>8</td>
<td>2500</td>
<td>1241</td>
<td>9.10</td>
<td>160.90</td>
</tr>
<tr>
<td>9</td>
<td>3000</td>
<td>1495</td>
<td>10.34</td>
<td>159.66</td>
</tr>
<tr>
<td>10</td>
<td>3500</td>
<td>1748</td>
<td>11.04</td>
<td>158.96</td>
</tr>
<tr>
<td>11</td>
<td>1500</td>
<td>750</td>
<td>11.40</td>
<td>158.60</td>
</tr>
<tr>
<td>12</td>
<td>2000</td>
<td>998</td>
<td>10.76</td>
<td>159.24</td>
</tr>
<tr>
<td>13</td>
<td>2500</td>
<td>1246</td>
<td>10.38</td>
<td>159.62</td>
</tr>
<tr>
<td>14</td>
<td>3000</td>
<td>1499</td>
<td>11.19</td>
<td>158.81</td>
</tr>
<tr>
<td>15</td>
<td>3500</td>
<td>1748</td>
<td>11.04</td>
<td>158.96</td>
</tr>
<tr>
<td>16</td>
<td>1500</td>
<td>750</td>
<td>11.40</td>
<td>158.60</td>
</tr>
<tr>
<td>17</td>
<td>2000</td>
<td>1003</td>
<td>12.35</td>
<td>157.65</td>
</tr>
<tr>
<td>18</td>
<td>2500</td>
<td>1246</td>
<td>10.38</td>
<td>159.62</td>
</tr>
<tr>
<td>19</td>
<td>3000</td>
<td>1500</td>
<td>11.40</td>
<td>158.60</td>
</tr>
<tr>
<td>20</td>
<td>3500</td>
<td>1748</td>
<td>11.04</td>
<td>158.96</td>
</tr>
</tbody>
</table>

Results:
Mean Sample Volume = 11.05 ml
Standard Deviation = 1.0004 ml
Solid volume based on a 95% confidence interval = 11.05 ± 0.047 ml
Solid density = 2.97 gm/ml

From these results we conclude:

Solid Volume of the Sample = 11.05 ml
True Dead Volume in the Sample Chamber = 158.9 ml

The confidence interval assumes normally distributed error in the individual observations about the true mean. Since the true standard deviation is not known, a two-tailed t distribution with 2.5%
probability in each tail and nineteen degrees of freedom was employed in the calculation of the confidence interval.

The procedure for operating this apparatus is straightforward and presented in Appendix B. Before each data run the molecular sieve sample is regenerated by heating the sample to 350 °C and applying a vacuum ( < 1 Torr) for a minimum of twelve hours. After regeneration the temperature of the sample is stabilized at the desired experimental temperature. Injection of the gaseous phase adsorbate from the charge chamber to the sample chamber is accomplished by opening valve (V3). The quantity of adsorbate in the sample chamber is increased in a stepwise fashion and data are collected after equilibrium is reached in the sample chamber. Equilibrium was assumed to exist when the pressure in the sample chamber remained constant for at least a period of one hour. In general, an equilibrium state was reached after a period of six to eight hours. The amount adsorbed may then be determined by performing a mass balance (See Appendix C).

C. Multicomponent Equilibrium Apparatus

Modification of the pure component equilibrium apparatus to enable it to gather multicomponent data was accomplished by the addition of a gas sampling and analysis section (See Fig. 4-8, 4-9, and 4-10). This gas sampling section was comprised of a Perkin-Elmer MGA-1100 medical gas analyzer (MGA), a dual channel strip chart recorder (SC), MGA gas
sampling probe (PR), two three way valves (V5 and V6), a MGA sampling volume (SV), and a rotary vacuum pump (V). Since the multicomponent system (N2-O2-Ar-5A) has four degrees of freedom the gas phase concentrations of at least two components are required (plus the temperature and total pressure) to fully define the system. It should be clear that air is to be injected into the sample chamber in all experiments, therefore, the molar ratios of N2:O2:Ar remain constant in the sample chamber. The advantage of this approach is that it should more closely simulate the actual gas concentrations in a PSA column.

Measurement of the gas phase concentrations poses a challenge. Direct measurement of the gas phase concentrations with the medical gas analyzer (MGA) would not allow accurate determination of the total mass removed from the sample chamber. This difficulty was overcome by allowing a small portion of the gas mixture to fill the previously evacuated MGA sampling volume (SV) so that a determination of the exact amount of mass of each component removed from the sample chamber (C1) could be made. The isolated gas mixture in the sampling volume (SV) is then permitted to flow through the gas sampling probe, and subsequently, to the MGA for concentration analysis.

The experimental technique adopted here represents somewhat of a departure from tradition methods. A traditional approach, considering only the binary system of nitrogen-oxygen, would dictate injecting the proper amounts of the pure gases so as to maintain the total pressure constant but vary the gas phase mole fractions from 0 to 1.0. A second
traditional approach would involve maintaining the gas phase concentrations constant and varying the pressure. Both traditional techniques require the injection of pure gases which could create areas of severe concentration heterogeneity. This difficulty is usually avoided through use of a circulation pump.

The approach of this work involves the injection of a homogenous mixture; therefore, the sample chamber is much less likely to possess the severe localized concentration gradients as the traditional system would experience without the circulation pump. Our approach minimizes the complexity of the experiment without compromising the validity of the experimental results provided a sufficient period for gaseous diffusion is allowed. Also, as previously mentioned, the data obtained in this manner should approximate the concentrations in a PSA column. Comparison of the results of this work with other work will validate this technique.

The first step in the modification of the pure component apparatus was to determine the MGA sampling volume which would minimize the gas sampling time, i.e. the volume of gas to be extracted, but allow ample time for the MGA to reach a steady state condition and thus provide stable signals at the strip chart recorder. The calibrated gas sampling probes used with the MGA covered four pressure ranges (See Table 9).
Table 9. Pressure range of the MGA gas sampling probes.

<table>
<thead>
<tr>
<th>Probe No.</th>
<th>Pressure Range (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>140 to 214</td>
</tr>
<tr>
<td>2</td>
<td>214 to 326</td>
</tr>
<tr>
<td>3</td>
<td>326 to 497</td>
</tr>
<tr>
<td>4</td>
<td>497 to 760</td>
</tr>
</tbody>
</table>

This selection of probes permitted gas analysis from 140 Torr to the high pressure constraint of the apparatus, 75 psia. Gas analysis above atmospheric pressure was possible by venting the sample to the atmosphere, while simultaneously, withdrawing a small portion. Tests were conducted at various pressures above and below atmospheric pressure with pure gases and with air to ensure the technique would provide accurate readings. These tests showed the probes would give accurate reading of their calibrated range. During these tests the minimum sampling time was determined to be approximately three seconds when using probe number one. An additional constraint on the system requires that during the sampling process the pressure in the sample volume must remain within the calibrated range of the probe. The MGA draws approximately 1 ml/sec of sampling gas and has a response time of 100 milliseconds. Assuming the ideal gas law applies, solution of two simultaneous equations based on the conditions of minimized sample volume and minimum allowable sample pressure gave the following result,

Theoretical MGA sample volume = 12 ml
The apparatus was modified and the actual MGA sampling volume was calculated, instead of measured by a displacement technique, since the volume consisted almost entirely of 1/4" OD tubing. The calculated volume was,

Actual MGA sampling volume = 12.9484 ml

The strip chart recorder and MGA were calibrated as a system using nitrogen, oxygen, and air. Air allowed the calibration of the argon signal.

The operational procedure of this apparatus is similar to that of the pure component equilibrium apparatus and is presented in detail in Appendix B. The basic difference involves the removal of a small gas sample for gas concentration analysis. The frequent MGA gas sampling probe changes required to ensure an accurate signal from the MGA increased the complexity of this experiment. The final results were obtained by a mass balance (See Appendix C).

D. Dual Column PSA Apparatus

A bench-scale, dual column PSA air separation apparatus was constructed (See Fig. 4-11 and 4-12). The unit was comprised of two identical columns (CL1 and CL2), seven solenoid valves (V1-7), three mass flowmeters (F1-3), a purge orifice (O), four pressure transducers (P1-4), a plenum chamber (P), a manual needle valve (V8), an inlet
pressure gauge (PG), and a medical gas analyzer (MS) for monitoring the product concentration. The unit was operated at 24°C and then at -40°C to evaluate the effects of low temperature on system performance. The apparatus was entirely computer controlled and constructed of stainless steel tubing and valves. The unit was mounted horizontally to a wooden framework for convenient access.

The three flowmeters monitored the mass flow in the inlet, exhaust, and product flows. At 24°C the flowmeter was configured to monitor the exhaust flow from one column, and at -40°C the flowmeter was configured to monitor the flow from both columns. These units were calibrated with a Singer DTM-200 volumetric flowmeter used as a standard. All units gave linear and reproducible outputs.

The columns of molecular sieve were contained within 1" O.D. thin wall stainless steel tubing approximately 8.5" in length and 0.965" I.D. The sieve was secured by stainless steel screens on each end of the column supported by heavy metal springs, such that, movement of the molecular sieve bed during the pressure fluctuations of each cycle was highly unlikely.

The molecular sieve pellets were loaded into the columns by a method known as "snowpacking". This technique involves passing the pellets through a funnel in which screens of various sizes have been placed perpendicular to the flow. The method is simple and proved to give the greatest packing density. The columns were packed with the
following amounts of molecular sieve,

<table>
<thead>
<tr>
<th></th>
<th>24°C</th>
<th>-40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed A</td>
<td>82.07 gm</td>
<td>78.0 gm</td>
</tr>
<tr>
<td>Bed B</td>
<td>80.35 gm</td>
<td>84.7 gm</td>
</tr>
</tbody>
</table>

Data acquisition and valve control were accomplished through use of a PDP11/03 computer which precisely controlled the valve sequencing and collected ten channels of data. The data signals consisted of three flowmeter signals, four pressure transducer signals, and three gas concentration signals representing the composition of the product flow. Information required for control of each experimental run, such as cycle time, step times, etc., was stored in an input file which was read by the main control program prior to each run.

Several parameters of the system could be varied to investigate their effect on the oxygen concentration in the product flow. The configuration (6-step or 2-step) and cycle time were easily varied by changes to the computer program input file. The bed temperature was controlled by adjustment of the temperature setting on the environmental chamber. The PSA system was operated at two temperatures: 24°C and -40°C. The product flowrate was controlled by valve (V8) and monitored by flowmeter (F3). The purge flow was varied by installation of one of three different diameter orifices (0.010", 0.020", and 0.029").
inlet pressure was held constant at 25 psia throughout this work.

Since this experiment was computer controlled the operating procedure was quite simple and is described in Appendix B. Desired operating parameters were entered into an input data file (XBASE.DAT) which was read by the main control program (TT.FOR). This program is shown in Appendix C. Once the control program is initiated the PSA unit operates based entirely upon commands originated at the PDP11/03 computer which are further processed by electronics interface boxes. As the PSA unit is operating the data channels are displayed on the screen of a VT-54 terminal in engineering units. For this work data was collected once the oxygen concentration in the product reached a steady state value which was usually after about thirty minutes of operation, although this time lengthened somewhat when operating at -40°C. For actual data collection to commence the simply depresses the line feed key at the VT-54 terminal. The data for each run was stored on floppy diskettes initially and then transfered to the main facility computer for analysis.

Operation at -40°C posed some special problems due to traces of water in the feed air. These traces caused significant degradation of the sieve requiring them to be repacked. This problem was eliminated by switching to bottled air and placing a molecular sieve 13X trap before the inlet.
Breakthrough experiments were conducted by using one column of the PSA apparatus. The bed temperature for the breakthrough runs were 24°C and -40°C, and the bed pressures were -14.7 psia and 25 psia. The gases used were air and oxygen so as to simulate as closely as possible the actual conditions of the PSA process.
FIG 4-1. ELECTRON MICROGRAPH OF MOLECULAR SIEVE 5A (20X40) MESH PELLET (20X MAGNIFICATION).
FIG 4-2. ELECTRON MICROGRAPH OF MOLECULAR SIEVE 5A (20X40) MESH PELLET (50X MAGNIFICATION).
FIG 4-3. ELECTRON MICROGRAPH OF MOLECULAR SIEVE 5A (20X40) MESH PELLET (90X MAGNIFICATION).
FIG 4-4. ELECTRON MICROGRAPH OF MOLECULAR SIEVE 5A (20X40) MESH CRUSHED PELLET (800X MAGNIFICATION).
FIG 4-5. ELECTRON MICROGRAPH OF MOLECULAR SIEVE 5A (20X40) MESH CRUSHED PELLET (1000X MAGNIFICATION).
FIG 4-6. PURE COMPONENT EQUILIBRIUM APPARATUS. C1. SAMPLE CHAMBER, C2. CHARGE CHAMBER, E. PRESSURE TRANSDUCER ELECTRONICS BOX, G. BOTTLED GAS, H. HEATER, P1 AND P2. PRESSURE TRANSDUCERS, R1 AND R2. DIGITAL READOUTS, S. STRIP CHART RECORDER, T. ENVIRONMENTAL TEST CHAMBER, T1 AND T2. THERMOCOUPLES, V. VACUUM PUMP, V1-4. MANUAL VALVES, AND X. VARIAC.
FIG 4-8. MULTICOMPONENT EQUILIBRIUM APPARATUS. C1. SAMPLE CHAMBER, C2. CHARGE CHAMBER, E. PRESSURE TRANSDUCER ELECTRONICS BOX, G. BOTTLED GAS, H. HEATER, P1 AND P2. PRESSURE TRANSDUCERS, R1 AND R2. DIGITAL READOUTS, S. STRIP CHART RECORDER, T. ENVIRONMENTAL TEST CHAMBER, T1 AND T2 THERMOCOUPLES, V. VACUUM PUMP, V1-4. MANUAL VALVES, X. VARIAC, MGA. MEDICAL GAS ANALYZER, SC. MGA STRIP CHART RECORDER, PR. MGA GAS SAMPLING PROBE, SV. MGA SAMPLING VOLUME, AND V5-6. THREE-WAY VALVES.
FIG 4-10. PHOTOGRAPH OF THE MULTICOMPONENT EQUILIBRIUM APPARATUS WITH SAMPLE CHAMBER INSERTED INTO THE ENVIRONMENTAL TEST CHAMBER.
FIG 4-12. PHOTOGRAPH OF THE PSA AIR SEPARATION UNIT.
CHAPTER V

DATA AND RESULTS

A. Pure Component Isotherms

The pure component isotherms of nitrogen and oxygen on Union Carbide molecular sieve 5A (20X40 mesh) at temperatures of 24, -40, and -70°C and up to pressures of approximately 3300 Torr were obtained by a volumetric technique with the pure component equilibrium apparatus described in Chapter IV (See Fig. 5-1 through 5-6). Calculation of the amount adsorbed was determined by performing a mass balance. The data presented show excellent reproducibility. At the temperatures of this work nitrogen adsorption is greater than oxygen adsorption, although as the temperature is lowered oxygen adsorption increases dramatically (See Fig. 5-7 through 5-9). The nitrogen and oxygen isotherms have been grouped together in Fig. 5-10 and 5-11 to show their temperature dependence.

As a validation of the measurement technique and the apparatus employed, the data of this work has been presented with other reported data (67,68,69) (See Fig. 5-12 through 5-15). The data correlates well with the Union Carbide Corporation oxygen and nitrogen data at 0 and 30 °C (69). Peterson (68) used Union Carbide molecular sieve 5A which he analyzed to be 70% exchanged with Ca++. Correlation with Peterson's nitrogen data at 25°C is excellent.
The best fitting equations for the oxygen and nitrogen data were the Langmuir and Sips equations, respectively. The results are shown below,

\[ q = \frac{P_1 p}{P_2 + P_1 p}, \quad q = \frac{P_1 p}{P_3 + P_2 p} \]

where,

- \( q \) has units of ml STP/gm.
- \( p \) is Torr.

Table 11. Best fit parameters for the pure component data.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temp. (C)</th>
<th>Run</th>
<th>P1 X 10</th>
<th>P2 X 10</th>
<th>P3</th>
<th>Minimum Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>24</td>
<td>1</td>
<td>0.4730</td>
<td>0.4832</td>
<td>1.0</td>
<td>0.0695</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>0.4617</td>
<td>0.4747</td>
<td>&quot;</td>
<td>0.1200</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>All</td>
<td>0.4669</td>
<td>0.4629</td>
<td>&quot;</td>
<td>0.3050</td>
</tr>
<tr>
<td></td>
<td>&quot; -40</td>
<td>1</td>
<td>2.311</td>
<td>2.247</td>
<td>&quot;</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>&quot; -40</td>
<td>All</td>
<td>2.340</td>
<td>2.318</td>
<td>&quot;</td>
<td>2.01</td>
</tr>
<tr>
<td></td>
<td>&quot; -70</td>
<td>1</td>
<td>6.638</td>
<td>5.629</td>
<td>&quot;</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td>&quot; -70</td>
<td>2</td>
<td>6.273</td>
<td>5.345</td>
<td>&quot;</td>
<td>0.396</td>
</tr>
<tr>
<td></td>
<td>&quot; -70</td>
<td>All</td>
<td>6.501</td>
<td>5.513</td>
<td>&quot;</td>
<td>19.9</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>24</td>
<td>1</td>
<td>4.696</td>
<td>4.947</td>
<td>0.8264</td>
<td>0.765</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>2</td>
<td>5.020</td>
<td>5.612</td>
<td>0.8210</td>
<td>0.134</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>All</td>
<td>4.755</td>
<td>5.164</td>
<td>0.8263</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>&quot; -40</td>
<td>1</td>
<td>84.20</td>
<td>83.78</td>
<td>0.6573</td>
<td>2.23</td>
</tr>
<tr>
<td></td>
<td>&quot; -40</td>
<td>All</td>
<td>73.60</td>
<td>75.77</td>
<td>0.6775</td>
<td>0.133</td>
</tr>
<tr>
<td></td>
<td>&quot; -40</td>
<td>All</td>
<td>83.95</td>
<td>82.22</td>
<td>0.6455</td>
<td>3.17</td>
</tr>
<tr>
<td></td>
<td>&quot; -70</td>
<td>1</td>
<td>345.6</td>
<td>277.8</td>
<td>0.5509</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>&quot; -70</td>
<td>2</td>
<td>349.1</td>
<td>280.2</td>
<td>0.5496</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>&quot; -70</td>
<td>All</td>
<td>348.0</td>
<td>279.8</td>
<td>0.5500</td>
<td>1.75</td>
</tr>
</tbody>
</table>

Note: Points of desorption have been included in the analysis where "All" appears.

The actual fit of these equations to the data may be observed by viewing Fig. 5-16 through 5-21. In subsequent calculations these equations are employed to represent the data.
B. Heat of Adsorption

The heat of adsorption for pure nitrogen and oxygen on molecular sieve 5A was determined through use of the Clausius-Clapeyron equation,

\[ \frac{dP}{dT} \mid_c = \frac{\Delta H_a}{T(V_g - V_a)} \]

The ideal gas law is assumed to apply and the volume of the adsorbed layer is assumed to be negligible (compared to the gas volume). The final equation is,

\[ \Delta H_a = R \left[ \frac{d \ln p}{d(1/T)} \right]_c \]

The values for \[ \frac{d \ln p}{d(1/T)} \] were determined from the slopes of the isosteric loading lines when \( \ln p \) is plotted versus \( 1/T \) (See Fig. 5-22 and 5-23). The isosteric heat of adsorption for pure oxygen and nitrogen is plotted versus quantity adsorbed (See Fig. 5-24). The \( H_a \) for oxygen is nearly independent of the quantity adsorbed suggesting adsorption which occurs on an energetically homogeneous surface. The gradual rise in \( H_a \) as the loading increases has been observed for nonpolar molecules and was attributed to intermolecular interactions between the sorbate molecules (34). The initial heat of sorption for oxygen extrapolated to the \( y \)-axis is 3.37 kcal/mol which is in agreement with reported values of 3.30 kcal/mol (31, 41).
For nitrogen the high values of $H_a$ at low loading is explained by the strong quadrupole-cation interactions with the active sites. These interactions diminish as the active sites become filled. For oxygen at high loading, i.e. $> 55$ ml STP/gm, a gradual increase in $H_a$ is observed, probably due to intermolecular interactions. The general trends shown in Fig. 5-24, that is, decreasing $H_a$ for a molecule with a strong quadrupole moment and increasing $H_a$ for a nonpolar molecule are expected results (31). The difference between the value of $H_a$ and the heat of vaporization represents the energy of the combined interactions between the zeolite framework and the molecule, i.e. dispersion, repulsion, electrostatic-quadrupole interaction, etc.

C. Correlation and Prediction of Pure Component Isotherms

By application of the statistical thermodynamic model the pure component data were correlated and the data of Union Carbide (69) were predicted with a reasonable degree of accuracy. The pure component equation based on the statistical thermodynamic theory is,

$$
\sigma = \frac{2}{(m-1)!} \frac{K_p + \sum_{i=2}^{m} \frac{(K_p)(1-2B/V)^i}{i!} + \sum_{i=2}^{m} \frac{(K_p)(1-mB/V)^i}{i!}}{1 + \sum_{i=2}^{m} \frac{(K_p)(1-2B/V)^i}{i!} + \sum_{i=2}^{m} \frac{(K_p)(1-mB/V)^i}{i!}}$

where $m \leq V/B$ (m is an integer).
The exponential factor shown in the equation in Chapter III has been omitted because its effect has been shown to be small (46). The two parameters which must be determined before this equation can be applied are $K$, Henry's Law constant, and $B$ the effective molecular volume.

The values of $K$ are found by analysis of the slope of the pure component isotherm in the region in which Henry's Law applies, i.e. the slope of the isotherm at low concentration. For oxygen, derivatives of the Langmuir equation were taken and $p$ was set equal to zero to find $K$. For nitrogen the value of $K$ was assumed to be the slope of the line from the origin to the first data point. This may have introduced some error in the analysis since the nitrogen isotherm rises steeply in the low pressure region. The values of $K$ obtained by this method are shown in Figure 5-25 with other reported values in the literature (46). The $K$ values obtained from data of this work agree with other literature values.

In the prediction of pure component isotherms of nitrogen and oxygen $K$ values will be needed over a wide range of temperatures. Therefore, the $K$ values previously obtained were fitted to the linearized form of the vant Hoff equation,

$$K = K_0 \exp \left( \frac{q_0}{RT} \right)$$

by a linear least squares technique. The resulting values for $K$ and $q$ are presented below (See Table 12).
Table 12. Values of \(K_0\) and \(q_0\) giving the temperature dependence of \(K\).

<table>
<thead>
<tr>
<th>System</th>
<th>(K_0) (molecules/cavity Torr)</th>
<th>(q_0) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2-5A</td>
<td>(9.0209 \times 10^{-7})</td>
<td>4.52</td>
</tr>
<tr>
<td>O2-5A</td>
<td>(1.4050 \times 10^{-6})</td>
<td>3.37</td>
</tr>
</tbody>
</table>

The only other parameter required is \(B\). This value is found by a method suggested by Ruthven (46) in which the isotherms are superimposed on a family of theoretical isotherm curves (See Fig. 5-26). The isotherm data must be plotted on the same coordinate system as the theoretical curves. The values for \(B\) and \(K\) are tabulated (See Table 13).

Table 13. Henry's Law constants and effective molecular volumes calculated from the pure component isotherms.

<table>
<thead>
<tr>
<th>System</th>
<th>(T(K))</th>
<th>(K) (molecules/cavity Torr)</th>
<th>(V/B)</th>
<th>(B) (cu.Angstroms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2-5A</td>
<td>203.15</td>
<td>0.06585</td>
<td>11</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>233.15</td>
<td>0.01557</td>
<td>10</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>297.15</td>
<td>0.001902</td>
<td>8</td>
<td>97</td>
</tr>
<tr>
<td>O2-5A</td>
<td>203.15</td>
<td>0.005952</td>
<td>20</td>
<td>38.8</td>
</tr>
<tr>
<td></td>
<td>233.15</td>
<td>0.002031</td>
<td>20</td>
<td>38.8</td>
</tr>
<tr>
<td></td>
<td>297.15</td>
<td>0.0004234</td>
<td>20</td>
<td>38.8</td>
</tr>
</tbody>
</table>
With these parameters identified the pure component isotherm data were correlated with reasonable results (See Fig. 5-27 through 5-32). To be able to predict isotherms of nitrogen and oxygen at other temperatures B was curve fit to a quadratic equation as a function of 1/T (See Fig. 5-33):

\[ R = \left(\frac{1}{T}\right)^{10} \]  
\[ B = 5.465 R - 64.56 H + 252.4 \]

With B and K defined for any temperature within the range of the original data we may predict other pure component isotherms.

The isotherms of Union Carbide (69) were predicted by the method above (See Fig. 5-34 through 5-38). The prediction for the oxygen isotherms at 273.15K and 238.15K are in excellent agreement, even the extrapolated prediction at 303.15K is in good agreement. In the case of nitrogen the prediction gives good agreement at low pressures but at higher pressures the predicted curve deviates slightly from the actual data.

D. Prediction of the Multicomponent Data

The multicomponent equilibrium apparatus described in Chapter IV was employed in the collection of adsorption data for air on molecular sieve 5A at 24, -40, and -70°C (See Fig. 5-39 through 5-41). The data at all temperatures show excellent reproducibility. The isotherm for
oxygen in the mixture appears to tend toward a saturation value at the lower temperatures. The argon loading is negligible at all temperatures when compared to the loading of the other components. The nitrogen mixture isotherm at the lower temperatures does not exhibit the marked curvature of the pure component isotherm at these temperatures.

In Figure 5-42 through 5-47 each component of the multicomponent mixture is plotted as quantity adsorbed versus its partial pressure in the mixture. The data plotted in this fashion display excellent reproducibility. This is evidenced by the argon data at very low partial pressures (See Fig. 5-47). Figures 5-48 through 5-50 show the partial pressures of nitrogen and oxygen in the multicomponent mixture plotted with the pure component isotherms. From these plots the departure from ideality of the mixture is evident at the lower temperatures. At 24°C both oxygen and nitrogen appear not to interact significantly since the mixture isotherms and the pure component isotherms are in most cases identical. For oxygen at higher pressure some interaction is occurring (See Fig. 5-48). We may conclude that at 24°C the lower concentration of molecules within the cavities of the zeolite permit each species to act independently. At the lower temperatures it is clear that significant intermolecular interactions are occurring.
The separation factors for this data are presented in Figure 5-51. At lower temperatures the separation factor exhibits a definite temperature dependence, i.e., the separation factor is higher for the lower temperatures. We may conclude that the separation factor is inversely proportional to temperature at low pressures (<1 atm.) and at higher pressures (>1 atm.) the separation factor is nearly independent of temperature. The results shown on the plot agree with the published separation factor from the work of Domine and Hay (67).

In Figures 5-52 through 5-54 the multicomponent data were predicted by use of the binary statistical thermodynamic model where K and B are derived from the pure component data. At 24 °C the prediction gives excellent results, but at the lower temperatures deviation from the prediction is obvious. It should be noted that the model gives a reasonable prediction in the low pressure regime, i.e., where ideal behavior would be expected. Argon has been neglected in this prediction to minimize the complexity of the model. The assumption of a binary mixture should produce valid results since argon sorption is negligible.

In Figures 5-55 and 5-56 the value of B, the effective molecular volume, for oxygen and nitrogen was adjusted slightly and improved results were obtained. In Figure 5-57 the apparent effective molecular volumes for nitrogen and oxygen as a pure component and as a components in a binary mixture are plotted versus 1/T. This plot indicates that the apparent effective molecular volume of the nitrogen molecules is greater in a mixture with oxygen than for the pure component at the same
temperature. The trend of decreasing molecular volume with temperature for the nitrogen molecule still exists. The oxygen molecules in the binary mixture are apparently packed more tightly than might otherwise be expected due to the reduction in the apparent effective molecular volume at the lower temperatures.

For prediction of binary data at other temperatures but the same total molar ratio, it may be of value to use curve fitted values for $B$:

$$R = (1/T) \left( 10^{-1} \right) \text{K}^{-1}$$

$$BN_2 = 1.454 R - 26.835 R + 170.8$$

$$BO_2 = 4.463 R - 45.858 R + 142.5$$

where,

- $BN_2$ = effective molecular volume for nitrogen in a binary mixture with the composition of air.
- $BO_2$ = effective molecular volume for oxygen in a binary mixture with the composition of air.

An attempt to predict the multicomponent data based on IAST theory lead to results similar to those obtained from the statistical thermodynamic model. The spreading pressure was calculated through use of the pure component isotherm fitting equations. The results of the predictions were obtained by an analytical method and are shown on Fig. 5-58 through 5-60. The prediction at $240^\circ$ is in excellent agreement with the observed data but at the lower temperatures the difference between
the prediction and the data are of approximately the same magnitude as those encountered when using the statistical thermodynamic model. The nonideality of the mixture at low temperature is quite evident. A prediction of the N2-O2 adsorption at 24 °C based on a statistical thermodynamic model is shown in Fig 5-112.

E. Breakthrough Experiments

Typical breakthrough data runs are shown on Fig. 5-61 through 5-68 for a flowrate of 25 SLPM. The runs were made using two column pressures: 25 psia and atmospheric pressure. The gases used were air and oxygen so that the actual conditions of the PSA process could be approximated. Figure 5-69 shows a typical velocity/distance lag time plot which accounts for the time the gases are flowing through the associated piping. This lag time correction must be applied to the raw data to arrive at the true breakthrough time. This measurement is approached in the same manner as the column breakthrough experiments except the column of molecular sieve is absent. The spikes in the medical gas analyzer signal at about the one second mark in Figure 5-69 are due to this unit's pressure sensitivity upon switching of the gas flows. The final breakthrough results are shown below (See Fig. 5-70 through 5-73):
Table 14. Breakthrough (B.T.) experiment results at 24°C.

<table>
<thead>
<tr>
<th>Flowrate (SLPM)</th>
<th>N2 B.T. (sec)</th>
<th>O2 B.T. (sec)</th>
<th>1% N2 (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High Pressure (25 psia)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>49.81</td>
<td>30.81</td>
<td>144.91</td>
</tr>
<tr>
<td>2.5</td>
<td>31.97</td>
<td>17.77</td>
<td>87.27</td>
</tr>
<tr>
<td>6.2</td>
<td>13.32</td>
<td>7.62</td>
<td>42.12</td>
</tr>
<tr>
<td>13.0</td>
<td>4.97</td>
<td>2.2</td>
<td>14.23</td>
</tr>
<tr>
<td>25.0</td>
<td>2.55</td>
<td>0.68</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>Low Pressure (14.4 psia)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>45.0</td>
<td>15.2</td>
<td>77.7</td>
</tr>
<tr>
<td>6.2</td>
<td>13.02</td>
<td>4.06</td>
<td>23.4</td>
</tr>
<tr>
<td>13.0</td>
<td>4.79</td>
<td>1.59</td>
<td>9.8</td>
</tr>
<tr>
<td>25.0</td>
<td>2.59</td>
<td>0.86</td>
<td>5.87</td>
</tr>
</tbody>
</table>

Table 15. Breakthrough (B.T.) experiment results at -40°C.

<table>
<thead>
<tr>
<th>Flowrate (SLPM)</th>
<th>N2 B.T. (sec)</th>
<th>O2 B.T. (sec)</th>
<th>1% N2 (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High Pressure (25 psia)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>137.3</td>
<td>60.55</td>
<td></td>
</tr>
<tr>
<td>6.2</td>
<td>38.89</td>
<td>14.66</td>
<td>244.96</td>
</tr>
<tr>
<td>13.0</td>
<td>12.81</td>
<td>4.49</td>
<td>95.26</td>
</tr>
<tr>
<td>25.0</td>
<td>6.71</td>
<td>2.07</td>
<td>50.02</td>
</tr>
<tr>
<td></td>
<td>Low Pressure (14.4 psia)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>127.9</td>
<td>39.0</td>
<td>586.5</td>
</tr>
<tr>
<td>6.2</td>
<td>37.7</td>
<td>13.8</td>
<td>167.0</td>
</tr>
<tr>
<td>13.0</td>
<td>11.8</td>
<td>4.3</td>
<td>87.7</td>
</tr>
<tr>
<td>25.0</td>
<td>6.05</td>
<td>1.0</td>
<td>42.4</td>
</tr>
</tbody>
</table>

Our rationale will be to analyze the data based on one of the flowrates and examine the data for any differences due to the pressure or temperature of the experiment. We will assume a hypothetical case of
high pressure feed flow at 25 SLPM and a low pressure purge flow of 25 SLPM and analyze the effect of reduced temperature, i.e. 24°C to -40°C.

Reading from the above tables for 25 SLPM breakthrough runs at 24°C the time for high pressure nitrogen breakthrough, oxygen breakthrough, and 1% nitrogen concentration in the effluent are 2.55, 0.68, and 6.8 seconds, respectively. In comparison at 25 SLPM and -40°C these times at high pressure nitrogen breakthrough, oxygen breakthrough, and 1% nitrogen concentration in the effluent are 6.71, 1.0, and 42.4 seconds, respectively. It appears the lowered temperature has caused the nitrogen breakthrough period to lengthen by a factor of 2.6 and the period to reach 1% nitrogen in the effluent by a factor of 6.2.

The nitrogen breakthrough experiment relates to the high pressure feed step in the actual PSA process, and the oxygen breakthrough and attainment of 1% nitrogen in the effluent relates to the purge step in the actual PSA process. Inspection of the curves in Figures 5-74 and 5-75 shows that the lower temperature has increased the overall time for nitrogen breakthrough to occur but the length of the mass transfer front remains about the same at both temperatures. On the other hand, the mass transfer front at -40°C in the oxygen breakthrough experiment has lengthened considerably. This dramatic effect may possibly explain the reason for the observed reduction in system performance at -40°C. The increased length of the front may be due to a significant decrease in intracrystalline diffusion rate for nitrogen.
F. Dual Column PSA Experiments (2-Step and 6-Step Cycle)

Figures 5-76 through 5-87 show some typical data sets from the miniature PSA system configured for 2-step operation. A system optimized at $24^\circ C$ was operated at $-40^\circ C$ to determine the effects of temperature. The data are presented in an alternating fashion, in that, the effect of reducing the operating temperature may be seen conveniently on each following page. Observing Figures 5-76 and 5-77, it can be seen that the inlet flowrate for the system at $-40^\circ C$ is slightly greater due to the volume change at low temperature as we attempt to maintain the inlet pressure constant. The exhaust flowmeter (F2) was configured in the run at $24^\circ C$ to monitor one of the column exhaust flows and at $-40^\circ C$ the flowmeter was setup to monitor exhaust flows from both columns. Since the flowmeter was outside its temperature range of operation at $-40^\circ C$ its absolute readings are questionable. The actual exhaust flow was determined by a mass balance over one cycle based on the readings of the inlet flowmeter (F1) and the product flowmeter (F3). From Figures 5-80, 5-81, 5-84, and 5-85 it is observed that the product oxygen concentration is stable even though the product flowrate is fluctuating.

With optimum system parameters for operation at $24^\circ C$ the ambient temperature was varied and the reduced performance reported by Miller et al. was observed (See Fig. 5-88). The significant decline in oxygen product concentration begins at approximately $-10^\circ C$ as the ambient
temperature is decreased. A limited number of runs were conducted at temperatures above ambient temperature up to 50°C with only a slight reduction in system performance observed.

Variation of purge flow, cycle time, and temperature was accomplished to determine their effect on the system performance (See Fig. 5-89 through 5-91). The purge flow with the 0.020" orifice installed gave the best performance overall. The 2-step system configuration giving the highest purity of oxygen (94.2%) at 24°C had a 0.020" diameter purge orifice and operated on a six second cycle time. An improvement in performance at -40°C by lengthening the cycle time is worth noting, although attainment of 95% oxygen concentration was not observed (See Figure 5-90). This improvement was predicted by the breakthrough curves. The effect of product flowrate and temperature on the above 2-step system configuration giving highest purity is shown in Figures 5-92 through 5-95. The reduction in oxygen concentration with increased product flow occurs in all runs (See Figures 5-92 through 5-95).

A typical data set for a 6-step experiment is shown on Figures 5-96 through 5-107. With this system configuration all flows are much more stable. In Figures 5-96 and 5-97 the 6-step system appears dependent on the purge flowrate but not as dependent on cycle time. The effect of cycle time and temperature on the 6-step/cycle system is shown in Figure 5-108. Oxygen recovery at 24°C is higher for the six-step system when compared to the 2-step but at -40°C they appear to be about
the same (See Fig. 5-109 through 5-111). The data may not be conclusive because breakthrough data were unavailable for guidance on getting the step times.
FIG 5-1. OXYGEN ON MOLECULAR SIEVE 5A AT 24°C
FIG 5-2. OXYGEN ON MOLECULAR SIEVE 5A AT -40°C
FIG 5-3. OXYGEN ON MOLECULAR SIEVE 5A AT -70°C
FIG 5-4. NITROGEN ON MOLECULAR SIEVE 5A AT 24°C
FIG 5-5. NITROGEN ON MOLECULAR SIEVE 5A AT -40°C
FIG 5-6. NITROGEN ON MOLECULAR SIEVE 5A AT -70°C
FIG 5-7. PURE NITROGEN AND OXYGEN ON MOLECULAR SIEVE 5A AT 24°C.
FIG 5-8. PURE NITROGEN AND OXYGEN ON MOLECULAR SIEVE 5A AT -40°C.
FIG 5-9. PURE NITROGEN AND OXYGEN ON MOLECULAR SIEVE 5A AT -70°C.
FIG 5-10. OXYGEN ISOTHERMS ON MOLECULAR SIEVE 5A.
FIG 5-11. NITROGEN ISOTHERMS ON MOLECULAR SIEVE 5A.
FIG 5-12. OXYGEN ISOTHERM ON MOLECULAR SIEVE 5A AT 24°C SHOWN WITH THE DATA OF UNION CARBIDE AT LOW PRESSURE.
FIG 5-13. OXYGEN ISOTHERM ON MOLECULAR SIEVE 5A AT 24°C SHOWN WITH THE DATA OF UNION CARBIDE.
FIG 5-14. NITROGEN ISOTHERM ON MOLECULAR SIEVE 5A AT 24°C SHOWN WITH THE DATA PETERSON AT 25°C.
FIG 5-15. NITROGEN ISOTHERM ON MOLECULAR SIEVE 5A AT 24°C SHOWN WITH DATA OF UNION CARBIDE.
FIG 5-16. FITTING A LANGMUIR EQUATION TO THE OXYGEN-5A DATA AT 24°C.
FIG 5-17. FITTING A LANGMUIR EQUATION TO THE OXYGEN-5A DATA AT -40°C.
FIG 5-18. FITTING A LANGMUIR EQUATION TO THE OXYGEN-5A DATA AT -70°C.
FIG 5-19. FITTING A SIPS EQUATION TO THE NITROGEN-5A DATA AT 24°C.
FIG 5-20. FITTING A SIPS EQUATION TO THE NITROGEN-5A DATA AT -40°C.
FIG 5-21. FITTING A SIPS EQUATION TO THE NITROGEN-5A DATA AT -70°C.
FIG 5-22. ISOSTERES FOR OXYGEN ON MOLECULAR SIEVE 5A.
FIG 5-23. ISOSTHERES FOR NITROGEN ON MOLECULAR SIEVE 5A.
FIG 5-24. ISOSTERIC HEAT OF ADSORPTION FOR NITROGEN AND OXYGEN ON MOLECULAR SIEVE 5A.
FIG 5-25. VANT HOFF PLOT SHOWING TEMPERATURE DEPENDENCE OF $K$. 

$K$ (MOLECULES/CAVITY TORR) 

$1 \times 10^{-1}$ $10^{-2}$ $10^{-3}$ $10^{-4}$ $3.0$ $4.0$ $5.0$ $6.0$ $7.0$ 

$1/T (1000)$ $(1/ K)$ 

1 = OXYGEN-5A (THIS WORK) 

2 = OTHERS 

3 = NITROGEN-5A (THIS WORK) 

4 = OTHERS
FIG 5-28. THEORETICAL EQUILIBRIUM CURVES CALCULATED USING THE STATISTICAL THERMODYNAMIC MODEL.
FIG 5-27. CORRELATION OF OXYGEN SORPTION ON MOLECULAR SIEVE 5A AT 24°C USING A STATISTICAL THERMODYNAMIC MODEL WHERE: $K = 0.0004234$, $B = 38.8$, AND $m = 20$. 
FIG 5-28. CORRELATION OF OXYGEN SORPTION ON MOLECULAR SIEVE 5A AT -40°C USING A STATISTICAL THERMODYNAMIC MODEL WHERE: $K = 0.002031$, $\beta = 38.8$, AND $m = 20$. 
FIG 5-29. CORRELATION OF OXYGEN SORPTION ON MOLECULAR SIEVE 5A AT -70°C USING A STATISTICAL THERMODYNAMIC MODEL WHERE: $K = 0.005952$, $B = 38.8$, $m = 20$. 
FIG 5-30. CORRELATION OF NITROGEN SORPTION ON MOLECULAR SIEVE 5A AT 24°C USING A STATISTICAL THERMODYNAMIC MODEL WHERE: K=0.001802, B=97, AND m=8.
FIG 5-31. CORRELATION OF NITROGEN SORPTION ON MOLECULAR SIEVE 5A AT -40°C USING A STATISTICAL THERMODYNAMIC MODEL WHERE: K=0.01557, B=76, AND m=10.
FIG 5-32. CORRELATION OF NITROGEN SORPTION ON MOLECULAR SIEVE 5A AT -70°C USING A STATISTICAL THERMODYNAMIC MODEL WHERE: K=0.06585, B=87, AND m=11.
FIG 5-33. TEMPERATURE DEPENDENCE OF THE APPARENT EFFECTIVE MOLECULAR VOLUME FOR PURE NITROGEN AND OXYGEN ON MOLECULAR SIEVE 5A.
FIG 5-34. PREDICTION OF UNION CARBIDE DATA FOR OXYGEN-5A SORPTION AT 0°C USING A STATISTICAL THERMODYNAMIC MODEL WHERE: \(K=0.0006968, B=38.8, m=20\).
FIG 5-35. PREDICTION OF UNION CARBIDE DATA FOR OXYGEN-5A SORPTION AT -35°C USING A STATISTICAL THERMODYNAMIC MODEL WHERE: K=0.001735, B=38.8, n=20.
FIG 5-36. PREDICTION OF UNION CARBIDE DATA FOR OXYGEN-5A SORPTION AT 30°C USING A STATISTICAL THERMODYNAMIC MODEL WHERE: K=0.0003771, B=38.8, m=20.
FIG 5-37. PREDICTION OF UNION CARBIDE DATA FOR NITROGEN-5A SORPTION AT 0°C USING A STATISTICAL THERMODYNAMIC MODEL WHERE: $K=0.003711$, $B=89.3$, $m=8$. 
FIG 5-38. PREDICTION OF UNION CARBIDE DATA FOR NITROGEN-5A SORPTION AT -35°C USING A STATISTICAL THERMODYNAMIC MODEL WHERE: $K=0.01281$, $B=77.8$, $m=10$. 
FIG 5-39. AIR-5A AT 24°C WHERE THE TOTAL MOLAR RATIO OF NITROGEN, OXYGEN, AND ARGON WITHIN THE SYSTEM IS CONSTANT AT 78.14 : 20.92 : 0.94, RESPECTIVELY.
FIG 5-40. AIR-5A AT -40°C WHERE THE TOTAL MOLAR RATIO OF NITROGEN, OXYGEN, AND ARGON WITHIN THE SYSTEM IS CONSTANT AT 78.14 : 20.92 : 0.94, RESPECTIVELY.
FIG 5-41. AIR-5A AT -70°C WHERE THE TOTAL MOLAR RATIO OF NITROGEN, OXYGEN, AND ARGON WITHIN THE SYSTEM IS CONSTANT AT 78.14 : 20.92 : 0.94, RESPECTIVELY.
FIG 5-42. MULTICOMPONENT DATA FOR THE SYSTEM AIR-5A AT 24°C.
FIG 5-43. MULTICOMPONENT DATA FOR THE SYSTEM AIR-5A AT -40°C.
FIG 5-44. MULTICOMPONENT DATA FOR THE SYSTEM AIR-5A AT -70°C.
FIG 5-45. NITROGEN LOADING AT 24, -40, AND -70°C FOR THE AIR-5A SYSTEM.
FIG 5-46. OXYGEN LOADING AT 24, -40, AND -70°C FOR THE AIR-5A SYSTEM.
FIG 5-47. ARGON LOADING AT 24, -40, AND -70°C FOR THE AIR-5A SYSTEM.
FIG 5-48. PURE AND MULTICOMPONENT DATA OF NITROGEN AND OXYGEN ON MOLECULAR SIEVE 5A AT 24°C.
Fig 5-49. Pure and multicomponent data of nitrogen and oxygen on molecular sieve 5A at -40°C.
FIG 5-50. PURE AND MULTICOMPONENT DATA OF NITROGEN AND OXYGEN ON MOLECULAR SIEVE 5A AT -70°C.
FIG 5-51. SEPARATION FACTORS FOR THE BINARY MIXTURE OF NITROGEN AND OXYGEN ON MOLECULAR SIEVE 5A.
FIG 5-52. PREDICTION OF NITROGEN-OXYGEN ADSORPTION ON MOLECULAR SIEVE 5A AT 24°C USING A STATISTICAL THERMODYNAMIC MODEL WITH PURE COMPONENT PARAMETERS.
FIG 5-53. PREDICTION OF NITROGEN-OXYGEN ADSORPTION ON MOLECULAR SIEVE 5A AT -40°C USING A STATISTICAL THERMODYNAMIC MODEL WITH PURE COMPONENT PARAMETERS.
FIG 5-54. PREDICTION OF NITROGEN-OXYGEN ADSORPTION ON MOLECULAR SIEVE 5A AT ~70°C USING A STATISTICAL THERMODYNAMIC MODEL WITH PURE COMPONENT PARAMETERS.
FIG 5-55. PREDICTION OF N2-O2 SORPTION AT -40°C USING A STATISTICAL THERMODYNAMIC MODEL WITH ADJUSTED EFFECTIVE MOLECULAR VOLUMES (BO2 = 28, BN2 = 82.5).
FIG 5-56. PREDICTION OF N₂-O₂ SORPTION AT -70 °C USING A STATISTICAL THERMODYNAMIC MODEL WITH ADJUSTED EFFECTIVE MOLECULAR VOLUMES (B₀₂ = 25, BN₂ = 74).
FIG 5-57. APPARENT EFFECTIVE MOLECULAR VOLUME FOR N2 AND O2 AS PURE COMPONENTS AND IN A N2-O2-AR MIXTURE WITH TOTAL MOLAR RATIO OF 78.14 : 20.92 : 0.94.
FIG 5-58. PREDICTION OF N2-O2 SORPTION ON MOLECULAR SIEVE 5A AT 24°C USING THE IDEAL ADSORBED SOLUTION THEORY.
FIG 5-59. PREDICTION OF N₂-O₂ SORPTION ON MOLECULAR SIEVE 5Å AT -40°C USING THE IDEAL ADSORBED SOLUTION THEORY.
FIG 5-60. PREDICTION OF N2-02 SORPTION ON MOLECULAR SIEVE 5A AT -70°C USING THE IDEAL ADSORBED SOLUTION THEORY.
FIG 5-61. RUN 102021: COLUMN NITROGEN BREAKTHROUGH AT 24°C, 25 SLPM, AND BED PRESSURE OF 25 PSIA.
FIG 5-82. RUN 102712: COLUMN NITROGEN BREAKTHROUGH AT 24°C, 25 SLPM, AND BED PRESSURE OF APPROXIMATELY 18.5 PSIA.
FIG 5-63. RUN 102023: COLUMN OXYGEN BREAKTHROUGH AT 24°C, 25 SLPM, AND BED PRESSURE OF 25 PSIA.
FIG 5-64. RUN 102714 : COLUMN OXYGEN BREAKTHROUGH AT 24°C, 25 SLPM, AND BED PRESSURE OF APPROXIMATELY 18.5 PSIA.
FIG 5-65. RUN 110407: COLUMN NITROGEN BREAKTHROUGH AT -40°C, 25 SLPM, AND BED PRESSURE OF 25 PSIA.
FIG 5-66. RUN 110413: COLUMN NITROGEN BREAKTHROUGH AT -40°C, 25 SLPM, AND BED PRESSURE OF APPROXIMATELY 18.5 PSIA.
FIG 5-67. RUN 110408: COLUMN OXYGEN BREAKTHROUGH AT -40°C, 25 SLPM, AND BED PRESSURE OF 25 PSIA.
FIG 5-68. RUN 110412: COLUMN OXYGEN BREAKTHROUGH AT -40°C, 25 SLPM, AND BED PRESSURE OF APPROXIMATELY 18.5 PSIA.
FIG 5-69. RUN 102709: MEASUREMENT OF DISTANCE/VELOCITY LAG TIME AT 25 SLPM.
FIG 5-70. DEPENDENCE OF NITROGEN BREAKTHROUGH ON FLOW RATE AT 24\textdegree\text{C} AND BED PRESSURE OF 25 PSIA.
FIG 5-71. DEPENDENCE OF OXYGEN BREAKTHROUGH ON FLOWRATE AT 24°C AND BED PRESSURE OF 25 PSIA.
FIG 5-72. DEPENDENCE OF NITROGEN BREAKTHROUGH ON FLOWRATE AT -40°C AND BED PRESSURE OF 25 PSIA.
FIG 5-73. DEPENDENCE OF OXYGEN BREAKTHROUGH ON FLOWRATE AT -40°C AND BED PRESSURE OF 25 PSIA.
FIG 5-74. EFFECT OF TEMPERATURE ON NITROGEN AND OXYGEN BREAKTHROUGH FOR A FLOWRATE OF 25 SLPM AND BED PRESSURE OF 25 PSIA.
FIG 5-75. EFFECT OF TEMPERATURE ON NITROGEN AND OXYGEN BREAKTHROUGH FOR A FLOW RATE OF 13 SLPM AND BED PRESSURE OF 25 PSIA.
FIG 5-76. AIR FLOW INTO THE PSA UNIT OPERATING AT 24°C AND CONFIGURED FOR A 2 STEP CYCLE, 6 SEC. CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-77. AIR FLOW INTO THE PSA UNIT OPERATING AT -40°C AND CONFIGURED FOR A 2 STEP CYCLE, 6 SEC. CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-78. EXHAUST FLOW FROM THE PSA UNIT OPERATING AT 24°C AND CONFIGURED FOR A 2 STEP CYCLE, 6 SEC. CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-79. EXHAUST FLOW FROM THE PSA UNIT OPERATING AT -40°C AND CONFIGURED FOR A 2 STEP CYCLE, 6 SEC. CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-80. PRODUCT FLOW FROM THE PSA UNIT OPERATING AT 24°C AND CONFIGURED FOR A 2 STEP CYCLE, 6 SEC CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-81. PRODUCT FLOW FROM THE PSA UNIT OPERATING AT -40°C AND CONFIGURED FOR A 2 STEP CYCLE, 6 SEC CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-82. PRODUCT N2 FROM THE PSA UNIT OPERATING AT 24°C AND CONFIGURED FOR A 2 STEP CYCLE, 6 SEC. CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-83. PRODUCT N2 FROM THE PSA UNIT OPERATING AT -40°C AND CONFIGURED FOR A 2 STEP CYCLE, 6 SEC. CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-84. PRODUCT O2 FROM THE PSA UNIT OPERATING AT 24°C AND CONFIGURED FOR A 2 STEP CYCLE, 6 SEC. CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-85. PRODUCT O2 FROM THE PSA UNIT OPERATING AT -40°C AND CONFIGURED FOR A 2 STEP CYCLE, 6 SEC. CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-86. PRODUCT AR FROM THE PSA UNIT OPERATING AT 24°C AND CONFIGURED FOR A 2 STEP CYCLE, 6 SEC. CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-87. PRODUCT AR FROM THE PSA UNIT OPERATING AT -40°C AND CONFIGURED FOR A 2 STEP CYCLE, 6 SEC. CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-88 EFFECT OF BED TEMPERATURE ON A PSA UNIT CONFIGURED FOR A 2 STEP CYCLE, 6 SEC. CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOWRATE.
FIG 5-89. EFFECT OF CYCLE TIME AND TEMPERATURE ON THE PSA UNIT CONFIGURED FOR 2 STEPS/CYCLE, 0.010" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-90. EFFECT OF CYCLE TIME AND TEMPERATURE ON THE PSA UNIT CONFIGURED FOR 2 STEPS/CYCLE, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-81. EFFECT OF CYCLE TIME AND TEMPERATURE ON THE PSA UNIT CONFIGURED FOR 2 STEPS/CYCLE, 0.029" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-92. EFFECT OF PRODUCT FLOWRATE AND TEMPERATURE ON THE PSA UNIT CONFIGURED FOR 2 STEPS/CYCLE, 8 SEC. CYCLE TIME, AND 0.020" PURGE ORIFICE.
FIG 5-93. EFFECT OF PRODUCT FLOW RATE AND TEMPERATURE ON THE PSA UNIT CONFIGURED FOR 2 STEPS/CYCLE, 18 SEC. CYCLE TIME, AND 0.020" ORIFICE.
FIG 5-94. EFFECT OF PRODUCT FLOWRATE AND CYCLE TIME ON THE PSA UNIT OPERATING AT 24°C AND CONFIGURED FOR 2 STEPS/CYCLE AND 0.020" PURGE ORIFICE.
FIG 5-85. EFFECT OF PRODUCT FLOWRATE AND CYCLE TIME ON THE PSA UNIT OPERATING AT -40°C AND CONFIGURED FOR 2 STEPS/CYCLE AND 0.020" PURGE ORIFICE.
FIG 5-96. INLET FLOW FOR PSA UNIT CONFIGURATION: 24°C, 6 STEP CYCLE (1SEC, 3SEC, 1SEC), 10 SEC CYCLE TIME, 0.020" PURGE ORIFICE AND 100 SCCM PRODUCT FLOW.
FIG 5-97. INLET FLOW FOR PSA UNIT CONFIGURATION: -40°C, 6 STEP CYCLE (1SEC, 3SEC, 1SEC), 10 SEC CYCLE TIME, 0.020" PURGE ORIFICE AND 100 SCCM PRODUCT FLOW.
FIG 5-88. EXHAUST FLOW FOR PSA UNIT CONFIGURATION: 24°C, 6 STEP CYCLE (1SEC, 3SEC, 1SEC), 10SEC CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-99. EXHAUST FLOW FOR PSA UNIT CONFIGURATION:
-40°C, 6 STEP CYCLE (1SEC, 3SEC, 1SEC), 10 SEC CYCLE TIME,
0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-100. PRODUCT FLOW FOR PSA UNIT CONFIGURATION: 24°C, 6 STEP CYCLE (1SEC, 3SEC, 1SEC), 10 SEC CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-101. PRODUCT FLOW FOR PSA UNIT CONFIGURATION: -40°C, 6 STEP CYCLE (1SEC, 3SEC, 1SEC), 10 SEC CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-102. PRODUCT N2% FOR PSA UNIT CONFIGURATION: 24°C, 6 STEP CYCLE (1SEC, 3SEC, 1SEC), 10 SEC CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-103. PRODUCT \( N_2 \)% FOR PSA UNIT CONFIGURATION:
-40°C, 8 STEP CYCLE (1SEC, 3SEC, 1SEC), 10 SEC CYCLE TIME,
0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-104. PRODUCT O2% FOR PSA UNIT CONFIGURATION: 24°C, 8 STEP CYCLE (1SEC, 3SEC, 1SEC), 10 SEC CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-105. PRODUCT O2% FOR PSA UNIT CONFIGURATION: -40°C, 6 STEP CYCLE (1SEC, 3SEC, 1SEC), 10 SEC CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-106. PRODUCT AR% FOR PSA UNIT CONFIGURATION: 24°C, 6 STEP CYCLE (1SEC, 3SEC, 1SEC), 10 SEC CYCLE TIME, 0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-107. PRODUCT AR% FOR PSA UNIT CONFIGURATION: 
-40°C, 8 STEP CYCLE (1SEC, 3SEC, 1SEC), 10 SEC CYCLE TIME, 
0.020" PURGE ORIFICE, AND 100 SCCM PRODUCT FLOW.
FIG 5-108. EFFECT OF CYCLE TIME AND TEMPERATURE ON THE PSA UNIT CONFIGURED FOR 8 STEP OPERATION AND 100 SCCM PRODUCT FLOW.
FIG 5-109. EFFECT OF PRODUCT FLOWRATE AND TEMPERATURE ON OXYGEN RECOVERY FOR A 2 STEP SYSTEM WITH A CYCLE TIME OF 8 SEC AND A 0.020" PURGE ORIFICE.
FIG 5-110. COMPARISON OF OXYGEN RECOVERY BETWEEN A 2 STEP AND 8 STEP SYSTEM OPERATING AT 24°C.
FIG 5-111. COMPARISON OF OXYGEN RECOVERY BETWEEN A 2 STEP AND 6 STEP SYSTEM OPERATING AT -40°C.
FIG 5-112. PREDICTION OF O₂-N₂ ADSORPTION ON MOLEcular SIEVE 5A AT 24 C BASED ON THE DATA OF THIS WORK AND A STATISTICAL THERMODYNAMIC MODEL.

O₂ COMPONENT LOADING

N₂ COMPONENT LOADING

TOTAL LOADING
CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1. The pure component isotherms of nitrogen and oxygen on molecular sieve 5A were correlated by a statistical thermodynamic model.

2. The pure isotherm data of Union Carbide (69) were predicted with reasonable accuracy using a statistical thermodynamic model with parameters determined from the pure component isotherm data of this work.

3. The multicomponent isotherms for the nitrogen and oxygen on molecular sieve 5A were predicted at 24°C by a statistical thermodynamic model and the IAST theory using the pure component data of this model.

4. The surface of the molecular sieve 5A is energetically heterogeneous to the nitrogen molecule and homogeneous toward the oxygen molecule. This is evident by viewing the plot of $H_a$ versus loading (See Figure 5-24).

5. The breakthrough data taken at 24 and -40°C shows that the length of the mass transfer front during adsorption, i.e. nitrogen breakthrough experiments, remains nearly constant. On the contrary, the length of the mass transfer front during desorption, i.e. oxygen breakthrough, is much greater at -40°C.

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A decrease in the rate of diffusion of the nitrogen molecules during desorption may account for the reduced performance of PSA systems at lower temperatures.

6. Optimum performance of a PSA system at \(-40^\circ C\) requires lengthening of the cycle time. The optimum cycle times for the six step and two step system are nearly the same. Slightly higher oxygen product concentrations and oxygen recoveries were observed for six step system in comparison to the two step.

7. The separation factor for nitrogen-oxygen is constant above 1000 Torr and temperature dependent below 1000 Torr where it is inversely proportional to the temperature.

8. There is no improvement in the separation of argon at \(-40^\circ C\).

9. At 24\(^\circ\)C the O2-N2-5A system may be considered ideal.
B. Recommendations

1. The nonideality of the binary mixture of nitrogen and oxygen at low temperature should be investigated to determine the nature of the interaction of these molecules. Possibly, an extension to existing models could be used to predict sorption at these lower temperatures.

2. The effect of the argon in the multicomponent mixture with nitrogen and oxygen should be investigated to ensure the validity of neglecting argon in the present analysis.

3. The PSA unit used in this study should be run at $-40^\circ$C to determine if greater oxygen concentrations can be achieved by optimization of the purge flow through use of an automatic flow controller.

4. Additional experimentation and analysis of the breakthrough curves at $-40^\circ$C should be conducted to determine the underlying causes of the significantly longer nitrogen desorption.

5. Further studies comparing the two step and the six step cycle should be undertaken.
APPENDIX

A NOMENCLATURE
B OPERATING PROCEDURE
C DATA AND CALCULATIONS
APPENDIX A

NOMENCLATURE

A = area

a = activity for an ideal gas \((p/kT)\)

\(a\) = number of cavities with \(s\) sorbate molecules

B = effective molecular volume (cu. Angstroms)

c = sorbate concentration (molecules/cavity)

C = canonical ensemble partition function

D = zeolitic diffusivity (cm. sq./sec)

\(D_0\) = "" at zero concentration

\(D_0\) = constant in units of \((\text{molecules})(\text{cm.sq.})(\text{cavity})(\text{sec})\)

\(D_0\) = pre-exponential factor \((\text{molecules})(\text{cm.sq.})(\text{cavity})(\text{sec})\)

E = diffusional activation energy

G = Gibbs free energy

H = enthalpy

\(H_a\) = isosteric heat of adsorption

K = Henry's Law constant \((c=Kp)\) \((\text{molecules/cavity/Torr})\)

\(K_0\) = pre-exponential factor giving temperature dependence of K \((\text{molecules/cavity})\) \((\text{dyne/cm.sq.})\)

k = Boltzmann's constant

m = maximum number of molecules per cavity \(\text{(saturation limit)}\)
\((m \leq V/B)\)
m = mass of sorbate adsorbed or desorbed during time, t

m = mass adsorbed or desorbed when time approaches infinity.

M = number of cavities

N = total number of sorbate molecules in the system

N = average number of molecules in the macroscopic system

n = number of molecules adsorbed by a crystal

P = total pressure

P = high pressure

H

P = low pressure

L

p = partial pressure

q(s) = site partition function

Q = subsystem of grand partition functions

qc = limiting isosteric heat of sorption at zero concentration

r = equivalent radius of a zeolite crystal

R = universal gas constant

r = position vector in the Sutherland potential

S = entropy

s = number of sorbate molecules occluded in a cavity

T = temperature, °K

t = dummy variable

U = internal energy

Us = potential energy for the subsystem
\( V_a \) = volume of the adsorbate

\( V_g \) = volume of the adsorbate in the gas phase

\( V \) = volume of the zeolite type A alpha cavity
(776 cu. Angstroms)

\( Z(s) \) = configuration integral for a system of \( s \) sorbate molecules in one molecular sieve 5A cavity

\( Z(i,j) \) = configuration integral for a system of \( i \) molecules of species A and \( j \) molecules of species B within a molecular sieve 5A cavity

\( \alpha \) = separation factor

\( \varepsilon \) = void fraction

\( \theta \) = fractional coverage

\( \lambda \) = \( \exp(\mu/kT) \)

\( \mu \) = chemical potential

\( \sigma, \xi \) = molecular constants in the potential energy function

\( \tau \) = charge

\( \phi \) = angle between the axis of the quadrupole and the line between the centers of the two molecules

\( \omega \) = polarizability

\( \Pi \) = spreading pressure

Subscripts

A = component A

B = component B

i = number of molecules of species A
j = number of molecules of species B
APPENDIX B
OPERATING PROCEDURES

A. Brief Description of the Pure Component Apparatus Operating Procedure

(1) Regenerate the adsorbent by heating to a temperature of 350°C while applying a vacuum of < 1 Torr for twelve hours. Close valve (V4), set the temperature controller on the environmental test chamber (T) and allow the sample to stabilize at the desired experimental temperature (See Fig. 4-6).

(2) Open valve (V2) to permit the gaseous adsorbate (pure nitrogen or oxygen) to enter the previously evacuated charge chamber (C2).

(3) Close valve (V2) and annotate the temperature and initial pressure of the charge chamber (C2).

(4) Ensure the adsorbent temperature (T1) is stable at the desired temperature of the experiment.

(5) Inject a portion of the gaseous adsorbate from the charge chamber (C2) into the sample chamber (C1) by slightly opening valve (V3).

(6) Monitor the sample chamber (C1) pressure through use of the strip chart recorder (S) to determine when equilibrium has been reached. In this work equilibrium required a minimum of six to eight hours for each data point.

(7) Annotate the final pressure in the charge chamber (C2) and the equilibrium pressure in the sample chamber (C1).

(8) The above procedure is repeated until the equilibrium pressure within the sample chamber (C1) reaches the high limit of the
calibrated range of the pressure transducers.

B. Brief Description of the Multicomponent Apparatus Operating Procedure

(1) Follow step (1) through (6) as shown in the operating procedure for the pure component apparatus but use valve (V1) to draw vacuum on the sample chamber (C1) during the regeneration step (See Fig. 4-8). Air is permitted to enter the charge volume (C2).

(2) Monitor the pressure in the sample chamber (C1) to determine when equilibrium has been attained.

(3) Evacuate the MGA sampling volume (SV) by placing valve (V6) in the proper position.

(4) Evacuate the MGA sampling probe (PR) by proper positioning of valves (V5 and V6).

(5) Annotate the pressure in the sample chamber (C1) at equilibrium. Open valve (V1) momentarily to draw a small sample of gas from the sample chamber (C1) into the MGA sampling volume (SV).

(6) Annotate the pressure in the sample chamber (C1) immediately after the gas sample has been removed.

(7) Open valve (V5) to allow the gas sample to enter the gas sampling probe (PR) and the MGA for analysis.

(8) Evacuate the sampling volume (SV) and the MGA gas sampling probe (PR) by positioning valves (V5 and V6).

(9) Repeat the above procedure to obtain other data points.

C. Brief Description of the PSA Unit Operating Procedure

229
(1) Edit the data file XBASE.DAT to set the experimental configuration and the number of data channels.

(2) Install the proper purge orifice for the desired configuration.

(3) Set the inlet air regulator at 25 psia.

(4) Ensure all data channels give the proper outputs and the calibration factors for each channel are correct.

(5) Begin the experiment by running the main control program TT.FOR.

(6) Set the product flow rate.

(7) After a stable oxygen concentration is observed in the product flow, depress the "line feed" key on the VT-54 terminal to begin the data collection process.

(8) The data is displayed to the screen of the VT-54 in engineering units and stored on a floppy diskette in A/D counts.
### APPENDIX C

**DATA AND CALCULATIONS**

Table 17. Nitrogen-5A at 24°C (Run 1).

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>0.325</td>
</tr>
<tr>
<td>50</td>
<td>0.940</td>
</tr>
<tr>
<td>88</td>
<td>1.645</td>
</tr>
<tr>
<td>156</td>
<td>2.769</td>
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<tr>
<td>223</td>
<td>3.794</td>
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<tr>
<td>339</td>
<td>5.454</td>
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<td>432</td>
<td>6.617</td>
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<td>9.158</td>
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<td>690</td>
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<tr>
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<td>10.905</td>
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<td>959</td>
<td>12.196</td>
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<td>16.731</td>
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<td>27.072</td>
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<tr>
<td>3439</td>
<td>28.041</td>
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Table 18. Nitrogen-5A at 24°C (Run 2)

<table>
<thead>
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<th>Quantity Adsorbed (ml STP/gm)</th>
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<tr>
<td>143</td>
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<tr>
<td>274</td>
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<td>415</td>
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<td>563</td>
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<td>750</td>
<td>10.316</td>
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<tr>
<td>1117</td>
<td>13.287</td>
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<td>1355</td>
<td>15.502</td>
</tr>
<tr>
<td>1712</td>
<td>18.148</td>
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<tr>
<td>2120</td>
<td>20.779</td>
</tr>
<tr>
<td>2508</td>
<td>23.017</td>
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<td>2901</td>
<td>25.039</td>
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<tr>
<td>3196</td>
<td>26.575</td>
</tr>
<tr>
<td>3382</td>
<td>27.541</td>
</tr>
</tbody>
</table>

Table 19. Nitrogen-5A at -40°C (Run 1)

<table>
<thead>
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<th>Pressure (Torr)</th>
<th>Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>4.651</td>
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<tr>
<td>100</td>
<td>14.812</td>
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<tr>
<td>395</td>
<td>30.593</td>
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<td>3320</td>
<td>64.144</td>
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</table>
Table 20. Nitrogen-5A at -40°C (Run 1 Desorption)

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2389</td>
<td>58.409</td>
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<tr>
<td>1779</td>
<td>53.469</td>
</tr>
<tr>
<td>1376</td>
<td>49.241</td>
</tr>
</tbody>
</table>

Table 21. Nitrogen-5A at -40°C (Run 2)

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>175</td>
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<td>553</td>
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<td>45.126</td>
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<tr>
<td>1676</td>
<td>52.256</td>
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Table 22. Nitrogen-5A at -70°C (Run 1)

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
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<tr>
<td>174</td>
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<tr>
<td>454</td>
<td>56.236</td>
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<tr>
<td>931</td>
<td>67.720</td>
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<tr>
<td>1505</td>
<td>75.246</td>
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<tr>
<td>2032</td>
<td>80.253</td>
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<tr>
<td>2457</td>
<td>83.693</td>
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<tr>
<td>2808</td>
<td>85.847</td>
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<tr>
<td>3087</td>
<td>87.232</td>
</tr>
<tr>
<td>3299</td>
<td>88.081</td>
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</table>
Table 23. Nitrogen-5A at -70°C (Run 1 Desorption)

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2400</td>
<td>83.123</td>
</tr>
<tr>
<td>1795</td>
<td>78.697</td>
</tr>
<tr>
<td>1412</td>
<td>74.574</td>
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</table>

Table 24. Nitrogen-5A at -70°C (Run 2)

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>20.783</td>
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<tr>
<td>172</td>
<td>40.084</td>
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<tr>
<td>444</td>
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<td>1402</td>
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<tr>
<td>1934</td>
<td>80.104</td>
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Table 25. Oxygen-5A at 24°C (Run 1)

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Quantity Adsorbed (ml STP/gm)</th>
</tr>
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<tbody>
<tr>
<td>249</td>
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<tr>
<td>495</td>
<td>2.318</td>
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<td>757</td>
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<td>2141</td>
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<td>2544</td>
<td>10.736</td>
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<td>3025</td>
<td>12.528</td>
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<tr>
<td>3320</td>
<td>13.560</td>
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<tr>
<td>3511</td>
<td>14.197</td>
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<tr>
<td>3620</td>
<td>14.561</td>
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</tbody>
</table>

234
Table 26. Oxygen-5A at 24°C (Run 2)

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>119</td>
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<tr>
<td>352</td>
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<td>677</td>
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<td>4.195</td>
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<td>7.558</td>
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<tr>
<td>2105</td>
<td>8.769</td>
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<td>2648</td>
<td>10.988</td>
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<td>3074</td>
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<td>3356</td>
<td>13.447</td>
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<td>3532</td>
<td>14.054</td>
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<tr>
<td>3625</td>
<td>14.476</td>
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</tbody>
</table>

Table 27. Oxygen-5A at -40°C (Run 1)

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>183</td>
<td>4.228</td>
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<tr>
<td>307</td>
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<tr>
<td>488</td>
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<td>720</td>
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<td>905</td>
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<td>1458</td>
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<td>1929</td>
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<td>3268</td>
<td>43.812</td>
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</table>
### Table 28. Oxygen-5A at -40°C (Run 1 Desorption)

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2581</td>
<td>37.932</td>
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<tr>
<td>1996</td>
<td>31.620</td>
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<tr>
<td>1546</td>
<td>26.480</td>
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<tr>
<td>1241</td>
<td>23.426</td>
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</table>

### Table 29. Oxygen-5A at -70°C (Run 1)

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>176</td>
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<tr>
<td>342</td>
<td>19.252</td>
</tr>
<tr>
<td>532</td>
<td>27.040</td>
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<td>682</td>
<td>32.742</td>
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<tr>
<td>833</td>
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<td>1257</td>
<td>48.164</td>
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<td>56.334</td>
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<td>62.263</td>
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<tr>
<td>2301</td>
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<tr>
<td>3165</td>
<td>75.512</td>
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<tr>
<td>3305</td>
<td>76.575</td>
</tr>
</tbody>
</table>

### Table 30. Oxygen-5A at -70°C (Run 1 Desorption)

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2813</td>
<td>72.341</td>
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<tr>
<td>2234</td>
<td>65.919</td>
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<td>1836</td>
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<td>49.760</td>
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236
### Table 31. Oxygen-5A at -70°C (Run 2)

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Quantity Adsorbed (ml STP/gm)</th>
</tr>
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<tbody>
<tr>
<td>285</td>
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<td>543</td>
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<td>3077</td>
<td>72.724</td>
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### Table 32. Isosteric heat of adsorption for oxygen

<table>
<thead>
<tr>
<th>Quantity Adsorbed (ml STP/gm)</th>
<th>$\Delta H_a$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>3371</td>
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<td>2.5</td>
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<tr>
<td>5.0</td>
<td>3378</td>
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</tr>
<tr>
<td>15.0</td>
<td>3398</td>
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<tr>
<td>20.0</td>
<td>3317</td>
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<tr>
<td>25.0</td>
<td>3352</td>
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<tr>
<td>30.0</td>
<td>3392</td>
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<td>35.0</td>
<td>3438</td>
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<tr>
<td>40.0</td>
<td>3490</td>
</tr>
<tr>
<td>45.0</td>
<td>3551</td>
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</tbody>
</table>
Table 33. Isosteric heat of adsorption for nitrogen

<table>
<thead>
<tr>
<th>Quantity Adsorbed (ml STP/gm)</th>
<th>- Ha (cal/mol)</th>
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</thead>
<tbody>
<tr>
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<tr>
<td>50.0</td>
<td>4683</td>
</tr>
<tr>
<td>55.0</td>
<td>4683</td>
</tr>
<tr>
<td>60.0</td>
<td>4715</td>
</tr>
<tr>
<td>65.0</td>
<td>4787</td>
</tr>
</tbody>
</table>

Table 34. Air-5A at 24°C (Run 1) (Total Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Total Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>169</td>
<td>2.356</td>
</tr>
<tr>
<td>372</td>
<td>4.727</td>
</tr>
<tr>
<td>585</td>
<td>7.072</td>
</tr>
<tr>
<td>882</td>
<td>9.713</td>
</tr>
<tr>
<td>1252</td>
<td>12.651</td>
</tr>
<tr>
<td>1836</td>
<td>16.860</td>
</tr>
<tr>
<td>2405</td>
<td>20.507</td>
</tr>
<tr>
<td>2803</td>
<td>22.745</td>
</tr>
<tr>
<td>3051</td>
<td>24.048</td>
</tr>
</tbody>
</table>
### Table 35. Air-5A at 24°C (Run 1) (Nitrogen Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Nitrogen Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>169</td>
<td>2.024</td>
</tr>
<tr>
<td>372</td>
<td>4.068</td>
</tr>
<tr>
<td>585</td>
<td>6.092</td>
</tr>
<tr>
<td>882</td>
<td>8.373</td>
</tr>
<tr>
<td>1252</td>
<td>10.962</td>
</tr>
<tr>
<td>1836</td>
<td>14.581</td>
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<tr>
<td>2405</td>
<td>17.715</td>
</tr>
<tr>
<td>2803</td>
<td>19.579</td>
</tr>
<tr>
<td>3051</td>
<td>20.845</td>
</tr>
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</table>

### Table 36. Air-5A at 24°C (Run 1) (Oxygen Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Oxygen Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>169</td>
<td>0.319</td>
</tr>
<tr>
<td>372</td>
<td>0.633</td>
</tr>
<tr>
<td>585</td>
<td>0.938</td>
</tr>
<tr>
<td>882</td>
<td>1.283</td>
</tr>
<tr>
<td>1252</td>
<td>1.617</td>
</tr>
<tr>
<td>1836</td>
<td>2.185</td>
</tr>
<tr>
<td>2405</td>
<td>2.674</td>
</tr>
<tr>
<td>2803</td>
<td>2.935</td>
</tr>
<tr>
<td>3051</td>
<td>3.067</td>
</tr>
</tbody>
</table>
### Table 37. Air-5A at 24°C (Run 1) (Argon Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Argon Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>169</td>
<td>0.014</td>
</tr>
<tr>
<td>372</td>
<td>0.026</td>
</tr>
<tr>
<td>585</td>
<td>0.042</td>
</tr>
<tr>
<td>882</td>
<td>0.057</td>
</tr>
<tr>
<td>1252</td>
<td>0.072</td>
</tr>
<tr>
<td>1836</td>
<td>0.094</td>
</tr>
<tr>
<td>2405</td>
<td>0.118</td>
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<tr>
<td>2803</td>
<td>0.131</td>
</tr>
<tr>
<td>3051</td>
<td>0.136</td>
</tr>
</tbody>
</table>

### Table 38. Air-5A at -40°C (Run 1) (Total Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Total Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>168</td>
<td>10.325</td>
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<tr>
<td>280</td>
<td>15.960</td>
</tr>
<tr>
<td>444</td>
<td>22.661</td>
</tr>
<tr>
<td>666</td>
<td>29.558</td>
</tr>
<tr>
<td>1184</td>
<td>39.684</td>
</tr>
<tr>
<td>1670</td>
<td>46.584</td>
</tr>
<tr>
<td>2110</td>
<td>51.516</td>
</tr>
<tr>
<td>2457</td>
<td>54.410</td>
</tr>
<tr>
<td>2731</td>
<td>56.748</td>
</tr>
<tr>
<td>2968</td>
<td>58.392</td>
</tr>
<tr>
<td>3118</td>
<td>59.615</td>
</tr>
</tbody>
</table>
### Table 39. Air-5A at -40°C (Run 1) (Nitrogen Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Nitrogen Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>168</td>
<td>8.629</td>
</tr>
<tr>
<td>280</td>
<td>13.351</td>
</tr>
<tr>
<td>444</td>
<td>18.985</td>
</tr>
<tr>
<td>666</td>
<td>24.838</td>
</tr>
<tr>
<td>1184</td>
<td>33.375</td>
</tr>
<tr>
<td>1670</td>
<td>39.189</td>
</tr>
<tr>
<td>2110</td>
<td>43.697</td>
</tr>
<tr>
<td>2457</td>
<td>46.078</td>
</tr>
<tr>
<td>2731</td>
<td>48.033</td>
</tr>
<tr>
<td>2968</td>
<td>49.462</td>
</tr>
<tr>
<td>3118</td>
<td>50.634</td>
</tr>
</tbody>
</table>

### Table 40. Air-5A at -40°C (Run 1) (Oxygen Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Oxygen Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>168</td>
<td>1.626</td>
</tr>
<tr>
<td>280</td>
<td>2.501</td>
</tr>
<tr>
<td>444</td>
<td>3.526</td>
</tr>
<tr>
<td>666</td>
<td>4.522</td>
</tr>
<tr>
<td>1184</td>
<td>6.041</td>
</tr>
<tr>
<td>1670</td>
<td>7.080</td>
</tr>
<tr>
<td>2110</td>
<td>7.485</td>
</tr>
<tr>
<td>2457</td>
<td>7.968</td>
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<tr>
<td>2731</td>
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<tr>
<td>2968</td>
<td>8.538</td>
</tr>
<tr>
<td>3118</td>
<td>8.588</td>
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</table>
Table 41. Air-5A at -40°C (Run 1) (Argon Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Argon Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>168</td>
<td>0.069</td>
</tr>
<tr>
<td>280</td>
<td>0.107</td>
</tr>
<tr>
<td>444</td>
<td>0.153</td>
</tr>
<tr>
<td>666</td>
<td>0.197</td>
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<tr>
<td>1184</td>
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<td>1670</td>
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<td>2110</td>
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<td>2731</td>
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<tr>
<td>2968</td>
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<tr>
<td>3118</td>
<td>0.393</td>
</tr>
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</table>

Table 42. Air-5A at -70°C (Run 1) (Total Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Total Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>168</td>
<td>24.632</td>
</tr>
<tr>
<td>290</td>
<td>35.617</td>
</tr>
<tr>
<td>427</td>
<td>44.188</td>
</tr>
<tr>
<td>634</td>
<td>53.462</td>
</tr>
<tr>
<td>1060</td>
<td>63.913</td>
</tr>
<tr>
<td>1536</td>
<td>71.236</td>
</tr>
<tr>
<td>1981</td>
<td>76.284</td>
</tr>
<tr>
<td>2400</td>
<td>79.439</td>
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<tr>
<td>2705</td>
<td>81.648</td>
</tr>
<tr>
<td>2943</td>
<td>83.142</td>
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</table>
Table 43. Air-5A at -70°C (Run 1) (Nitrogen Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Nitrogen Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>168</td>
<td>20.030</td>
</tr>
<tr>
<td>290</td>
<td>29.048</td>
</tr>
<tr>
<td>427</td>
<td>36.146</td>
</tr>
<tr>
<td>634</td>
<td>43.859</td>
</tr>
<tr>
<td>1060</td>
<td>52.596</td>
</tr>
<tr>
<td>1536</td>
<td>58.827</td>
</tr>
<tr>
<td>1981</td>
<td>63.152</td>
</tr>
<tr>
<td>2400</td>
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<tr>
<td>2705</td>
<td>67.803</td>
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<tr>
<td>2943</td>
<td>69.217</td>
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Table 44. Air-5A at -70°C (Run 1) (Oxygen Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Oxygen Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>168</td>
<td>4.415</td>
</tr>
<tr>
<td>290</td>
<td>6.295</td>
</tr>
<tr>
<td>427</td>
<td>7.704</td>
</tr>
<tr>
<td>634</td>
<td>9.198</td>
</tr>
<tr>
<td>1060</td>
<td>10.837</td>
</tr>
<tr>
<td>1536</td>
<td>11.875</td>
</tr>
<tr>
<td>1981</td>
<td>12.568</td>
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<tr>
<td>2400</td>
<td>12.973</td>
</tr>
<tr>
<td>2705</td>
<td>13.243</td>
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<tr>
<td>2943</td>
<td>13.315</td>
</tr>
<tr>
<td>Total Pressure (Torr)</td>
<td>Quantity Argon Adsorbed (ml STP/gm)</td>
</tr>
<tr>
<td>----------------------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>168</td>
<td>0.192</td>
</tr>
<tr>
<td>290</td>
<td>0.275</td>
</tr>
<tr>
<td>427</td>
<td>0.338</td>
</tr>
<tr>
<td>634</td>
<td>0.405</td>
</tr>
<tr>
<td>1060</td>
<td>0.480</td>
</tr>
<tr>
<td>1536</td>
<td>0.533</td>
</tr>
<tr>
<td>1981</td>
<td>0.565</td>
</tr>
<tr>
<td>2400</td>
<td>0.590</td>
</tr>
<tr>
<td>2705</td>
<td>0.602</td>
</tr>
<tr>
<td>2943</td>
<td>0.611</td>
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</table>

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Total Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>194</td>
<td>2.736</td>
</tr>
<tr>
<td>1169</td>
<td>11.691</td>
</tr>
<tr>
<td>1908</td>
<td>17.247</td>
</tr>
<tr>
<td>2467</td>
<td>20.497</td>
</tr>
<tr>
<td>2829</td>
<td>22.678</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Nitrogen Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>194</td>
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<tr>
<td>1169</td>
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</tr>
<tr>
<td>1908</td>
<td>14.917</td>
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<tr>
<td>2467</td>
<td>17.685</td>
</tr>
<tr>
<td>2829</td>
<td>19.598</td>
</tr>
</tbody>
</table>
Table 48. Air-5A at 24°C (Run 2) (Oxygen Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Oxygen Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>194</td>
<td>0.369</td>
</tr>
<tr>
<td>1169</td>
<td>1.516</td>
</tr>
<tr>
<td>1908</td>
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</tr>
<tr>
<td>2467</td>
<td>2.695</td>
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<tr>
<td>2829</td>
<td>2.952</td>
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</table>

Table 49. Air-5A at 24°C (Run 2) (Argon Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Argon Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>194</td>
<td>0.016</td>
</tr>
<tr>
<td>1169</td>
<td>0.067</td>
</tr>
<tr>
<td>1908</td>
<td>0.099</td>
</tr>
<tr>
<td>2467</td>
<td>0.117</td>
</tr>
<tr>
<td>2829</td>
<td>0.128</td>
</tr>
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</table>

Table 50. Air-5A at -40°C (Run 2) (Total Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Total Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>199</td>
<td>12.048</td>
</tr>
<tr>
<td>325</td>
<td>18.012</td>
</tr>
<tr>
<td>458</td>
<td>23.163</td>
</tr>
<tr>
<td>687</td>
<td>30.087</td>
</tr>
<tr>
<td>1200</td>
<td>40.048</td>
</tr>
<tr>
<td>1707</td>
<td>47.059</td>
</tr>
<tr>
<td>2151</td>
<td>51.723</td>
</tr>
<tr>
<td>2513</td>
<td>54.953</td>
</tr>
<tr>
<td>2808</td>
<td>57.098</td>
</tr>
</tbody>
</table>
Table 51. Air-5A at -40°C (Run 2) (Nitrogen Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Nitrogen Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>199</td>
<td>10.060</td>
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<tr>
<td>325</td>
<td>15.062</td>
</tr>
<tr>
<td>458</td>
<td>19.410</td>
</tr>
<tr>
<td>687</td>
<td>25.263</td>
</tr>
<tr>
<td>1200</td>
<td>33.695</td>
</tr>
<tr>
<td>1707</td>
<td>39.537</td>
</tr>
<tr>
<td>2151</td>
<td>43.485</td>
</tr>
<tr>
<td>2513</td>
<td>46.255</td>
</tr>
<tr>
<td>2808</td>
<td>48.283</td>
</tr>
</tbody>
</table>

Table 52. Air-5A at -40°C (Run 2) (Oxygen Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Oxygen Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>199</td>
<td>1.907</td>
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<tr>
<td>325</td>
<td>2.828</td>
</tr>
<tr>
<td>458</td>
<td>3.598</td>
</tr>
<tr>
<td>687</td>
<td>4.629</td>
</tr>
<tr>
<td>1200</td>
<td>6.084</td>
</tr>
<tr>
<td>1707</td>
<td>7.199</td>
</tr>
<tr>
<td>2151</td>
<td>7.882</td>
</tr>
<tr>
<td>2513</td>
<td>8.320</td>
</tr>
<tr>
<td>2808</td>
<td>8.433</td>
</tr>
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</table>
### Table 53. Air-5A at \(-40^\circ\text{C}\) (Run 2) (Argon Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Argon Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>199</td>
<td>0.081</td>
</tr>
<tr>
<td>325</td>
<td>0.122</td>
</tr>
<tr>
<td>458</td>
<td>0.156</td>
</tr>
<tr>
<td>687</td>
<td>0.196</td>
</tr>
<tr>
<td>1200</td>
<td>0.269</td>
</tr>
<tr>
<td>1707</td>
<td>0.323</td>
</tr>
<tr>
<td>2151</td>
<td>0.356</td>
</tr>
<tr>
<td>2513</td>
<td>0.377</td>
</tr>
<tr>
<td>2808</td>
<td>0.382</td>
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</table>

### Table 54. Air-5A at \(-70^\circ\text{C}\) (Run 2) (Total Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Total Quantity Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>171</td>
<td>25.049</td>
</tr>
<tr>
<td>289</td>
<td>35.728</td>
</tr>
<tr>
<td>443</td>
<td>45.251</td>
</tr>
<tr>
<td>688</td>
<td>55.163</td>
</tr>
<tr>
<td>1122</td>
<td>65.464</td>
</tr>
<tr>
<td>1608</td>
<td>72.520</td>
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<tr>
<td>2053</td>
<td>76.911</td>
</tr>
<tr>
<td>2431</td>
<td>80.141</td>
</tr>
<tr>
<td>2731</td>
<td>82.298</td>
</tr>
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</table>
Table 55. Air-5A at -70°C (Run 2) (Nitrogen Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Nitrogen Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>171</td>
<td>20.363</td>
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<tr>
<td>289</td>
<td>29.131</td>
</tr>
<tr>
<td>443</td>
<td>37.020</td>
</tr>
<tr>
<td>688</td>
<td>45.240</td>
</tr>
<tr>
<td>1122</td>
<td>53.892</td>
</tr>
<tr>
<td>1608</td>
<td>59.895</td>
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<tr>
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<td>63.736</td>
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<td>66.398</td>
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<tr>
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</tbody>
</table>

Table 56. Air-5A at -70°C (Run 2) (Oxygen Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Oxygen Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>171</td>
<td>4.491</td>
</tr>
<tr>
<td>289</td>
<td>6.321</td>
</tr>
<tr>
<td>443</td>
<td>7.885</td>
</tr>
<tr>
<td>688</td>
<td>9.503</td>
</tr>
<tr>
<td>1122</td>
<td>11.079</td>
</tr>
<tr>
<td>1608</td>
<td>12.082</td>
</tr>
<tr>
<td>2053</td>
<td>12.609</td>
</tr>
<tr>
<td>2431</td>
<td>13.148</td>
</tr>
<tr>
<td>2731</td>
<td>13.303</td>
</tr>
</tbody>
</table>
Table 57. Air-5A at -70°C (Run 2) (Argon Loading)

<table>
<thead>
<tr>
<th>Total Pressure (Torr)</th>
<th>Quantity Argon Adsorbed (ml STP/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>171</td>
<td>0.195</td>
</tr>
<tr>
<td>289</td>
<td>0.276</td>
</tr>
<tr>
<td>443</td>
<td>0.346</td>
</tr>
<tr>
<td>688</td>
<td>0.420</td>
</tr>
<tr>
<td>1122</td>
<td>0.494</td>
</tr>
<tr>
<td>1608</td>
<td>0.542</td>
</tr>
<tr>
<td>2053</td>
<td>0.566</td>
</tr>
<tr>
<td>2431</td>
<td>0.594</td>
</tr>
<tr>
<td>2731</td>
<td>0.601</td>
</tr>
</tbody>
</table>
Determination of Sample True Volume and True Density by Helium Displacement

Sample: Union Carbide Molecular Sieve 5A (20x40 mesh) at 297.15K

Number of Data Points: 20
Sample weight (gm) = 32.8
Volume of Sample Chamber (ml) = 170.0
Volume of the Charge Chamber (ml) = 158.6

<table>
<thead>
<tr>
<th>Point No.</th>
<th>Initial Pressure (Torr)</th>
<th>Final Pressure (Torr)</th>
<th>Moles Added (gm mol*10**3)</th>
<th>Calculated Total Volume (ml)</th>
<th>Calculated Sample Chamber Volume (ml)</th>
<th>Calculated Sample Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1500</td>
<td>750.0</td>
<td>12.838</td>
<td>317.20</td>
<td>158.60</td>
<td>11.40</td>
</tr>
<tr>
<td>2</td>
<td>2000</td>
<td>1008.0</td>
<td>17.117</td>
<td>314.68</td>
<td>156.08</td>
<td>13.92</td>
</tr>
<tr>
<td>3</td>
<td>2500</td>
<td>1246.0</td>
<td>21.396</td>
<td>318.22</td>
<td>159.62</td>
<td>10.38</td>
</tr>
</tbody>
</table>

Point No: 4
250
<table>
<thead>
<tr>
<th>POINT NO: 5</th>
<th>INITIAL PRESSURE (TORR): 3500</th>
<th>FINAL PRESSURE (TORR): 1743</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOLES ADDED (GM MOL*10**3): 29.955</td>
<td>CALCULATED TOTAL VOLUME (ML): 318.47</td>
<td></td>
</tr>
<tr>
<td>CALCULATED SAMPLE CHAMBER VOLUME (ML): 159.87</td>
<td>CALCULATED SAMPLE VOLUME (ML): 10.13</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>POINT NO: 6</th>
<th>INITIAL PRESSURE (TORR): 1500</th>
<th>FINAL PRESSURE (TORR): 750</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOLES ADDED (GM MOL*10**3): 12.838</td>
<td>CALCULATED TOTAL VOLUME (ML): 317.20</td>
<td></td>
</tr>
<tr>
<td>CALCULATED SAMPLE CHAMBER VOLUME (ML): 158.60</td>
<td>CALCULATED SAMPLE VOLUME (ML): 11.40</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>POINT NO: 7</th>
<th>INITIAL PRESSURE (TORR): 2000</th>
<th>FINAL PRESSURE (TORR): 998</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOLES ADDED (GM MOL*10**3): 17.117</td>
<td>CALCULATED TOTAL VOLUME (ML): 317.84</td>
<td></td>
</tr>
<tr>
<td>CALCULATED SAMPLE CHAMBER VOLUME (ML): 159.24</td>
<td>CALCULATED SAMPLE VOLUME (ML): 10.76</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>POINT NO: 8</th>
<th>INITIAL PRESSURE (TORR): 2500</th>
<th>FINAL PRESSURE (TORR): 1241</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOLES ADDED (GM MOL*10**3): 21.396</td>
<td>CALCULATED TOTAL VOLUME (ML): 319.50</td>
<td></td>
</tr>
<tr>
<td>CALCULATED SAMPLE CHAMBER VOLUME (ML): 160.90</td>
<td>CALCULATED SAMPLE VOLUME (ML): 9.10</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>POINT NO: 9</th>
<th>INITIAL PRESSURE (TORR): 3000</th>
<th>FINAL PRESSURE (TORR): 1495</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOLES ADDED (GM MOL*10**3): 25.676</td>
<td>CALCULATED TOTAL VOLUME (ML): 318.26</td>
<td></td>
</tr>
<tr>
<td>CALCULATED SAMPLE VOLUME (ML): 10.34</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CALCULATED SAMPLE CHAMBER VOLUME (ML) = 159.66
CALCULATED SAMPLE VOLUME (ML) = 10.34

POINT NO: 10
INITIAL PRESSURE (TORR) = 3500.
FINAL PRESSURE (TORR) = 1748.
MOLES ADDED (GM MOL*10**3) = 29.955
CALCULATED TOTAL VOLUME (ML) = 317.56
CALCULATED SAMPLE CHAMBER VOLUME (ML) = 158.96
CALCULATED SAMPLE VOLUME (ML) = 11.04

POINT NO: 11
INITIAL PRESSURE (TORR) = 1500.
FINAL PRESSURE (TORR) = 750.
MOLES ADDED (GM MOL*10**3) = 12.838
CALCULATED TOTAL VOLUME (ML) = 317.20
CALCULATED SAMPLE CHAMBER VOLUME (ML) = 158.60
CALCULATED SAMPLE VOLUME (ML) = 11.40

POINT NO: 12
INITIAL PRESSURE (TORR) = 2000.
FINAL PRESSURE (TORR) = 998.
MOLES ADDED (GM MOL*10**3) = 17.117
CALCULATED TOTAL VOLUME (ML) = 317.84
CALCULATED SAMPLE CHAMBER VOLUME (ML) = 159.24
CALCULATED SAMPLE VOLUME (ML) = 10.76

POINT NO: 13
INITIAL PRESSURE (TORR) = 2500.
FINAL PRESSURE (TORR) = 1246.
MOLES ADDED (GM MOL*10**3) = 21.396
CALCULATED TOTAL VOLUME (ML) = 318.22
CALCULATED SAMPLE CHAMBER VOLUME (ML) = 159.62
CALCULATED SAMPLE VOLUME (ML) = 10.38

POINT NO: 14
INITIAL PRESSURE (TORR) = 3000.
FINAL PRESSURE (TORR) = 1499.
MOLES ADDED (GM MOL*10**3) = 25.676
CALCULATED TOTAL VOLUME (ML) = 317.41
CALCULATED SAMPLE CHAMBER VOLUME (ML) = 158.81
CALCULATED SAMPLE VOLUME (ML) = 11.19
POINT NO: 15
INITIAL PRESSURE (TORR)= 3500.
FINAL PRESSURE (TORR)= 1748.
MOLES ADDED (GM MOL*10**3)= 29.955
CALCULATED TOTAL VOLUME (ML)= 317.56
CALCULATED SAMPLE CHAMBER VOLUME (ML)= 158.96
CALCULATED SAMPLE VOLUME (ML)= 11.04

POINT NO: 16
INITIAL PRESSURE (TORR)= 1500.
FINAL PRESSURE (TORR)= 752.
MOLES ADDED (GM MOL*10**3)= 12.838
CALCULATED TOTAL VOLUME (ML)= 316.36
CALCULATED SAMPLE CHAMBER VOLUME (ML)= 157.76
CALCULATED SAMPLE VOLUME (ML)= 12.24

POINT NO: 17
INITIAL PRESSURE (TORR)= 2000.
FINAL PRESSURE (TORR)= 1003.
MOLES ADDED (GM MOL*10**3)= 17.117
CALCULATED TOTAL VOLUME (ML)= 316.25
CALCULATED SAMPLE CHAMBER VOLUME (ML)= 157.65
CALCULATED SAMPLE VOLUME (ML)= 12.35

POINT NO: 18
INITIAL PRESSURE (TORR)= 2500.
FINAL PRESSURE (TORR)= 1246.
MOLES ADDED (GM MOL*10**3)= 21.396
CALCULATED TOTAL VOLUME (ML)= 318.22
CALCULATED SAMPLE CHAMBER VOLUME (ML)= 159.62
CALCULATED SAMPLE VOLUME (ML)= 10.38

POINT NO: 19
INITIAL PRESSURE (TORR)= 3000.
FINAL PRESSURE (TORR)= 1500.
MOLES ADDED (GM MOL*10**3)= 25.676
CALCULATED TOTAL VOLUME (ML)= 317.20
CALCULATED SAMPLE CHAMBER VOLUME (ML)= 158.60
CALCULATED SAMPLE VOLUME (ML)= 11.40

POINT NO: 20
INITIAL PRESSURE (TORR)= 3500.
FINAL PRESSURE (TORR)= 1748.
MOLES ADDED (GM MOL*10**3)= 29.955
CALCULATED TOTAL VOLUME (ML) = 317.56
CALCULATED SAMPLE CHAMBER VOLUME (ML) = 158.96
CALCULATED SAMPLE VOLUME (ML) = 11.04

MEAN SAMPLE VOLUME (ML) = 11.05
STANDARD DEVIATION (ML) = 1.0004
SAMPLE VOLUME WITH 95% CONFIDENCE INTERVAL (ML) = 11.05 PLUS OR MINUS 0.47
SAMPLE DENSITY (GM/ML) = 2.97

N2241.FOR
EQUILIBRIUM ADSORPTION PROGRAM
GEO GEORGE MILLER
23 JULY 83

DIMENSION PCHAR1(100),TCHARC(100),TSAMPC(100),PFINAL(100)
DIMENSION XMOLTO(100),XMOLIN(100),XMOLGA(100),XMOLAD(100)
DIMENSION VSTP(100),VOLWT(100),PCHAR2(100),ZI(100)
DIMENSION Z2(100),Z3(100)
OPEN(UNIT=1,NAME='N2241.GPH',TYPE='NEW',DISPOSE='SAVE')
OPEN(UNIT=7,NAME='N2241.RES',TYPE='NEW',DISPOSE='SAVE')

PCHAR1=INITIAL CHARGE CHAMBER PRESSURE (TORR)
PCHAR2=FINAL CHARGE CHAMBER PRESSURE (TORR)
Z1=INITIAL CHARGE CHAMBER PRESSURE Z FACTOR
Z2=FINAL CHARGE CHAMBER PRESSURE Z FACTOR
Z3=EQUILIBRIUM Z FACTOR
TCHARC=TEMP IN THE CHARGE CHAMBER (DEG C)
TSAMPC=TEMP IN THE SAMPLE CHAMBER (DEG C)
PFINAL=FINAL PRESSURE IN THE SAMPLE CHAMBER (TORR)
XMOLTO=TOTAL MOLES ADDED (GM MOL)
XMOLIN=MOLES ADDED (GM MOL)
XMOLGA=MOLES IN GAS PHASE (GM MOL)
XMOLAD=MOLES ADSORBED (GM MOL)
VSTP=VOLUME ADSORBED (ML STP)
VOLWT=VOLUME ADSORBED(ML STP)/WEIGHT OF SAMPLE (GM)
SAMWT=SAMPLE WEIGHT (GM)
VCHARC=VOLUME OF THE CHARGE CHAMBER (ML)
VSAMPC=VOLUME OF THE SAMPLE CHAMBER (ML)
VSAMPL=VOLUME OF SAMPLE (ML)
VSAMPT=TRUE DEAD VOLUME IN SAMPLE CHAMBER (ML)
NDATA=22
SAMWT=32.8
R=82.057
VCHARC=158.6
VSAMPC=170.0
VSAMPL=11.05
VSAMPT=VSAMPC-VSAMPL

INPUT: EXPERIMENT NO. 1

PCHAR1(1)=759.
PCHAR1(2)=691.
PCHAR1(3)=554.
PCHAR1(4)=760.
PCHAR1(5)=499.
PCHAR1(6)=759.
PCHAR1(7)=855.
PCHAR1(8)=900.
PCHAR1(9)=1000.
PCHAR1(10)=827.4
PCHAR1(11)=1298.
PCHAR1(12)=1292.7
PCHAR1(13)=1546.3
PCHAR1(14)=1551.4
PCHAR1(15)=2063.4
PCHAR1(16)=2322.
PCHAR1(17)=2580.6
PCHAR1(18)=3097.7
PCHAR1(19)=3873.4
PCHAR1(20)=3847.6
PCHAR1(21)=3873.6
PCHAR1(22)=3873.4

PCHAR2(1)=686.
PCHAR2(2)=553.
PCHAR2(3)=395.
PCHAR2(4)=499.
PCHAR2(5)=256.
PCHAR2(6)=357.
PCHAR2(7)=562.
PCHAR2(8)=564.
PCHAR2(9)=680.
PCHAR2(10)=718.8
PCHAR2(11)=1106.7
PCHAR2(12)=1122.2
PCHAR2(13)=1189.4
PCHAR2(14)=1184.3
PCHAR2(15)=1463.5
PCHAR2(16)=1892.8
PCHAR2(17)=1949.6
PCHAR2(18)=2337.5
PCHAR2(19)=2859.8
PCHAR2(20)=3201.1
PCHAR2(21) = 3433.9
PCHAR2(22) = 3573.5

C
PFINAL(1) = 17.5
PFINAL(2) = 50.
PFINAL(3) = 88.
PFINAL(4) = 156.
PFINAL(5) = 223.
PFINAL(6) = 339.
PFINAL(7) = 432.
PFINAL(8) = 539.
PFINAL(9) = 651.
PFINAL(10) = 690.
PFINAL(11) = 759.
PFINAL(12) = 823.
PFINAL(13) = 959.
PFINAL(14) = 1142.9
PFINAL(15) = 1391.1
PFINAL(16) = 1577.3
PFINAL(17) = 1866.9
PFINAL(18) = 2197.9
PFINAL(19) = 2720.2
PFINAL(20) = 3066.7
PFINAL(21) = 3304.6
PFINAL(22) = 3439.

C
TCHARC(1) = 24.
TCHARC(2) = 25.
TCHARC(3) = 25.
TCHARC(4) = 25.
TCHARC(5) = 25.
TCHARC(6) = 25.
TCHARC(7) = 25.
TCHARC(8) = 25.
TCHARC(9) = 25.
TCHARC(10) = 23.
TCHARC(11) = 24.
TCHARC(12) = 24.
TCHARC(13) = 24.
TCHARC(14) = 24.
TCHARC(15) = 25.
TCHARC(16) = 24.
TCHARC(17) = 24.
TCHARC(18) = 24.
TCHARC(19) = 24.
TCHARC(20) = 24.
TCHARC(21) = 24.
TCHARC(22) = 24.

256
TSAMPC(1) = 25.
TSAMPC(2) = 25.
TSAMPC(3) = 25.
TSAMPC(4) = 25.
TSAMPC(5) = 25.
TSAMPC(6) = 25.
TSAMPC(7) = 25.
TSAMPC(8) = 25.
TSAMPC(9) = 25.
TSAMPC(10) = 25.
TSAMPC(11) = 25.
TSAMPC(12) = 25.
TSAMPC(13) = 25.
TSAMPC(14) = 25.
TSAMPC(15) = 25.
TSAMPC(16) = 25.
TSAMPC(17) = 25.
TSAMPC(18) = 25.
TSAMPC(19) = 25.
TSAMPC(20) = 25.
TSAMPC(21) = 25.
TSAMPC(22) = 25.

C

DO100 J = 1, NDATA
TCHARC(J) = TCHARC(J) + 273.15
TSAMPC(J) = TSAMPC(J) + 273.15
CONTINUE

TOTAL = 0.
DO101 J = 1, NDATA
Z1(J) = (-2.565068585E-07 * PCHAR1(J)) + 1.00000
XMOL1 = ((PCHAR1(J) / 760.) * VCHARC) / (R * TCHARC(J) * Z1(J))
Z2(J) = (-2.565068585E-07 * PCHAR2(J)) + 1.00000
XMOL2 = ((PCHAR2(J) / 760.) * VCHARC) / (R * TCHARC(J) * Z2(J))
XMOLIN(J) = XMOL1 - XMOL2
XMOLTO(J) = TOTAL + XMOLIN(J)
TOTAL = XMOLTO(J)
Z3(J) = (-2.565068585E-07 * PFINAL(J)) + 1.00000
XMOLGA(J) = ((PFINAL(J) / 760.) * VSAMPT) / (R * TSAMPC(J) * Z3(J))
XMOLAD(J) = XMOLTO(J) - XMOLGA(J)
VSTP(J) = XMOLAD(J) * R * 273.15
VOLWT(J) = VSTP(J) / SAMWT
CONTINUE

DO103 J = 1, NDATA
XMOLIN(J) = XMOLIN(J) * 1000.
XMOLTO(J) = XMOLTO(J) * 1000.
XMOLGA(J) = XMOLGA(J) * 1000.
XMOLAD(J) = XMOLAD(J) * 1000.
CONTINUE
WRITE(7, 15)
15 FORMAT(///,1X,'G.W.MILLER')
WRITE(7,18)
18 FORMAT(1X,'USAF SCHOOL OF AEROSPACE MEDICINE')
WRITE(7,19)
19 FORMAT(1X,'CREW TECHNOLOGY DIVISION')
WRITE(7,20)
20 FORMAT(1X,'BROOKS AFB,TEXAS')
WRITE(7,16)
16 FORMAT(///,1X,'ADSORPTION ISOTHERM EXPERIMENT NO.1')
WRITE(7,1)
1 FORMAT(1X,'NITROGEN ON UNION CARBIDE MOLECULAR SIEVE 5A (20X40
1MESH) AT 24 DEG C')
WRITE(7,2) NDATA
2 FORMAT(///,1X,'NUMBER OF DATA POINTS=',I3)
WRITE(7,3) SAMWT
3 FORMAT(1X,'SAMPLE WEIGHT (GM)=' ,F6.1)
WRITE(7,4) VCHARC
4 FORMAT(1X,'VOLUME OF CHARGE CHAMBER (ML)=' ,F6.1)
WRITE(7,5) VSAMPC
5 FORMAT(1X,'VOLUME OF SAMPLE CHAMBER W/O ZEOLITE (ML)=' ,F6.1)
WRITE(7,6) VSAMPL
6 FORMAT(1X,'TRUE VOLUME OF SAMPLE (ML)=' ,F6.2)
WRITE(7,7) VSAMPT
7 FORMAT(1X,'TRUE DEAD VOLUME OF SAMPLE CHAMBER (ML)=' ,F6.1)
DO105 J=1,NDATA
WRITE(7,8)J
8 FORMAT(///,1X,'POINT NO:=' ,I3)
WRITE(7,500) PCHR1(J),XMOL1N(J)
500 FORMAT(1X,'INITIAL CHARGE PRES (TORR)=' ,F7.1,4X,'MOLES ADDED (G
1MOL*10**3)=' ,F9.4)
WRITE(7,501) PCHR2(J),XMOLTOL(J)
501 FORMAT(1X,'FINAL CHARGE PRES (TORR)=' ,F7.1,6X,'TOTAL MOLES (GM
1MOL*10**3)=' ,F9.4)
WRITE(7,502) TCHR1(J),XMOLG1(J)
502 FORMAT(1X,'CHARGE CHAMBER TEMP(K)=' ,F7.2,8X,'MOLES IN GAS PHASE
1(GM MOL*10**3)=' ,F9.4)
WRITE(7,11) PFINAL(J),XMOLAD(J)
11 FORMAT(1X,'EQUILIBRIUM PRES (TORR)=' ,F7.1,7X,'MOLES ADSORBED (G
1MOL*10**3)=' ,F9.4)
WRITE(7,12) TSAMPC(J),VSTP(J)
12 FORMAT(1X,'SAMPLE CHAMBER TEMP(K)=' ,F7.2,8X,'VOLUME ADSORBED (M
1L) S.T.P.=' ,F9.4)
WRITE(7,13) Z1(J),Z3(J)
13 FORMAT(1X,'INITIAL CHARGE PRES Z=' ,F8.5,8X,'EQUILIBRIUM PRES Z=
1',F8.5)
WRITE(7,600) Z2(J),VOLWT(J)
600 FORMAT(1X,'FINAL CHARGE PRES Z=' ,F8.5,10X,'(ML)S.T.P./GM OF ZEO
1LITE=' ,F8.3)
105 CONTINUE
N2241.RES
G.W.MILLER
USAF SCHOOL OF AEROSPACE MEDICINE
CREW TECHNOLOGY DIVISION
BROOKS AFB, TEXAS

**ADSORPTION ISOTHERM EXPERIMENT NO.1**
NITROGEN ON UNION CARBIDE MOLECULAR SIEVE 5A (20X40 MESH) AT 24 DEG C
NUMBER OF DATA POINTS = 22
SAMPLE WEIGHT (GM) = 32.8
VOLUME OF CHARGE CHAMBER (ML) = 158.6
VOLUME OF SAMPLE CHAMBER W/O ZEOLITE (ML) = 170.0
TRUE VOLUME OF SAMPLE (ML) = 11.05
TRUE DEAD VOLUME OF SAMPLE CHAMBER (ML) = 158.9

**POINT NO: 1**
INITIAL CHARGE PRES (TORR) = 759
FINAL CHARGE PRES (TORR) = 686.0
CHARGE CHAMBER TEMP (K) = 297.15
EQUILIBRIUM PRES (TORR) = 17.5
SAMPLE CHAMBER TEMP (K) = 298.15
INITIAL CHARGE PRES Z = 0.99981
FINAL CHARGE PRES Z = 0.9999

**MOLES ADDED (GM MOL*10**3)**
0.6250
TOTAL MOLES (GM MOL*10**3) = 0.6250
MOLES IN GAS PHASE (GM MOL*10**3) = 0.1496
MOLES ADSORBED (GM MOL*10**3) = 0.4754
VOLUME ADSORBED (ML) S.T.P. = 10.6556
EQUILIBRIUM PRES Z = 1.0000

**POINT NO: 2**
INITIAL CHARGE PRES (TORR) = 691
FINAL CHARGE PRES (TORR) = 553.0
CHARGE CHAMBER TEMP (K) = 298.15
EQUILIBRIUM PRES (TORR) = 50.0
SAMPLE CHAMBER TEMP (K) = 298.15
INITIAL CHARGE PRES Z = 0.99982
FINAL CHARGE PRES Z = 0.99986

**MOLES ADDED (GM MOL*10**3)**
1.1775
TOTAL MOLES (GM MOL*10**3) = 1.8025
MOLES IN GAS PHASE (GM MOL*10**3) = 0.4274
MOLES ADSORBED (GM MOL*10**3) = 1.3751
VOLUME ADSORBED (ML) S.T.P. = 30.8203
EQUILIBRIUM PRES Z = 0.9999

**POINT NO: 3**
INITIAL CHARGE PRES (TORR) = 554
FINAL CHARGE PRES (TORR) = 395.0
CHARGE CHAMBER TEMP (K) = 298.15
EQUILIBRIUM PRES (TORR) = 88.0
SAMPLE CHAMBER TEMP (K) = 298.15
INITIAL CHARGE PRES Z = 0.99986
FINAL CHARGE PRES Z = 0.99993
FINAL CHARGE PRES Z = 0.99990 (ML) S.T.P./GM OF ZEOLITE = 1.645

POINT NO: 4
INITIAL CHARGE PRES (TORR) = 760
FINAL CHARGE PRES (TORR) = 499.0
CHARGE CHAMBER TEMP (K) = 298.15
EQUILIBRIUM PRES (TORR) = 156.0
INITIAL CHARGE PRES Z = 0.99981
FINAL CHARGE PRES Z = 0.99987
MOLES ADDED (GM MOL*10**3) = 2.2270
TOTAL MOLES (GM MOL*10**3) = 5.3861
MOLES IN GAS PHASE (GM MOL*10**3) = 4.0524
MOLES ADSORBED (GM MOL*10**3) = 1.3336
VOLUME ADSORBED (ML) S.T.P. = 90.8304

POINT NO: 5
INITIAL CHARGE PRES (TORR) = 499
FINAL CHARGE PRES (TORR) = 256.0
CHARGE CHAMBER TEMP (K) = 298.15
EQUILIBRIUM PRES (TORR) = 223.0
SAMPLE CHAMBER TEMP (K) = 298.15
INITIAL CHARGE PRES Z = 0.99987
FINAL CHARGE PRES Z = 0.99993
MOLES ADDED (GM MOL*10**3) = 2.0731
TOTAL MOLES (GM MOL*10**3) = 7.4592
MOLES IN GAS PHASE (GM MOL*10**3) = 5.9528
MOLES ADSORBED (GM MOL*10**3) = 1.5065
VOLUME ADSORBED (ML) S.T.P. = 124.4586

POINT NO: 6
INITIAL CHARGE PRES (TORR) = 759
FINAL CHARGE PRES (TORR) = 357.0
CHARGE CHAMBER TEMP (K) = 298.15
EQUILIBRIUM PRES (TORR) = 339.0
SAMPLE CHAMBER TEMP (K) = 297.15
INITIAL CHARGE PRES Z = 0.99997
FINAL CHARGE PRES Z = 0.99998
MOLES ADDED (GM MOL*10**3) = 3.4300
TOTAL MOLES (GM MOL*10**3) = 10.8893
MOLES IN GAS PHASE (GM MOL*10**3) = 8.9065
MOLES ADSORBED (GM MOL*10**3) = 1.9828
VOLUME ADSORBED (ML) S.T.P. = 178.8891

POINT NO: 7
INITIAL CHARGE PRES (TORR) = 855
FINAL CHARGE PRES (TORR) = 562.0
CHARGE CHAMBER TEMP (K) = 298.15
EQUILIBRIUM PRES (TORR) = 432.0
SAMPLE CHAMBER TEMP (K) = 297.15
INITIAL CHARGE PRES Z = 0.99997
FINAL CHARGE PRES Z = 0.99998
MOLES ADDED (GM MOL*10**3) = 2.5001
TOTAL MOLES (GM MOL*10**3) = 9.3893
MOLES IN GAS PHASE (GM MOL*10**3) = 7.3708
MOLES ADSORBED (GM MOL*10**3) = 9.6285
VOLUME ADSORBED (ML) S.T.P. = 217.0439

POINT NO: 8
INITIAL CHARGE PRES (TORR) = 900
FINAL CHARGE PRES (TORR) = 564.0
CHARGE CHAMBER TEMP (K) = 298.15
EQUILIBRIUM PRES (TORR) = 539.0
SAMPLE CHAMBER TEMP (K) = 297.15
INITIAL CHARGE PRES Z = 0.99997
FINAL CHARGE PRES Z = 0.99998
MOLES ADDED (GM MOL*10**3) = 2.8671
TOTAL MOLES (GM MOL*10**3) = 16.2564
MOLES IN GAS PHASE (GM MOL*10**3) = 14.6239
MOLES ADSORBED (GM MOL*10**3) = 11.6325
VOLUME ADSORBED (ML) S.T.P. = 260.7303

POINT NO: 9
INITIAL CHARGE PRES (TORR) = 1000
FINAL CHARGE PRES Z = 0.99986
MOLES ADDED (GM MOL*10**3) = 2.7307

260
FINAL CHARGE PRES (TORR) = 680.0
TOTAL MOLES (GM MOL*10**3) = 18.9871
CHARGE CHAMBER TEMP(K) = 298.15
MOLES IN GAS PHASE (GM MOL*10**3) = 5.5848
EQUILIBRIUM PRES (TORR) = 651.0
MOLES ADSORBED (GM MOL*10**3) = 13.4023
SAMPLE CHAMBER TEMP(K) = 297.15
VOLUME ADSORBED (ML) S.T.P. = 300.3973
INITIAL CHARGE PRES Z = 0.999774
EQUILIBRIUM PRES Z = 0.99983
FINAL CHARGE PRES Z = 0.99982
(ML)S.T.P./GM OF ZEOLITE = 9.158

POINT NO: 10

INITIAL CHARGE PRES (TORR) = 827
MOLES ADDED (GM MOL*10**3) = 0.9330
FINAL CHARGE PRES (TORR) = 718.8
TOTAL MOLES (GM MOL*10**3) = 19.9201
CHARGE CHAMBER TEMP(K) = 296.15
MOLES IN GAS PHASE (GM MOL*10**3) = 5.9195
EQUILIBRIUM PRES (TORR) = 690.0
MOLES ADSORBED (GM MOL*10**3) = 14.0006
SAMPLE CHAMBER TEMP(K) = 297.15
VOLUME ADSORBED (ML) S.T.P. = 313.8082
INITIAL CHARGE PRES Z = 0.99979
EQUILIBRIUM PRES Z = 0.99982
FINAL CHARGE PRES Z = 0.99982
(ML)S.T.P./GM OF ZEOLITE = 9.567

POINT NO: 11

INITIAL CHARGE PRES (TORR) = 1298
MOLES ADDED (GM MOL*10**3) = 1.6383
FINAL CHARGE PRES (TORR) = 1106.7
TOTAL MOLES (GM MOL*10**3) = 21.5583
CHARGE CHAMBER TEMP(K) = 297.15
MOLES IN GAS PHASE (GM MOL*10**3) = 6.5115
EQUILIBRIUM PRES (TORR) = 759.0
MOLES ADSORBED (GM MOL*10**3) = 15.0468
SAMPLE CHAMBER TEMP(K) = 297.15
VOLUME ADSORBED (ML) S.T.P. = 337.6755
INITIAL CHARGE PRES Z = 0.99967
EQUILIBRIUM PRES Z = 0.99981
FINAL CHARGE PRES Z = 0.99972
(ML)S.T.P./GM OF ZEOLITE = 10.282

POINT NO: 12

INITIAL CHARGE PRES (TORR) = 1292
MOLES ADDED (GM MOL*10**3) = 1.4601
FINAL CHARGE PRES (TORR) = 1122.2
TOTAL MOLES (GM MOL*10**3) = 23.0185
CHARGE CHAMBER TEMP(K) = 297.15
MOLES IN GAS PHASE (GM MOL*10**3) = 7.0607
EQUILIBRIUM PRES (TORR) = 823.0
MOLES ADSORBED (GM MOL*10**3) = 15.9578
SAMPLE CHAMBER TEMP(K) = 297.15
VOLUME ADSORBED (ML) S.T.P. = 357.6755
INITIAL CHARGE PRES Z = 0.99967
EQUILIBRIUM PRES Z = 0.99979
FINAL CHARGE PRES Z = 0.99971
(ML)S.T.P./GM OF ZEOLITE = 10.905

POINT NO: 13

INITIAL CHARGE PRES (TORR) = 1546
MOLES ADDED (GM MOL*10**3) = 3.0567
FINAL CHARGE PRES (TORR) = 1184.3
TOTAL MOLES (GM MOL*10**3) = 26.0751
CHARGE CHAMBER TEMP(K) = 297.15
MOLES IN GAS PHASE (GM MOL*10**3) = 8.2277
EQUILIBRIUM PRES (TORR) = 959.0
MOLES ADSORBED (GM MOL*10**3) = 17.8413
SAMPLE CHAMBER TEMP(K) = 297.15
VOLUME ADSORBED (ML) S.T.P. = 400.0292
INITIAL CHARGE PRES Z = 0.99969
EQUILIBRIUM PRES Z = 0.99975
FINAL CHARGE PRES Z = 0.99969
(ML)S.T.P./GM OF ZEOLITE = 12.196

POINT NO: 14

INITIAL CHARGE PRES (TORR) = 1551
MOLES ADDED (GM MOL*10**3) = 3.1440
FINAL CHARGE PRES (TORR) = 1184.3
TOTAL MOLES (GM MOL*10**3) = 29.2192
CHARGE CHAMBER TEMP(K) = 297.15
MOLES IN GAS PHASE (GM MOL*10**3) = 9.8060
EQUILIBRIUM PRES (TORR) = 1142.9
MOLES ADSORBED (GM MOL*10**3) = 19.4132
SAMPLE CHAMBER TEMP(K) = 297.15
VOLUME ADSORBED (ML) S.T.P. = 435.1248
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<tr>
<th>POINT NO: 15</th>
<th>INITIAL CHARGE PRES (TORR) = 2063</th>
<th>FINAL CHARGE PRES (TORR) = 1463.5</th>
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<tr>
<td>CHARGE CHAMBER TEMP (K) = 298.15</td>
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<tr>
<td>SAMPLE CHAMBER TEMP (K) = 297.15</td>
<td>MOLES IN GAS PHASE (GMOL*10**3) = 11.9363</td>
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<tr>
<td>INITIAL CHARGE PRES Z = 0.99947</td>
<td>MOLES ADSORBED (GMOL*10**3) = 22.4046</td>
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<tr>
<td>FINAL CHARGE PRES Z = 0.99962</td>
<td>VOLUME ADSORBED (ML) S.T.P. = 502.1730</td>
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<tr>
<td>MOLES ADDED (GM MOL*10**3) = 5.1217</td>
<td>EQUILIBRIUM PRES Z = 0.99964</td>
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<tr>
<td>TOTAL MOLES (GM MOL*10**3) = 34.3408</td>
<td>(ML) S.T.P./GM OF ZEOLITE = 13.266</td>
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<tr>
<td>MOLES IN GAS PHASE (GMOL*10**3) = 11.9363</td>
<td>MOLES ADSORBED (GMOL*10**3) = 22.4046</td>
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<tr>
<td>SAMPLE CHAMBER TEMP (K) = 297.15</td>
<td>VOLUME ADSORBED (ML) S.T.P. = 502.1730</td>
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<tr>
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<td>FINAL CHARGE PRES Z = 0.99962</td>
<td>(ML) S.T.P./GM OF ZEOLITE = 13.266</td>
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<tr>
<th>POINT NO: 16</th>
<th>INITIAL CHARGE PRES (TORR) = 2322</th>
<th>FINAL CHARGE PRES (TORR) = 1892.8</th>
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<tr>
<td>CHARGE CHAMBER TEMP (K) = 297.15</td>
<td>EQUILIBRIUM PRES (TORR) = 1577.3</td>
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<tr>
<td>SAMPLE CHAMBER TEMP (K) = 297.15</td>
<td>MOLES IN GAS PHASE (GMOL*10**3) = 13.5346</td>
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<tr>
<td>INITIAL CHARGE PRES Z = 0.99940</td>
<td>MOLES ADSORBED (GMOL*10**3) = 24.4835</td>
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</tr>
<tr>
<td>FINAL CHARGE PRES Z = 0.99951</td>
<td>VOLUME ADSORBED (ML) S.T.P. = 548.7704</td>
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<tr>
<td>MOLES ADDED (GM MOL*10**3) = 3.6773</td>
<td>EQUILIBRIUM PRES Z = 0.99960</td>
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</tr>
<tr>
<td>TOTAL MOLES (GM MOL*10**3) = 38.0181</td>
<td>(ML) S.T.P./GM OF ZEOLITE = 16.731</td>
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<tr>
<td>MOLES IN GAS PHASE (GMOL*10**3) = 13.5346</td>
<td>MOLES ADSORBED (GMOL*10**3) = 24.4835</td>
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<tr>
<td>SAMPLE CHAMBER TEMP (K) = 297.15</td>
<td>VOLUME ADSORBED (ML) S.T.P. = 548.7704</td>
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<tr>
<td>INITIAL CHARGE PRES Z = 0.99940</td>
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<tr>
<td>FINAL CHARGE PRES Z = 0.99951</td>
<td>(ML) S.T.P./GM OF ZEOLITE = 16.731</td>
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<tr>
<th>POINT NO: 17</th>
<th>INITIAL CHARGE PRES (TORR) = 2580</th>
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<td>CHARGE CHAMBER TEMP (K) = 297.15</td>
<td>EQUILIBRIUM PRES (TORR) = 1866.9</td>
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<tr>
<td>SAMPLE CHAMBER TEMP (K) = 297.15</td>
<td>MOLES IN GAS PHASE (GMOL*10**3) = 16.0208</td>
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<tr>
<td>INITIAL CHARGE PRES Z = 0.99934</td>
<td>MOLES ADSORBED (GMOL*10**3) = 27.4040</td>
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<tr>
<td>FINAL CHARGE PRES Z = 0.99950</td>
<td>VOLUME ADSORBED (ML) S.T.P. = 614.2301</td>
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<tr>
<td>MOLES ADDED (GM MOL*10**3) = 5.4067</td>
<td>EQUILIBRIUM PRES Z = 0.99952</td>
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</tr>
<tr>
<td>TOTAL MOLES (GM MOL*10**3) = 49.9401</td>
<td>(ML) S.T.P./GM OF ZEOLITE = 18.727</td>
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</tr>
<tr>
<td>MOLES IN GAS PHASE (GMOL*10**3) = 16.0208</td>
<td>MOLES ADSORBED (GMOL*10**3) = 27.4040</td>
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</tr>
<tr>
<td>SAMPLE CHAMBER TEMP (K) = 297.15</td>
<td>VOLUME ADSORBED (ML) S.T.P. = 614.2301</td>
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<tr>
<td>INITIAL CHARGE PRES Z = 0.99934</td>
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<tr>
<td>FINAL CHARGE PRES Z = 0.99950</td>
<td>(ML) S.T.P./GM OF ZEOLITE = 18.727</td>
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<tr>
<th>POINT NO: 18</th>
<th>INITIAL CHARGE PRES (TORR) = 3097</th>
<th>FINAL CHARGE PRES (TORR) = 2337.5</th>
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<td>SAMPLE CHAMBER TEMP (K) = 297.15</td>
<td>MOLES IN GAS PHASE (GMOL*10**3) = 18.8629</td>
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<tr>
<td>INITIAL CHARGE PRES Z = 0.99921</td>
<td>MOLES ADSORBED (GMOL*10**3) = 31.0772</td>
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<tr>
<td>FINAL CHARGE PRES Z = 0.99940</td>
<td>VOLUME ADSORBED (ML) S.T.P. = 696.5603</td>
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<tr>
<td>MOLES ADDED (GM MOL*10**3) = 6.5153</td>
<td>EQUILIBRIUM PRES Z = 0.99944</td>
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<tr>
<td>TOTAL MOLES (GM MOL*10**3) = 49.9401</td>
<td>(ML) S.T.P./GM OF ZEOLITE = 21.237</td>
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</tr>
<tr>
<td>MOLES IN GAS PHASE (GMOL*10**3) = 18.8629</td>
<td>MOLES ADSORBED (GMOL*10**3) = 31.0772</td>
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<tr>
<td>SAMPLE CHAMBER TEMP (K) = 297.15</td>
<td>VOLUME ADSORBED (ML) S.T.P. = 696.5603</td>
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<tr>
<td>INITIAL CHARGE PRES Z = 0.99921</td>
<td>EQUILIBRIUM PRES Z = 0.99944</td>
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<tr>
<td>FINAL CHARGE PRES Z = 0.99940</td>
<td>(ML) S.T.P./GM OF ZEOLITE = 21.237</td>
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<tr>
<th>POINT NO: 19</th>
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<th>FINAL CHARGE PRES (TORR) = 2859.8</th>
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<tr>
<td>INITIAL CHARGE PRES Z = 0.99901</td>
<td>MOLES ADSORBED (GMOL*10**3) = 31.0772</td>
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<tr>
<td>FINAL CHARGE PRES Z = 0.99927</td>
<td>VOLUME ADSORBED (ML) S.T.P. = 696.5603</td>
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<tr>
<td>MOLES ADDED (GM MOL*10**3) = 8.6899</td>
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<tr>
<td>TOTAL MOLES (GM MOL*10**3) = 58.6300</td>
<td>(ML) S.T.P./GM OF ZEOLITE = 24.110</td>
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<tr>
<td>MOLES IN GAS PHASE (GMOL*10**3) = 18.8629</td>
<td>MOLES ADSORBED (GMOL*10**3) = 31.0772</td>
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<tr>
<td>SAMPLE CHAMBER TEMP (K) = 297.15</td>
<td>VOLUME ADSORBED (ML) S.T.P. = 696.5603</td>
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<tr>
<td>INITIAL CHARGE PRES Z = 0.99901</td>
<td>EQUILIBRIUM PRES Z = 0.99930</td>
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<tr>
<td>FINAL CHARGE PRES Z = 0.99927</td>
<td>(ML) S.T.P./GM OF ZEOLITE = 24.110</td>
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</tr>
<tr>
<td>Point No.</td>
<td>Initial Charge Pres (Torr)</td>
<td>Moles Added (Gmol*10^3)</td>
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<tr>
<td>----------</td>
<td>-----------------------------</td>
<td>--------------------------</td>
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<tr>
<td>20</td>
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**************************************************************************************************

C T241.FOR
C TERNARY EQUILIBRIUM ADSORPTION PROGRAM (AIR AT 24 C)
C G.W. MILLER
C 8 AUG 83
DIMENSION PCHAR1(IO0),TCHARC(IO0),TSAMPC(IO0),PFFINAL(IO0)
DIMENSION XMOLT0(IO0),XMOLIN(IO0),XMOLGA(IO0),XMOLAD(IO0)
DIMENSION VSTP(IO0),VOLWT(IO0),PCHAR2(IO0),Z1(IO0)
DIMENSION Z2(IO0),Z3(IO0),XN2MGA(IO0),XO2MGA(IO0),XARMGA(IO0)
DIMENSION Z4(IO0),TN2SAM(IO0),TO2SAM(IO0),TARSAM(IO0)
DIMENSION XN2ADD(IO0),XO2ADD(IO0),XARADD(IO0)
DIMENSION XN2GAS(IO0),XO2GAS(IO0),XARGAS(IO0)
DIMENSION XN2ADS(IO0),XO2ADS(IO0),XARADS(IO0)
DIMENSION VOLN2(IO0),VOLO2(IO0),VOLAR(IO0)
DIMENSION VOWTN2(IO0),VOWTO2(IO0),VOWTAR(IO0)
DIMENSION PMGAVO(IO0),XMOLRE(IO0),XN2REM(IO0)
DIMENSION XO2REM(IO0),XARREM(IO0),SEFFAC(IO0)
DIMENSION XMFO2A(IO0),XMFARA(IO0),XMFN2A(IO0)
C

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OPEN(UNIT=1,NAME='TAI241.DAT',TYPE='NEW',DISPOSE='SAVE')
OPEN(UNIT=2,NAME='TN2241.DAT',TYPE='NEW',DISPOSE='SAVE')
OPEN(UNIT=3,NAME='TO2241.DAT',TYPE='NEW',DISPOSE='SAVE')
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OPEN(UNIT=5,NAME='SEP241.DAT',TYPE='NEW',DISPOSE='SAVE')
OPEN(UNIT=7,NAME='T241.RES',TYPE='NEW',DISPOSE='SAVE')

C INPUT DATA FROM EXPERIMENT

C SAMWT-SAMPLE WEIGHT (GM)
C VCHARC-VOLUME OF THE CHARGE CHAMBER (ML)
C VSAMPC-VOLUME OF THE SAMPLE CHAMBER (ML)
C VSAMPL-VOLUME OF SAMPLE (ML)
C VSAMPI-TRUE DEAD VOLUME IN SAMPLE CHAMBER (ML)
C VOLMGA-VOLUME OF THE MGA SAMPLE CHAMBER (ML)
C PCHAR1-INITIAL CHARGE CHAMBER PRESSURE (TORR)
C PCHAR2-FINAL CHARGE CHAMBER PRESSURE (TORR)
C TCHARC-TEMP IN THE CHARGE CHAMBER (DEG C)
C TSAMPC-TEM IN THE SAMPLE CHAMBER (DEG C)
C PFINAL-EQUILIBRIUM PRESSURE IN THE SAMPLE CHAMBER (TORR)
C XN2MGA-MOLE FRACTION OF NITROGEN IN THE MGA SAMPLE VOLUME
C XO2MGA-MOLE FRACTION OF OXYGEN IN THE MGA SAMPLE VOLUME
C XARMGA-MOLE FRACTION OF ARGON IN THE MGA SAMPLE VOLUME
C PMGAVO-FINAL PRESSURE OF THE MGA SAMPLE VOLUME (TORR)

C CALCULATED VALUES

C Z1-INITIAL CHARGE CHAMBER PRESSURE Z FACTOR
C Z2-FINAL CHARGE CHAMBER PRESSURE Z FACTOR
C Z3=EQUILIBRIUM PRESSURE Z FACTOR
C Z4=MGA SAMPLE VOLUME Z FACTOR
C XMOLTO-TOTAL MOLES IN SAMPLE CHAMBER (GM MOL)
C TN2SAM-TOTAL MOLES OF NITROGEN IN THE SAMPLE CHAMBER (GM MOL)
C TO2SAM-TOTAL MOLES OF OXYGEN IN THE SAMPLE CHAMBER (GM MOL)
C TARSAM-TOTAL MOLES OF ARGON IN THE SAMPLE CHAMBER (GM MOL)
C XMOLIN-MOLES ADDED (GM MOL)
C XN2ADD-MOLES OF NITROGEN ADDED (GM MOL)
C XO2ADD-MOLES OF OXYGEN ADDED (GM MOL)
C XARADD-MOLES OF ARGON ADDED (GM MOL)
C XMOLGA-MOLE IN GAS PHASE (GM MOL)
C XN2GAS-MOLES OF NITROGEN IN THE GAS PHASE (GM MOL)
C XO2GAS-MOLES OF OXYGEN IN THE GAS PHASE (GM MOL)
C XARGAS-MOLES OF ARGON IN THE GAS PHASE (GM MOL)
C XMOLAD-MOLE ADSORBED (GM MOL)
C XN2ADS-MOLES OF NITROGEN ADSORBED (GM MOL)
C XO2ADS-MOLES OF OXYGEN ADSORBED (GM MOL)
C XARADS-MOLES OF ARGON ADSORBED (GM MOL)
C XMFN2A-MOLE FRACTION OF NITROGEN ADSORBED
C XMFO2A-MOLE FRACTION OF OXYGEN ADSORBED

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XMFARA=MOLE FRACTION OF ARGON ADSORBED
C VSTP=VOLUME ADSORBED (ML STP)
C VOLN2=VOLUME OF NITROGEN ADSORBED (ML STP)
C VLO2=VOLUME OF OXYGEN ADSORBED (ML STP)
C VOLAR=VOLUME OF ARGON ADSORBED (ML STP)
C VOLWT=VOLUME ADSORBED (ML STP)/WEIGHT OF SAMPLE (GM)
C VWTN2=VOLUME NITROGEN ADSORBED (ML STP)/WEIGHT OF SAMPLE (GM)
C WWT02=VOLUME OXYGEN ADSORBED (ML STP)/WEIGHT OF SAMPLE (GM)
C WWTAR=VOLUME ARGON ADSORBED (ML STP)/WEIGHT OF SAMPLE (GM)
C SEPFAC=SEPARATION FACTOR BETWEEN NITROGEN AND OXYGEN NEGLECTING ARGON.

NDATA=9
SAMWT=32.8
R=82.057
VCHARC=158.6
VSAMPC=170.0
VSAMPL=11.05
VSAMPT=VSAMPC-VSAMPL
VOLWGT=12.9484
AIRN2=0.7814
AIRO2=0.2092
AIRAR=0.0094

INPUT: EXPERIMENT NO.

PCHAR1(1)=763.1
PCHAR1(2)=1034.3
PCHAR1(3)=1789.3
PCHAR1(4)=2311.6
PCHAR1(5)=2802.9
PCHAR1(6)=3351.1
PCHAR1(7)=3868.3
PCHAR1(8)=3868.3
PCHAR1(9)=3868.3

PCHAR2(1)=189.
PCHAR2(2)=413.7
PCHAR2(3)=1142.9
PCHAR2(4)=1520.4
PCHAR2(5)=1856.6
PCHAR2(6)=1949.6
PCHAR2(7)=2534.
PCHAR2(8)=2901.2
PCHAR2(9)=3180.5

PFINAL(1)=169.
PFINAL(2)=372.
PFINAL(3)=585.
PFINAL(4)=882.
PFINAL(5)=1251.5
PFINAL(6)=1835.9
PFINAL(7)=2404.7
PFINAL(8)=2802.9
PFINAL(9)=3051.2

TCHARC(1)=25.
TCHARC(2)=24.
TCHARC(3)=25.
TCHARC(4)=24.
TCHARC(5)=25.
TCHARC(6)=24.
TCHARC(7)=24.
TCHARC(8)=24.
TCHARC(9)=24.

TSAMPC(1)=24.
TSAMPC(2)=25.
TSAMPC(3)=24.
TSAMPC(4)=25.
TSAMPC(5)=24.
TSAMPC(6)=24.
TSAMPC(7)=24.
TSAMPC(8)=24.
TSAMPC(9)=24.

XN2MGA(1)=0.5973
XN2MGA(2)=0.6157
XN2MGA(3)=0.6289
XN2MGA(4)=0.6457
XN2MGA(5)=0.6536
XN2MGA(6)=0.6705
XN2MGA(7)=0.6832
XN2MGA(8)=0.6906
XN2MGA(9)=0.6962

XO2MGA(1)=0.3847
XO2MGA(2)=0.3666
XO2MGA(3)=0.3551
XO2MGA(4)=0.3390
XO2MGA(5)=0.3314
XO2MGA(6)=0.3150
XO2MGA(7)=0.3031
XO2MGA(8)=0.2961
XO2MGA(9)=0.2907

XARMGA(1)=0.0180
XARMGA(2)=0.0177
XARMGA(3) = 0.0160
XARMGA(4) = 0.0153
XARMGA(5) = 0.0150
XARMGA(6) = 0.0145
XARMGA(7) = 0.0137
XARMGA(8) = 0.0133
XARMGA(9) = 0.0131

C
PMGAO(1) = 164.
PMGAO(2) = 359.
PMGAO(3) = 564.
PMGAO(4) = 847.
PMGAO(5) = 1205.
PMGAO(6) = 1753.1
PMGAO(7) = 2291.
PMGAO(8) = 2663.3
PMGAO(9) = 2890.9

C
DO100 J = 1, NDATA
TCAR(J) = TCHARC(J) + 273.15
TSAMPC(J) = TSAMPC(J) + 273.15
100 CONTINUE
TOTAL = 0.
T0N2 = 0.
TOTAL = 0.

C
DO101 J = 1, NDATA
Z1(J) = (-4.204836514E-07*PCHAR1(J)) + 1.00000
XMOL1 = ((PCHAR1(J)/760.)*VCHARC)/(R*TSAMPC(J)*Z1(J))
Z2(J) = (-4.204836514E-07*PCHAR2(J)) + 1.00000
XMOL2 = ((PCHAR2(J)/760.)*VCHARC)/(R*TSAMPC(J)*Z2(J))
XMOLTO(J) = TOTAL + XMOLIN(J)
TOTAL = XMOLTO(J)
XN2ADD(J) = AIRN2*XMOIN(J)
XO2ADD(J) = AIRO2*XMOIN(J)
XARADD(J) = AIRAR*XMOIN(J)
TN2SAM(J) = TOTN2 + XN2ADD(J)
TOTN2 = TN2SAM(J)
TO2SAM(J) = TOTO2 + XO2ADD(J)
TOTO2 = TO2SAM(J)
TARSAM(J) = TOTAR + XARADD(J)
TOTAR = TARSAM(J)
ZPURN2 = (-2.565068585E-07*PFINAL(J)) + 1.00000
ZPURO2 = (-8.33333328077E-07*PFINAL(J)) + 1.00000
ZPURAR = (-8.617666817E-07*PFINAL(J)) + 1.00000
Z3(J) = (ZPURN2*XN2MGA(J)) + (ZPURO2*XO2MGA(J)) + (ZPURAR*XARMGA(J))
XMOLGA(J) = ((PFINAL(J)/760.)*VSAMPT)/(R*TSAMPC(J)*Z3(J))
XN2GAS(J) = XMOLGA(J) * XN2MGA(J)  
XO2GAS(J) = XMOLGA(J) * XO2MGA(J)  
XARGAS(J) = XMOLGA(J) * XARMGA(J)  
XMOLAD(J) = XMOLTO(J) - XMOLGA(J)  
XN2ADS(J) = TN2SAM(J) - XN2GAS(J)  
XO2ADS(J) = TO2SAM(J) - XO2GAS(J)  
XARADS(J) = TARSAM(J) - XARGAS(J)  
XMFNA2(J) = XN2ADS(J) / XMULAD(J)  
XMFO2A(J) = XO2ADS(J) / XMOLAD(J)  
XMFARA(J) = XARADS(J) / XMOLAD(J)  
VSTP(J) = XMOLAD(J) * R * 273.15  
VOLN2(J) = XN2ADS(J) * R * 273.15  
VLOO2(J) = XO2ADS(J) * R * 273.15  
VOLAR(J) = XARADS(J) * R * 273.15  
VOLWT(J) = VSTP(J) / SAMWT  
VOWTN2(J) = VOLN2(J) / SAMWT  
VOT02(J) = VLOO2(J) / SAMWT  
VOTAR(J) = VOLAR(J) / SAMWT  
ZPURN2(J) = (-2.565068585E-07 * PMGAVOCJ) + 1.00000  
ZPUR02(J) = (-8.333332807E-07 * PMGAVOCJ) + 1.00000  
ZPURAR(J) = (-8.617667817E-07 * PMGAVOCJ) + 1.00000  
Z4(J) = (ZPURN2 * XN2MGA(J)) + (ZPUR02 * XO2MGA(J)) + (ZPURAR * XARMGA(J))  
XMOLRE(J) = ((PMGAVOCJ / 760.) * VOLMGA) / (R * TSAMPC(J) * ZkI(J))  
XN2REM(J) = XN2MGA(J) * XMOLRE(J)  
XO2REM(J) = XO2MGA(J) * XMOLRE(J)  
XARREM(J) = XARMGA(J) * XMOLRE(J)  
TOTAL - TOTAL = XMOLRE(J)  
TOTN2 = TOTN2 - XN2REM(J)  
TOT02 = TOT02 - XO2REM(J)  
TOTAR = TOTAR - XARREM(J)  
XX1 = XO2MGA(J) * XARMGA(J)  
XX2 = XMFO2A(J) * XMFARA(J)  
SEPFAC(J) = (XMFN2A(J) * XX1) / (XN2MGA(J) * XX2)
XO2ADS(J) = XO2ADS(J)*1000.
XARADS(J) = XARADS(J)*1000.
XMOLRE(J) = XMOLRE(J)*1000.
XN2REM(J) = XN2REM(J)*1000.
XO2REM(J) = XO2REM(J)*1000.
XARREM(J) = XARREM(J)*1000.

103 CONTINUE
   WRITE(7,15)
15 FORMAT(/,1X,'G.W.MILLER')
   WRITE(7,18)
18 FORMAT(1X,'USAF SCHOOL OF AEROSPACE MEDICINE')
   WRITE(7,19)
19 FORMAT(1X,'CREW TECHNOLOGY DIVISION')
   WRITE(7,20)
20 FORMAT(1X,'BROOKS AFB,Texas')
   WRITE(7,16)
16 FORMAT(/,1X,' ADSORPTION ISOTHERM EXPERIMENT NO.5')
   WRITE(7,1)
1  FORMAT(1X,'AIR ON UNION CARBIDE ZEOLITE 5A (20X40 MESH) AT 24 D
    1EG C')
   WRITE(7,2) NDATA
2 FORMAT(/,1X,'NUMBER OF DATA POINTS=',I3)
   WRITE(7,3) SAMWT
3 FORMAT(1X,'SAMPLE WEIGHT (GM)=',F6.1)
   WRITE(7,4) VCHARC
4 FORMAT(1X,'VOLUME OF CHARGE CHAMBER (ML)=',F6.1)
   WRITE(7,5) VSAMPC
5 FORMAT(1X,'VOLUME OF SAMPLE CHAMBER W/O ZEOLITE (ML)=',F6.1)
   WRITE(7,6) VSAMPL
6 FORMAT(1X,'VOLUME OF SAMPLE CHAMBER W/O SAMPLE (ML)=',F6.1)
   WRITE(7,7) VSAMPT
7 FORMAT(1X,'TRUE DEAD VOLUME OF SAMPLE CHAMBER (ML)=',F6.1)
   WRITE(7,8) AIRN2
850 FORMAT(1X,'MOLE FRACTION OF NITROGEN IN THE BOTTLED AIR=',,F7.4)
851 FORMAT(1X,'MOLE FRACTION OF OXYGEN IN THE BOTTLED AIR=',,F7.4)
   WRITE(7,8) AIR02
651 FORMAT(1X,'MOLE FRACTION OF ARGON IN THE BOTTLED AIR=',,F7.4)
   WRITE(7,8) AIRAR
852 FORMAT(1X,'MOLE FRACTION OF ARGON IN THE BOTTLED AIR=',,F7.4)
   WRITE(7,8) AIRAR
300 FORMAT(/,1X,'**********************************************************************')
   WRITE(7,8) AIRAR
301 FORMAT(1X,'**********************************************************************')
   WRITE(7,8) AIRAR
   DO105 J=1,NDATA
   WRITE(7,8) J
8 FORMAT(/,1X,'POINT NO=',I3,/)
WRITE(7,700) PCHAR1(J)
700 FORMAT(1X,'INITIAL CHARGE PRESSURE (TORR)=' ,F7.1)
WRITE(7,701) PCHAR2(J)
701 FORMAT(1X,'FINAL CHARGE PRESSURE (TORR)=' ,F7.1)
WRITE(7,702) TCHARG(J)
702 FORMAT(1X,'TEMPERATURE OF THE CHARGE CHAMBER (K)=' ,F7.2)
WRITE(7,706) HFINAL(J)
706 FORMAT(1X,'EQUILIBRIUM PRESSURE (TORR)=' ,F7.1)
WRITE(7,707) TSAMPC(J)
707 FORMAT(1X,'TEMPERATURE OF THE SAMPLE CHAMBER (K)=' ,F7.2)
WRITE(7,709) XN2MGA(J)
709 FORMAT(1X,'MOLE FRACTION NITROGEN IN THE MGA SAMPLE=' ,1X,F6.4)
WRITE(7,710) XO2MGA(J)
710 FORMAT(1X,'MOLE FRACTION OXYGEN IN THE MGA SAMPLE=' ,1X,F6.4)
WRITE(7,711) XARMGA(J)
711 FORMAT(1X,'MOLE FRACTION ARGON IN THE MGA SAMPLE=' ,1X,F6.4)
WRITE(7,712) PMGAVO(J)
712 FORMAT(1X,'MGA SAMPLE VOLUME PRESSURE (TORR)=' ,F7.1)
WRITE(7,713) Z1(J)
713 FORMAT(1X,'INITIAL CHARGE PRESSURE Z=' ,F8.5)
WRITE(7,714) Z2(J)
714 FORMAT(1X,'FINAL CHARGE PRESSURE Z=' ,F8.5)
WRITE(7,715) Z3(J)
715 FORMAT(1X,'EQUILIBRIUM PRESSURE Z=' ,F8.5)
WRITE(7,716) Z4(J)
716 FORMAT(1X,'MGA SAMPLE CHAMBER Z=' ,F8.5)
WRITE(7,717) XN2ADD(J)
717 FORMAT(1X,'MOLES OF NITROGEN ADDED (GM MOL*10**3)=' ,F10.4)
WRITE(7,718) XO2ADD(J)
718 FORMAT(1X,'MOLES OF OXYGEN ADDED (GM MOL*10**3)=' ,F10.4)
WRITE(7,719) XARADD(J)
719 FORMAT(1X,'MOLES OF ARGON ADDED (GM MOL*10**3)=' ,F10.4)
WRITE(7,720) XMOLIN(J)
720 FORMAT(1X,'TOTAL MOLES ADDED (GM MOL*10**3)=' ,F10.4)
WRITE(7,721) TNS2SAM(J)
721 FORMAT(1X,'TOTAL MOLES OF NITROGEN IN THE SAMPLE CHAMBER (GM MO L*10**3)=' ,F10.4)
WRITE(7,722) T02SAM(J)
722 FORMAT(1X,'TOTAL MOLES OF OXYGEN IN THE SAMPLE CHAMBER (GM MOL* 10**3)=' ,F10.4)
WRITE(7,723) TARSAM(J)
723 FORMAT(1X,'TOTAL MOLES OF ARGON IN THE SAMPLE CHAMBER (GM MOL*1 10**3)=' ,F10.4)
WRITE(7,724) XMOLTO(J)
724 FORMAT(1X,'TOTAL MOLES IN THE SAMPLE CHAMBER (GM MOL*10**3)=' ,F 110.4)
WRITE(7,725) XN2GAS(J)
270
725 FORMAT(1X,'MOLES OF NITROGEN IN THE GAS PHASE (GM MOL*10**3) = ', 1F10.4)
WRITE(7,726) XO2GAS(J)
726 FORMAT(1X,'MOLES OF OXYGEN IN THE GAS PHASE (GM MOL*10**3) = ', F10.4)
WRITE(7,727) XARGS(J)
727 FORMAT(1X,'MOLES OF ARGON IN THE GAS PHASE (GM MOL*10**3) = ', F10.4)
WRITE(7,728) XMOLGA(J)
728 FORMAT(1X,'TOTAL MOLES IN THE GAS PHASE (GM MOL*10**3) = ', F10.4)
WRITE(7,1451) XN2MGA(J)
729 FORMAT(1X,'MOLE FRACTION OF NITROGEN IN THE GAS PHASE = ', 2X, F6.14)
WRITE(7,730) XO2ADS(J)
730 FORMAT(1X,'MOLES OF NITROGEN ADSORBED (GM MOL*10**3) = ', F10.4)
WRITE(7,731) XARADS(J)
731 FORMAT(1X,'MOLES OF ARGON ADSORBED (GM MOL*10**3) = ', F10.4)
WRITE(7,732) XMOLAD(J)
732 FORMAT(1X,'TOTAL MOLES ADSORBED (GM MOL*10**3) = ', F10.4)
WRITE(7,733) XMFN2A(J)
733 FORMAT(1X,'MOLE FRACTION OF NITROGEN ADSORBED = ', 2X, F6.14)
WRITE(7,734) XMFO2A(J)
734 FORMAT(1X,'MOLE FRACTION OF OXYGEN ADSORBED = ', 2X, F6.14)
WRITE(7,735) XMFARA(J)
735 FORMAT(1X,'MOLE FRACTION OF ARGON ADSORBED = ', 2X, F6.14)
WRITE(7,736) VOLN2(J)
736 FORMAT(1X,'VOLUME OF NITROGEN ADSORBED (ML STP) = ', F10.3)
WRITE(7,737) VOLO2(J)
737 FORMAT(1X,'VOLUME OF OXYGEN ADSORBED (ML STP) = ', F10.3)
WRITE(7,738) VOLAR(J)
738 FORMAT(1X,'VOLUME OF ARGON ADSORBED (ML STP) = ', F10.3)
WRITE(7,739) VSTP(J)
739 FORMAT(1X,'TOTAL VOLUME ADSORBED (ML STP) = ', F10.3)
WRITE(7,740) VOWTN2(J)
740 FORMAT(1X,'VOLUME OF NITROGEN ADSORBED (ML STP/GM) = ', F9.3)
WRITE(7,741) VOWTO2(J)
741 FORMAT(1X,'VOLUME OF OXYGEN ADSORBED (ML STP/GM) = ', F9.3)
WRITE(7,742) VOWTAR(J)
742 FORMAT(1X,'VOLUME OF ARGON ADSORBED (ML STP/GM) = ', F9.3)
WRITE(7,743) VOLWT(J)
743 FORMAT(1X,'TOTAL VOLUME ADSORBED (ML STP/GM) = ', F9.3)
271
WRITE(7,754) X02REM(J)
754 FORMAT(1X,'MOLES OF OXYGEN REMOVED BY THE MGA (GM MOL*10**3)=', F10.5)
WRITE(7,755) XARREM(J)
755 FORMAT(1X,'MOLES OF ARGON REMOVED BY THE MGA (GM MOL*10**3)=', F110.5)
WRITE(7,756) XMOLRE(J)
756 FORMAT(1X,'TOTAL MOLES REMOVED BY THE MGA (GM MOL*10**3)=', F10.15)
WRITE(7,777) SEPFAC(J)
777 FORMAT(/,1X,'SEPARATION FACTOR BETWEEN NITROGEN AND OXYGEN=', F7.13)
WRITE(7,320)
320 FORMAT(1X, '************ DEFAULT VALUES ************')
105 CONTINUE
DO555 J=1,NDATA
WRITE(1,551) PFINAL(J),VOLWT(J)
551 FORMAT(F7.0,3X,F8.3)
555 CONTINUE
DO556 J=1,NDATA
WRITE(2,551) PFINAL(J),VOWTN2(J)
556 CONTINUE
DO557 J=1,NDATA
WRITE(3,551) PFINAL(J), VOWTO2(J)
557 CONTINUE
DO558 J=1,NDATA
WRITE(4,551) PFINAL(J), VOWTAR(J)
558 CONTINUE
DO559 J=1,NDATA
WRITE(5,551) PFINAL(J), SEPFAC(J)
559 CONTINUE
STOP
END

*********************************************************
T241.RES
G.W.MILLER
USAF SCHOOL OF AEROSPACE MEDICINE
CREW TECHNOLOGY DIVISION
BROOKS AFB,Texas

ADSORPTION ISOHERM EXPERIMENT NO.5
AIR ON UNION CARBIDE ZEOLITE 5A (20X40 MESH) AT 24 DEG C

272
NUMBER OF DATA POINTS = 9
SAMPLE WEIGHT (GM) = 32.8
VOLUME OF CHARGE CHAMBER (ML) = 158.6
VOLUME OF SAMPLE CHAMBER W/O ZEOLITE (ML) = 170.0
TRUE VOLUME OF SAMPLE (ML) = 11.05
MGA SAMPLE VOLUME (ML) = 12.95
TRUE DEAD VOLUME OF SAMPLE CHAMBER (ML) = 158.9
MOLE FRACTION OF NITROGEN IN THE BOTTLED AIR = 0.7814
MOLE FRACTION OF OXYGEN IN THE BOTTLED AIR = 0.2092
MOLE FRACTION OF ARGON IN THE BOTTLED AIR = 0.0094

POINT NO: 1

INPUT:
INITIAL CHARGE PRESSURE (TORR) = 763.0
FINAL CHARGE PRESSURE (TORR) = 189.0
TEMPERATURE OF THE CHARGE CHAMBER (K) = 298.15
EQUILIBRIUM PRESSURE (TORR) = 169.0
TEMPERATURE OF THE SAMPLE CHAMBER (K) = 297.15
MOLE FRACTION NITROGEN IN THE MGA SAMPLE = 0.5973
MOLE FRACTION OXYGEN IN THE MGA SAMPLE = 0.3847
MOLE FRACTION ARGON IN THE MGA SAMPLE = 0.0180
MGA SAMPLE VOLUME PRESSURE (TORR) = 164.0

OUTPUT:
INITIAL CHARGE PRESSURE Z = 0.99968
FINAL CHARGE PRESSURE Z = 0.99992
EQUILIBRIUM PRESSURE Z = 0.99992
MGA SAMPLE CHAMBER Z = 0.99992

MOLES OF NITROGEN ADDED (GM MOL*10**3) = 3.8274
MOLES OF OXYGEN ADDED (GM MOL*10**3) = 1.0247
MOLES OF ARGON ADDED (GM MOL*10**3) = 0.0460
TOTAL MOLES ADDED (GM MOL*10**3) = 4.8981

TOTAL MOLES OF NITROGEN IN THE SAMPLE CHAMBER (GM MOL*10**3) = 3.8274
TOTAL MOLES OF OXYGEN IN THE SAMPLE CHAMBER (GM MOL*10**3) = 1.0247
TOTAL MOLES OF ARGON IN THE SAMPLE CHAMBER (GM MOL*10**3) = 0.0460
TOTAL MOLES IN THE SAMPLE CHAMBER (GM MOL*10**3) = 4.8981

MOLES OF NITROGEN IN THE GAS PHASE (GM MOL*10**3) = 0.8659
MOLES OF OXYGEN IN THE GAS PHASE (GM MOL*10**3) = 0.5577
MOLES OF ARGON IN THE GAS PHASE (GM MOL*10**3) = 0.0261
TOTAL MOLES IN THE GAS PHASE (GM MOL*10**3) = 1.4497
MOLE FRACTION OF NITROGEN IN THE GAS PHASE = 0.5973
MOLE FRACTION OF OXYGEN IN THE GAS PHASE = 0.3847
MOLE FRACTION OF ARGON IN THE GAS PHASE = 0.0180

MOLES OF NITROGEN ADSORBED (GM MOL*10**3) = 2.9614
MOLES OF OXYGEN ADSORBED (GM MOL*10**3) = 0.4670
<table>
<thead>
<tr>
<th>MOLES OF ARGON ADSORBED (GM MOL*10**3)</th>
<th>0.0199</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOTAL MOLES ADSORBED (GM MOL*10**3)</td>
<td>3.4484</td>
</tr>
<tr>
<td>MOLE FRACTION OF NITROGEN ADSORBED= 0.8588</td>
<td></td>
</tr>
<tr>
<td>MOLE FRACTION OF OXYGEN ADSORBED= 0.1354</td>
<td></td>
</tr>
<tr>
<td>MOLE FRACTION OF ARGON ADSORBED= 0.0058</td>
<td></td>
</tr>
</tbody>
</table>

| VOLUME OF NITROGEN ADSORBED (ML STP)= 66.377 |
| VOLUME OF OXYGEN ADSORBED (ML STP)= 10.467 |
| VOLUME OF ARGON ADSORBED (ML STP)= 0.447 |
| TOTAL VOLUME ADSORBED (ML STP)= 77.291 |

| VOLUME OF NITROGEN ADSORBED (ML STP/GM)= 2.024 |
| VOLUME OF OXYGEN ADSORBED (ML STP/GM)= 0.319 |
| VOLUME OF ARGON ADSORBED (ML STP/GM)= 0.014 |
| TOTAL VOLUME ADSORBED (ML STP/GM)= 2.356 |

| MOLES OF NITROGEN REMOVED BY THE MGA (GM MOL*10**3)= 0.06845 |
| MOLES OF OXYGEN REMOVED BY THE MGA (GM MOL*10**3)= 0.04409 |
| MOLES OF ARGON REMOVED BY THE MGA (GM MOL*10**3)= 0.00206 |
| TOTAL MOLES REMOVED BY THE MGA (GM MOL*10**3)= 0.11460 |

| SEPARATION FACTOR BETWEEN NITROGEN AND OXYGEN= 4.100 |

**Point No: 2**

**Input:**
- INITIAL CHARGE PRESSURE (TORR)= 1034.3
- FINAL CHARGE PRESSURE (TORR)= 413.7
- TEMPERATURE OF THE CHARGE CHAMBER (K)= 297.15
- EQUILIBRIUM PRESSURE (TORR)= 372.0
- TEMPERATURE OF THE SAMPLE CHAMBER (K)= 298.15
- MOLE FRACTION NITROGEN IN THE MGA SAMPLE= 0.6157
- MOLE FRACTION OXYGEN IN THE MGA SAMPLE= 0.3666
- MOLE FRACTION ARGON IN THE MGA SAMPLE= 0.0177
- MGA SAMPLE VOLUME PRESSURE (TORR)= 359.0

**Output:**
- INITIAL CHARGE PRESSURE Z= 0.99957
- FINAL CHARGE PRESSURE Z= 0.99983
- EQUILIBRIUM PRESSURE Z= 0.99982
- MGA SAMPLE CHAMBER Z= 0.99983

| MOLES OF NITROGEN ADDED (GM MOL*10**3)= 4.1529 |
| MOLES OF OXYGEN ADDED (GM MOL*10**3)= 1.1118 |
| MOLES OF ARGON ADDED (GM MOL*10**3)= 0.0500 |
| TOTAL MOLES ADDED (GM MOL*10**3)= 5.3146 |

| TOTAL MOLES OF NITROGEN IN THE SAMPLE CHAMBER (GM MOL*10**3)= 7.9118 |
| TOTAL MOLES OF OXYGEN IN THE SAMPLE CHAMBER (GM MOL*10**3)= 2.0924 |
| TOTAL MOLES OF ARGON IN THE SAMPLE CHAMBER (GM MOL*10**3)= 0.0939 |

274
TOTAL MOLES IN THE SAMPLE CHAMBER (GM MOL*10**3)= 10.0981
MOLES OF NITROGEN IN THE GAS PHASE (GM MOL*10**3)= 1.9583
MOLES OF OXYGEN IN THE GAS PHASE (GM MOL*10**3)= 1.1660
MOLES OF ARGON IN THE GAS PHASE (GM MOL*10**3)= 0.0563
TOTAL MOLES IN THE GAS PHASE (GM MOL*10**3)= 3.1807
MOLE FRACTION OF NITROGEN IN THE GAS PHASE= 0.6157
MOLE FRACTION OF OXYGEN IN THE GAS PHASE= 0.3666
MOLE FRACTION OF ARGON IN THE GAS PHASE= 0.0177
MOLES OF NITROGEN ADSORBED (GM MOL*10**3)= 5.9534
MOLES OF OXYGEN ADSORBED (GM MOL*10**3)= 0.9264
MOLES OF ARGON ADSORBED (GM MOL*10**3)= 0.0376
TOTAL MOLES ADSORBED (GM MOL*10**3)= 6.9175
MOLE FRACTION OF NITROGEN ADSORBED= 0.8606
MOLE FRACTION OF OXYGEN ADSORBED= 0.1339
MOLE FRACTION OF ARGON ADSORBED= 0.0054
VOLUME OF NITROGEN ADSORBED (ML STP)= 133.440
VOLUME OF OXYGEN ADSORBED (ML STP)= 20.764
VOLUME OF ARGON ADSORBED (ML STP)= 8.444
TOTAL VOLUME ADSORBED (ML STP)= 155.047
VOLUME OF NITROGEN ADSORBED (ML STP/GM)= 4.068
VOLUME OF OXYGEN ADSORBED (ML STP/GM)= 0.633
VOLUME OF ARGON ADSORBED (ML STP/GM)= 0.026
TOTAL VOLUME ADSORBED (ML STP/GM)= 4.727
MOLES OF NITROGEN REMOVED BY THE MGA (GM MOL*10**3)= 0.15395
MOLES OF OXYGEN REMOVED BY THE MGA (GM MOL*10**3)= 0.09167
MOLES OF ARGON REMOVED BY THE MGA (GM MOL*10**3)= 0.00443
TOTAL MOLES REMOVED BY THE MGA (GM MOL*10**3)= 0.25005
SEPARATION FACTOR BETWEEN NITROGEN AND OXYGEN= 3.855
POINT NO: 3
INPUT:
INITIAL CHARGE PRESSURE (TORR)= 1789.3
FINAL CHARGE PRESSURE (TORR)= 1142.9
TEMPERATURE OF THE CHARGE CHAMBER (K)= 298.15
EQUILIBRIUM PRESSURE (TORR)= 585.0
TEMPERATURE OF THE SAMPLE CHAMBER (K)= 297.15
MOLE FRACTION NITROGEN IN THE MGA SAMPLE= 0.6289
MOLE FRACTION OXYGEN IN THE MGA SAMPLE= 0.3551
MOLE FRACTION ARGON IN THE MGA SAMPLE= 0.0160
MGA SAMPLE VOLUME PRESSURE (TORR)= 564.0
OUTPUT:
INITIAL CHARGE PRESSURE Z= 0.99925
275
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<tr>
<th>Parameter</th>
<th>Value</th>
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<td>Final charge pressure</td>
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<td>Equilibrium pressure</td>
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<td>MGA sample chamber pressure</td>
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<td>Moles of nitrogen added (GM mol*10**3)</td>
<td>4.3137</td>
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<td>Moles of oxygen added (GM mol*10**3)</td>
<td>1.1549</td>
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<tr>
<td>Moles of argon added (GM mol*10**3)</td>
<td>0.0519</td>
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<td>Total moles added (GM mol*10**3)</td>
<td>5.5205</td>
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<td>Total moles of nitrogen in the sample chamber (GM mol*10**3)</td>
<td>3.0715</td>
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<tr>
<td>Total moles of oxygen in the sample chamber (GM mol*10**3)</td>
<td>1.7823</td>
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<tr>
<td>Total moles of argon in the sample chamber (GM mol*10**3)</td>
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<td>Moles of nitrogen in the gas phase (GM mol*10**3)</td>
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<td>Moles of oxygen in the gas phase (GM mol*10**3)</td>
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<td>Moles of argon in the gas phase (GM mol*10**3)</td>
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<td>Total moles in the gas phase (GM mol*10**3)</td>
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<td>Mole fraction of nitrogen in the gas phase</td>
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<td>Mole fraction of oxygen in the gas phase</td>
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<td>Mole fraction of argon in the gas phase</td>
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<td>Moles of nitrogen adsorbed (GM mol*10**3)</td>
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<td>Moles of oxygen adsorbed (GM mol*10**3)</td>
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<td>Moles of argon adsorbed (GM mol*10**3)</td>
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<td>Mole fraction of nitrogen adsorbed</td>
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<td>Mole fraction of oxygen adsorbed</td>
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<td>Mole fraction of argon adsorbed</td>
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<td>Volume of nitrogen adsorbed (ML STP)</td>
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<td>Volume of oxygen adsorbed (ML STP)</td>
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<td>Volume of argon adsorbed (ML STP)</td>
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<td>Total volume adsorbed (ML STP)</td>
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<td>Volume of nitrogen adsorbed (ML STP/GM)</td>
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<td>Volume of oxygen adsorbed (ML STP/GM)</td>
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<td>Volume of argon adsorbed (ML STP/GM)</td>
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<td>Total volume adsorbed (ML STP/GM)</td>
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<td>Moles of nitrogen removed by the MGA (GM mol*10**3)</td>
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<td>Moles of oxygen removed by the MGA (GM mol*10**3)</td>
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<td>Moles of argon removed by the MGA (GM mol*10**3)</td>
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<td>Total moles removed by the MGA (GM mol*10**3)</td>
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<td>Separation factor between nitrogen and oxygen</td>
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<td>Point No: 4</td>
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276
INITIAL CHARGE PRESSURE (TORR) = 2311.6
FINAL CHARGE PRESSURE (TORR) = 1520.4
TEMPERATURE OF THE CHARGE CHAMBER (K) = 297.15
EQUILIBRIUM PRESSURE (TORR) = 882.0
TEMPERATURE OF THE SAMPLE CHAMBER (K) = 298.15
MOLE FRACTION NITROGEN IN THE MGA SAMPLE = 0.6457
MOLE FRACTION OXYGEN IN THE MGA SAMPLE = 0.3390
MOLE FRACTION ARGON IN THE MGA SAMPLE = 0.0153
MGA SAMPLE VOLUME PRESSURE (TORR) = 847.0

OUTPUT:
INITIAL CHARGE PRESSURE Z = 0.99903
FINAL CHARGE PRESSURE Z = 0.99936
EQUILIBRIUM PRESSURE Z = 0.99959
MGA SAMPLE CHAMBER Z = 0.99961

MOLES OF NITROGEN ADDED (GM MOL*10**3) = 5.2998
MOLES OF OXYGEN ADDED (GM MOL*10**3) = 1.4189
MOLES OF ARGON ADDED (GM MOL*10**3) = 0.0638
TOTAL MOLES ADDED (GM MOL*10**3) = 6.7824

TOTAL MOLES OF NITROGEN IN THE SAMPLE CHAMBER (GM MOL*10**3) = 17.1234
TOTAL MOLES OF OXYGEN IN THE SAMPLE CHAMBER (GM MOL*10**3) = 4.4345
TOTAL MOLES OF ARGON IN THE SAMPLE CHAMBER (GM MOL*10**3) = 0.1989
TOTAL MOLES IN THE SAMPLE CHAMBER (GM MOL*10**3) = 21.7568

MOLES OF NITROGEN IN THE GAS PHASE (GM MOL*10**3) = 4.8705
MOLES OF OXYGEN IN THE GAS PHASE (GM MOL*10**3) = 2.5571
MOLES OF ARGON IN THE GAS PHASE (GM MOL*10**3) = 0.1154
TOTAL MOLES IN THE GAS PHASE (GM MOL*10**3) = 7.5430
MOLE FRACTION OF NITROGEN IN THE GAS PHASE = 0.6457
MOLE FRACTION OF OXYGEN IN THE GAS PHASE = 0.3390
MOLE FRACTION OF ARGON IN THE GAS PHASE = 0.0153

MOLES OF NITROGEN ADSORBED (GM MOL*10**3) = 12.2529
MOLES OF OXYGEN ADSORBED (GM MOL*10**3) = 1.8775
MOLES OF ARGON ADSORBED (GM MOL*10**3) = 0.0834
TOTAL MOLES ADSORBED (GM MOL*10**3) = 14.2138
MOLE FRACTION OF NITROGEN ADSORBED = 0.8620
MOLE FRACTION OF OXYGEN ADSORBED = 0.1321
MOLE FRACTION OF ARGON ADSORBED = 0.0059

VOLUME OF NITROGEN ADSORBED (ML STP) = 274.635
VOLUME OF OXYGEN ADSORBED (ML STP) = 42.081
VOLUME OF ARGON ADSORBED (ML STP) = 1.870
TOTAL VOLUME ADSORBED (ML STP) = 318.586

VOLUME OF NITROGEN ADSORBED (ML STP/GM) = 8.373
VOLUME OF OXYGEN ADSORBED (ML STP/GM) = 1.283
VOLUME OF ARGON ADSORBED (ML STP/GM) = 0.057
TOTAL VOLUME ADSORBED (ML STP/GM) = 9.713

MOLES OF NITROGEN REMOVED BY THE MGA (GM MOL*10**3) = 0.38101
MOLES OF OXYGEN REMOVED BY THE MGA (GM MOL*10**3) = 0.20003
MOLES OF ARGON REMOVED BY THE MGA (GM MOL*10**3) = 0.00903
TOTAL MOLES REMOVED BY THE MGA (GM MOL*10**3) = 0.59007

SEPARATION FACTOR BETWEEN NITROGEN AND OXYGEN = 3.429

POINT NO: 5

INPUT:
INITIAL CHARGE PRESSURE (TORR) = 2802.9
FINAL CHARGE PRESSURE (TORR) = 1856.6
TEMPERATURE OF THE CHARGE CHAMBER (K) = 298.15
EQUILIBRIUM PRESSURE (TORR) = 1251.5
TEMPERATURE OF THE SAMPLE CHAMBER (K) = 297.15
MOLE FRACTION NITROGEN IN THE MGA SAMPLE = 0.6536
MOLE FRACTION OXYGEN IN THE MGA SAMPLE = 0.3314
MOLE FRACTION ARGON IN THE MGA SAMPLE = 0.0150
MGA SAMPLE VOLUME PRESSURE (TORR) = 1205.0

OUTPUT:
INITIAL CHARGE PRESSURE Z = 0.99882
FINAL CHARGE PRESSURE Z = 0.99922
EQUILIBRIUM PRESSURE Z = 0.99943
MGA SAMPLE CHAMBER Z = 0.99945

MOLES OF NITROGEN ADDED (GM MOL*10**3) = 6.3196
MOLES OF OXYGEN ADDED (GM MOL*10**3) = 1.6919
MOLES OF ARGON ADDED (GM MOL*10**3) = 0.0760
TOTAL MOLES ADDED (GM MOL*10**3) = 8.0876

TOTAL MOLES OF NITROGEN IN THE SAMPLE CHAMBER (GM MOL*10**3) = 23.0620
TOTAL MOLES OF OXYGEN IN THE SAMPLE CHAMBER (GM MOL*10**3) = 5.9264
TOTAL MOLES OF ARGON IN THE SAMPLE CHAMBER (GM MOL*10**3) = 0.2658
TOTAL MOLES IN THE SAMPLE CHAMBER (GM MOL*10**3) = 29.2543

MOLES OF NITROGEN IN THE GAS PHASE (GM MOL*10**3) = 7.0202
MOLES OF OXYGEN IN THE GAS PHASE (GM MOL*10**3) = 3.5595
MOLES OF ARGON IN THE GAS PHASE (GM MOL*10**3) = 0.1611
TOTAL MOLES IN THE GAS PHASE (GM MOL*10**3) = 10.7408
MOLE FRACTION OF NITROGEN IN THE GAS PHASE = 0.6536
MOLE FRACTION OF OXYGEN IN THE GAS PHASE = 0.3314
MOLE FRACTION OF ARGON IN THE GAS PHASE = 0.0150

MOLES OF NITROGEN ADSORBED (GM MOL*10**3) = 16.0419
MOLES OF OXYGEN ADSORBED (GM MOL*10**3) = 2.3669
MOLES OF ARGON ADSORBED (GM MOL*10**3) = 0.1047
TOTAL MOLES ADSORBED (GM MOL*10**3) = 18.5135
MOLE FRACTION OF NITROGEN ADSORBED = 0.8665
MOLE FRACTION OF OXYGEN ADSORBED = 0.1278
MOLE FRACTION OF ARGON ADSORBED = 0.0057

VOLUME OF NITROGEN ADSORBED (ML STP) = 359.560
VOLUME OF OXYGEN ADSORBED (ML STP) = 53.052
VOLUME OF ARGON ADSORBED (ML STP) = 2.348
TOTAL VOLUME ADSORBED (ML STP) = 414.960

VOLUME OF NITROGEN ADSORBED (ML STP/GM) = 10.962
VOLUME OF OXYGEN ADSORBED (ML STP/GM) = 1.617
VOLUME OF ARGON ADSORBED (ML STP/GM) = 0.072
TOTAL VOLUME ADSORBED (ML STP/GM) = 12.651

MOLES OF NITROGEN REMOVED BY THE MGA (GM MOL*10**3) = 0.55062
MOLES OF OXYGEN REMOVED BY THE MGA (GM MOL*10**3) = 0.27918
MOLES OF ARGON REMOVED BY THE MGA (GM MOL*10**3) = 0.01264
TOTAL MOLES REMOVED BY THE MGA (GM MOL*10**3) = 0.84244

SEPARATION FACTOR BETWEEN NITROGEN AND OXYGEN = 3.440

POINT NO: 6

INPUT:
INITIAL CHARGE PRESSURE (TORR) = 3351.1
FINAL CHARGE PRESSURE (TORR) = 1949.6
TEMPERATURE OF THE CHARGE CHAMBER (K) = 297.15
EQUILIBRIUM PRESSURE (TORR) = 1835.9
TEMPERATURE OF THE SAMPLE CHAMBER (K) = 297.15
MOLE FRACTION NITROGEN IN THE MGA SAMPLE = 0.6705
MOLE FRACTION OXYGEN IN THE MGA SAMPLE = 0.3150
MOLE FRACTION ARGON IN THE MGA SAMPLE = 0.0145
MGA SAMPLE VOLUME PRESSURE (TORR) = 1753.1

OUTPUT:
INITIAL CHARGE PRESSURE Z = 0.99859
FINAL CHARGE PRESSURE Z = 0.99918
EQUILIBRIUM PRESSURE Z = 0.99918
MGA SAMPLE CHAMBER Z = 0.99922

MOLES OF NITROGEN ADDED (GM MOL*10**3) = 9.3936
MOLES OF OXYGEN ADDED (GM MOL*10**3) = 2.5149
MOLES OF ARGON ADDED (GM MOL*10**3) = 0.1130
TOTAL MOLES ADDED (GM MOL*10**3) = 12.0215

TOTAL MOLES OF NITROGEN IN THE SAMPLE CHAMBER (GM MOL*10**3) = 31.9050
TOTAL MOLES OF OXYGEN IN THE SAMPLE CHAMBER (GM MOL*10**3) = 8.1621
TOTAL MOLES OF ARGON IN THE SAMPLE CHAMBER (GM MOL*10**3) = 0.3662
TOTAL MOLES IN THE SAMPLE CHAMBER (GM MOL*10**3) = 40.4334
MOLES OF NITROGEN IN THE GAS PHASE (GM *10**3)= 10.5672
MOLES OF OXYGEN IN THE GAS PHASE (GM *10**3)= 4.9645
MOLES OF ARGON IN THE GAS PHASE (GM *10**3)= 0.2285
TOTAL MOLES IN THE GAS PHASE (GM *10**3)= 15.7602
MOLE FRACTION OF NITROGEN IN THE GAS PHASE= 0.6705
MOLE FRACTION OF OXYGEN IN THE GAS PHASE= 0.3150
MOLE FRACTION OF ARGON IN THE GAS PHASE= 0.0145

MOLES OF NITROGEN ADSORBED (GM *10**3)= 21.3378
MOLES OF OXYGEN ADSORBED (GM *10**3)= 3.1977
MOLES OF ARGON ADSORBED (GM *10**3)= 0.1377
TOTAL MOLES ADSORBED (GM *10**3)= 24.6732
MOLE FRACTION OF NITROGEN ADSORBED= 0.8648
MOLE FRACTION OF OXYGEN ADSORBED= 0.1296
MOLE FRACTION OF ARGON ADSORBED= 0.0056

VOLUME OF NITROGEN ADSORBED (ML STP)= 478.263
VOLUME OF OXYGEN ADSORBED (ML STP)= 71.673
VOLUME OF ARGON ADSORBED (ML STP)= 3.086
TOTAL VOLUME ADSORBED (ML STP)= 553.022

VOLUME OF NITROGEN ADSORBED (ML STP/GM)= 14.581
VOLUME OF OXYGEN ADSORBED (ML STP/GM)= 2.185
VOLUME OF ARGON ADSORBED (ML STP/GM)= 0.094
TOTAL VOLUME ADSORBED (ML STP/GM)= 16.860

MOLES OF NITROGEN REMOVED BY THE MGA (GM *10**3)= 0.82197
MOLES OF OXYGEN REMOVED BY THE MGA (GM *10**3)= 0.38616
MOLES OF ARGON REMOVED BY THE MGA (GM *10**3)= 0.01778
TOTAL MOLES REMOVED BY THE MGA (GM *10**3)= 1.22591

SEPARATION FACTOR BETWEEN NITROGEN AND OXYGEN= 3.144

POINT NO: 7

INPUT:
INITIAL CHARGE PRESSURE (TORR)= 3868.3
FINAL CHARGE PRESSURE (TORR)= 2534.0
TEMPERATURE OF THE CHARGE CHAMBER (K)= 297.15
EQUILIBRIUM PRESSURE (TORR)= 2404.7
TEMPERATURE OF THE SAMPLE CHAMBER (K)= 297.15
MOLE FRACTION NITROGEN IN THE MGA SAMPLE= 0.6832
MOLE FRACTION OXYGEN IN THE MGA SAMPLE= 0.3031
MOLE FRACTION ARGON IN THE MGA SAMPLE= 0.0137
MGA SAMPLE VOLUME PRESSURE (TORR)= 2291.0

OUTPUT:
INITIAL CHARGE PRESSURE Z= 0.99837
FINAL CHARGE PRESSURE Z= 0.99893
EQUILIBRIUM PRESSURE Z= 0.99894
MGA SAMPLE CHAMBER 2 = 0.99899

MOLES OF NITROGEN ADDED (GM MOL*10**3) = 8.9474
MOLES OF OXYGEN ADDED (GM MOL*10**3) = 2.3954
MOLES OF ARGON ADDED (GM MOL*10**3) = 0.1076
TOTAL MOLES ADDED (GM MOL*10**3) = 11.4504

TOTAL MOLES OF NITROGEN IN THE SAMPLE CHAMBER (GM MOL*10**3) = 40.0304
TOTAL MOLES OF OXYGEN IN THE SAMPLE CHAMBER (GM MOL*10**3) = 10.1714
TOTAL MOLES OF ARGON IN THE SAMPLE CHAMBER (GM MOL*10**3) = 0.4561
TOTAL MOLES IN THE SAMPLE CHAMBER (GM MOL*10**3) = 50.6579

MOLES OF NITROGEN IN THE GAS PHASE (GM MOL*10**3) = 14.1066
MOLES OF OXYGEN IN THE GAS PHASE (GM MOL*10**3) = 6.2584
MOLES OF ARGON IN THE GAS PHASE (GM MOL*10**3) = 0.2829
TOTAL MOLES IN THE GAS PHASE (GM MOL*10**3) = 20.6479
MOLE FRACTION OF NITROGEN IN THE GAS PHASE = 0.6832
MOLE FRACTION OF OXYGEN IN THE GAS PHASE = 0.3031
MOLE FRACTION OF ARGON IN THE GAS PHASE = 0.0137

MOLES OF NITROGEN ADSORBED (GM MOL*10**3) = 25.9238
MOLES OF OXYGEN ADSORBED (GM MOL*10**3) = 3.9130
MOLES OF ARGON ADSORBED (GM MOL*10**3) = 0.1732
TOTAL MOLES ADSORBED (GM MOL*10**3) = 30.0100
MOLE FRACTION OF NITROGEN ADSORBED = 0.8638
MOLE FRACTION OF OXYGEN ADSORBED = 0.1304
MOLE FRACTION OF ARGON ADSORBED = 0.0058

VOLUME OF NITROGEN ADSORBED (ML STP) = 581.052
VOLUME OF OXYGEN ADSORBED (ML STP) = 87.706
VOLUME OF ARGON ADSORBED (ML STP) = 3.882
TOTAL VOLUME ADSORBED (ML STP) = 672.640

VOLUME OF NITROGEN ADSORBED (ML STP/GM) = 17.715
VOLUME OF OXYGEN ADSORBED (ML STP/GM) = 2.674
VOLUME OF ARGON ADSORBED (ML STP/GM) = 0.118
TOTAL VOLUME ADSORBED (ML STP/GM) = 20.507

MOLES OF NITROGEN REMOVED BY THE MGA (GM MOL*10**3) = 1.09477
MOLES OF OXYGEN REMOVED BY THE MGA (GM MOL*10**3) = 0.48569
MOLES OF ARGON REMOVED BY THE MGA (GM MOL*10**3) = 0.02195
TOTAL MOLES REMOVED BY THE MGA (GM MOL*10**3) = 1.60241

SEPARATION FACTOR BETWEEN NITROGEN AND OXYGEN = 2.942

POINT NO: 8
INPUT:
INITIAL CHARGE PRESSURE (TORR) = 3868.3
FINAL CHARGE PRESSURE (TORR) = 2901.2
TEMPERATURE OF THE CHARGE CHAMBER (K) = 297.15
EQUILIBRIUM PRESSURE (TORR) = 2802.9
TEMPERATURE OF THE SAMPLE CHAMBER (K) = 297.15
MOLE FRACTION NITROGEN IN THE MGA SAMPLE = 0.6906
MOLE FRACTION OXYGEN IN THE MGA SAMPLE = 0.2961
MOLE FRACTION ARGON IN THE MGA SAMPLE = 0.0133
MGA SAMPLE VOLUME PRESSURE (TORR) = 2663.3

OUTPUT:
INITIAL CHARGE PRESSURE Z = 0.99837
FINAL CHARGE PRESSURE Z = 0.99878
EQUILIBRIUM PRESSURE Z = 0.99878
MGA SAMPLE CHAMBER Z = 0.99884

MOLES OF NITROGEN ADDED (GM MOL*10**3) = 6.4860
MOLES OF OXYGEN ADDED (GM MOL*10**3) = 1.7365
MOLES OF ARGON ADDED (GM MOL*10**3) = 0.0780
TOTAL MOLES ADDED (GM MOL*10**3) = 8.3005

TOTAL MOLES OF NITROGEN IN THE SAMPLE CHAMBER (GM MOL*10**3) = 45.4217
TOTAL MOLES OF OXYGEN IN THE SAMPLE CHAMBER (GM MOL*10**3) = 11.4222
TOTAL MOLES OF ARGON IN THE SAMPLE CHAMBER (GM MOL*10**3) = 0.5121
TOTAL MOLES IN THE SAMPLE CHAMBER (GM MOL*10**3) = 57.3560

MOLES OF NITROGEN IN THE GAS PHASE (GM MOL*10**3) = 16.6234
MOLES OF OXYGEN IN THE GAS PHASE (GM MOL*10**3) = 7.1274
MOLES OF ARGON IN THE GAS PHASE (GM MOL*10**3) = 0.3201
TOTAL MOLES IN THE GAS PHASE (GM MOL*10**3) = 24.0710
MOLE FRACTION OF NITROGEN IN THE GAS PHASE = 0.6906
MOLE FRACTION OF OXYGEN IN THE GAS PHASE = 0.2961
MOLE FRACTION OF ARGON IN THE GAS PHASE = 0.0133

MOLES OF NITROGEN ADSORBED (GM MOL*10**3) = 28.7983
MOLES OF OXYGEN ADSORBED (GM MOL*10**3) = 4.2948
MOLES OF ARGON ADSORBED (GM MOL*10**3) = 0.1920
TOTAL MOLES ADSORBED (GM MOL*10**3) = 33.2851
MOLE FRACTION OF NITROGEN ADSORBED = 0.8652
MOLE FRACTION OF OXYGEN ADSORBED = 0.1290
MOLE FRACTION OF ARGON ADSORBED = 0.0058

VOLUME OF NITROGEN ADSORBED (ML STP) = 645.481
VOLUME OF OXYGEN ADSORBED (ML STP) = 96.263
VOLUME OF ARGON ADSORBED (ML STP) = 4.303
TOTAL VOLUME ADSORBED (ML STP) = 746.047

VOLUME OF NITROGEN ADSORBED (ML STP/GM) = 19.679
VOLUME OF OXYGEN ADSORBED (ML STP/GM) = 2.935
VOLUME OF ARGON ADSORBED (ML STP/GM) = 0.131
TOTAL VOLUME ADSORBED (ML STP/GM) = 22.745
MOLES OF NITROGEN REMOVED BY THE MGA (GM MOL*10**3) = 1.28665
MOLES OF OXYGEN REMOVED BY THE MGA (GM MOL*10**3) = 0.55166
MOLES OF ARGON REMOVED BY THE MGA (GM MOL*10**3) = 0.02478
TOTAL MOLES REMOVED BY THE MGA (GM MOL*10**3) = 1.86310

SEPARATION FACTOR BETWEEN NITROGEN AND OXYGEN = 2.876

POINT NO: 9
INPUT:
INITIAL CHARGE PRESSURE (TORR) = 3868.3
FINAL CHARGE PRESSURE (TORR) = 3180.5
TEMPERATURE OF THE CHARGE CHAMBER (K) = 297.15
EQUILIBRIUM PRESSURE (TORR) = 3051.2
TEMPERATURE OF THE SAMPLE CHAMBER (K) = 297.15
MOLE FRACTION NITROGEN IN THE MGA SAMPLE = 0.6962
MOLE FRACTION OXYGEN IN THE MGA SAMPLE = 0.2907
MOLE FRACTION ARGON IN THE MGA SAMPLE = 0.0131
MGA SAMPLE VOLUME PRESSURE (TORR) = 2890.9

OUTPUT:
INITIAL CHARGE PRESSURE Z = 0.99837
FINAL CHARGE PRESSURE Z = 0.99866
EQUILIBRIUM PRESSURE Z = 0.99868
MGA SAMPLE CHAMBER Z = 0.99875

MOLES OF NITROGEN ADDED (GM MOL*10**3) = 4.6134
MOLES OF OXYGEN ADDED (GM MOL*10**3) = 1.2351
MOLES OF ARGON ADDED (GM MOL*10**3) = 0.0555
TOTAL MOLES ADDED (GM MOL*10**3) = 5.9040

TOTAL MOLES OF NITROGEN IN THE SAMPLE CHAMBER (GM MOL*10**3) = 48.7485
TOTAL MOLES OF OXYGEN IN THE SAMPLE CHAMBER (GM MOL*10**3) = 12.1057
TOTAL MOLES OF ARGON IN THE SAMPLE CHAMBER (GM MOL*10**3) = 0.5429
TOTAL MOLES IN THE SAMPLE CHAMBER (GM MOL*10**3) = 61.3970

MOLES OF NITROGEN IN THE GAS PHASE (GM MOL*10**3) = 18.2446
MOLES OF OXYGEN IN THE GAS PHASE (GM MOL*10**3) = 7.6181
MOLES OF ARGON IN THE GAS PHASE (GM MOL*10**3) = 0.3433
TOTAL MOLES IN THE GAS PHASE (GM MOL*10**3) = 26.2059
MOLE FRACTION OF NITROGEN IN THE GAS PHASE = 0.6962
MOLE FRACTION OF OXYGEN IN THE GAS PHASE = 0.2907
MOLE FRACTION OF ARGON IN THE GAS PHASE = 0.0131

MOLES OF NITROGEN ADSORBED (GM MOL*10**3) = 30.5039
MOLES OF OXYGEN ADSORBED (GM MOL*10**3) = 4.4876
MOLES OF ARGON ADSORBED (GM MOL*10**3) = 0.1996
TOTAL MOLES ADSORBED (GM MOL*10**3) = 35.1911
MOLE FRACTION OF NITROGEN ADSORBED = 0.8668
MOLE FRACTION OF OXYGEN ADSORBED = 0.1275
MOLE FRACTION OF ARGON ADSORBED = 0.0057

VOLUME OF NITROGEN ADSORBED (ML STP) = 683.711
VOLUME OF OXYGEN ADSORBED (ML STP) = 100.584
VOLUME OF ARGON ADSORBED (ML STP) = 4.473
TOTAL VOLUME ADSORBED (ML STP) = 788.768

VOLUME OF NITROGEN ADSORBED (ML STP/GM) = 20.845
VOLUME OF OXYGEN ADSORBED (ML STP/GM) = 3.067
VOLUME OF ARGON ADSORBED (ML STP/GM) = 0.136
TOTAL VOLUME ADSORBED (ML STP/GM) = 24.048

MOLES OF NITROGEN REMOVED BY THE MGA (GM MOL*10**3) = 1.40806
MOLES OF OXYGEN REMOVED BY THE MGA (GM MOL*10**3) = 0.58794
MOLES OF ARGON REMOVED BY THE MGA (GM MOL*10**3) = 0.02649
TOTAL MOLES REMOVED BY THE MGA (GM MOL*10**3) = 2.02249

SEPARATION FACTOR BETWEEN NITROGEN AND OXYGEN = 2.840

*****************************************************************************
C RUTHVE.FOR
C PREDICTION OF PURE COMPONENT ISOTHERM DATA USING RUTHVEN'S EQN.
C
C OWNER: G.W.MILLER
C DATE: 20 FEB 84
C FILENAME: RUTHVE.FOR
C
IMPLICIT REAL * 8 (A-H,O-Z)
DIMENSION C(40),XNUM(20),XDEN(20),XP(40)
OPEN(UNIT=7,NAME='NEW.DAT',TYPE='NEW',DISPOSE='SAVE')

C NOMENCLATURE:
C C = AMOUNT ADSORBED [ML STP/GM(CRYSTAL+BINDER)]
C XK = HENRY'S CONSTANT(MOLECULES/(CAVITY*TORR))
C XP = PRESSURE (TORR)
C B = EFFECTIVE MOLECULAR VOLUME OR VAN DER WAALS COVOLUME (A**3)
C V = CAVITY VOLUME (A**3)
C M = MAXIMUM NO. OF MOLECULES/CAVITY (LESS THAN OR EQUAL TO V/B)

C INPUT:
C
XK = 0.01261D00
B = 77.63D00
V = 776.0D00
M = 10

C CALCULATIONS:

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XPP = 0.0
DO500 I=1,40
XP(II) = XPP + 100.
XPP = XP(II)
XKP = XK * XPP
XNUSUM = 0.0
XDESUM = 0.0
XNUM(I) = XKP
XDEN(I) = 1. + XKP
DO100 I=2,M
L = I
XNUM1 = (XKP**L) * ((( 1.- ((L*B)/V))**L)
PFAC1 = 1
MMIN1 = L - 1
DO200 J=1,MMIN1
K1 = J
PFAC1 = PFAC1 * K1
200 CONTINUE
XNUM(I) = XNUM1/PFAC1
100 CONTINUE
DO300 I=2,M
N = I
XNUM2 = (XKP**N) * ((( 1.-((N*B)/V))**N)
PFAC2 = 1
DO400 J=1,N
K2 = J
PFAC2 = PFAC2 * K2
400 CONTINUE
XDEN(I) = XNUM2/PFAC2
300 CONTINUE
DO600 I=1,M
XNUSUM = XNUSUM + XNUM(I)
XDESUM = XDESUM + XDEN(I)
600 CONTINUE
C(II) = XNUSUM / XDESUM
DO900 I=1,20
XNUM(I) = 0.0
XDEN(I) = 0.0
900 CONTINUE
500 CONTINUE
C
C OUTPUT TO DATA FILE:
C
DO1000 I=1,40
C(I)= C(I) * 11.2111
1000 CONTINUE
DO700 I=1,40
WRITE (7,800) XP(I),C(I)
700 CONTINUE
800     FORMAT (1X,F7.1,3X,F9.3)
        TYPE*, 'RENAME NEW DATA FILE'
        STOP
END

*****************************************************************************
C       RUBI24.FOR
C       PREDICTION OF BINARY DATA AT 297.15 K
C
C       OWNER: G.W. MILLER
C       DATE:  2 APR 84
C       FILENAME: RUBI24.FOR
C
C       IMPLICIT REAL * 8 (A-H,O-Z)
C       DIMENSION XP02(30),XPN2(30),XPT(30),CO2(30),CN2(30)
C       OPEN(UNIT=7,NAME='RBIN24.DAT',TYPE='NEW',DISPOSE='SAVE')
C       OPEN(UNIT=9,NAME='RBI024.DAT',TYPE='NEW',DISPOSE='SAVE')

C       NOMENCLATURE:
C
C       CO2   = AMT OXYGEN ADSORBED (MOLECULES/CAVITY)
C       CN2   = AMT NITROGEN ADSORBED (MOLECULES/CAVITY)
C       XK02  = HENRY CONSTANT FOR OXYGEN (MOLECULES/CAV*TORR)
C       XKN2  = HENRY CONSTANT FOR NITROGEN (MOLECULES/CAV*TORR)
C       BO2   = OXYGEN EFFECTIVE MOLECULAR VOLUME (Å**3)
C       BN2   = NITROGEN EFFECTIVE MOLECULAR VOLUME (Å**3)
C       V     = CAVITY VOLUME (Å**3)
C       MO2   = NUMBER OF OXYGEN MOLECULES PER CAVITY AT SATURATION
C       MN2   = "  NITROGEN  "  "  "  "  "
C       XP02  = OXYGEN PARTIAL PRESSURE (TORR)
C       XPN2  = NITROGEN PARTIAL PRESSURE (TORR)
C       NDATA = NUMBER OF DATA POINTS
C
C       INPUT:
C
C       XK02  = 0.0004234D00
C       XKN2  = 0.001902D00
C       BO2   = 38.8D00
C       BN2   = 97.D00
C       MO2   = 20
C       MN2   = 8
C       V     = 776.D00
C       NDATA = 14

C       XP02(1) = 65.1D00
C       XP02(2) = 75.2D00
C       XP02(3) = 135.8D00
C       XP02(4) = 207.7D00

C
C XPO2(5) = 299.2D00
C XPO2(6) = 403.2D00
C XPO2(7) = 415.5D00
C XPO2(8) = 578.3D00
C XPO2(9) = 619.1D00
C XPO2(10) = 728.9D00
C XPO2(11) = 755.5D00
C XPO2(12) = 829.9D00
C XPO2(13) = 847.2D00
C XPO2(14) = 887.2D00
C
C XPN2(1) = 100.9D00
C XPN2(2) = 115.3D00
C XPN2(3) = 229.9D00
C XPN2(4) = 367.9D00
C XPN2(5) = 569.8D00
C XPN2(6) = 747.2D00
C XPN2(7) = 817.2D00
C XPN2(8) = 1230.9D00
C XPN2(9) = 1261.2D00
C XPN2(10) = 1642.9D00
C XPN2(11) = 1676.7D00
C XPN2(12) = 1935.7D00
C XPN2(13) = 1944.1D00
C XPN2(14) = 2124.2D00
C
C CALCULATIONS:
C
DO 6 M=1,NDATA
XPT(M) = XPO2(M) + XPN2(M)
6 CONTINUE
BA = B02
BB = BN2
INUMJ = MN2 + 1
IDENJ = INUMJ
INUMI = MO2 + 1
IDENI = INUMI
DO100 III=1,NDATA
ICHECK = 0
XKAPA = XK02 * XPO2(III)
XKBPB = XKN2 * XPN2(III)
2222 XDEN = 0.0
XNUM = 0.0
C
C CALCULATION OF DOUBLE SUMMATION IN NUMERATOR:
C
DO200 J=1,INUMJ
JN = J - 1
XJN = JN
PFACJN = 1.
IF(JN) 9999,903,904
904 DO300 K=1,JN
KA = K
PFACJN = PFACJN * KA
300 CONTINUE
903 DO400 I=1,INUMI
IN = I - 1
XIN = IN
CHKERN = (XIN * BA) + (XJN * BB)
IF(CHKERN.GT.V) GO TO 400
MN = JN + IN
C2 = (XKAPA**IN) * (XKBPB**JN)
XMAJ1 = C2 * ((1.D00-((XIN*BA)/V)-((XJN*BB)/V))**MN)
PFACIN = 1.
IF(IN) 9999,919,911
911 DO912 K=1,IN
KB = K
PFACIN = PFACIN * KB
912 CONTINUE
919 IF(ICHECK) 9999,913,914
913 MGAS = IN
GO TO 915
914 MGAS = JN
915 CN = ((MGAS * XMAJ1) / PFACIN) * (1.D00 / PFACJN)
XNUM = XNUM + CN
400 CONTINUE
200 CONTINUE
C
C CALCULATION OF DOUBLE SUMMATION IN DENOMINATOR:
C
DO500 J=1,IDENJ
JD = J - 1
XJD = JD
PFACJD = 1.
IF(JD) 9999,916,917
917 DO600 K=1,JD
KC = K
PFACJD = PFACJD * KC
600 CONTINUE
916 DO700 I=1,IDENI
ID = I - 1
XID = ID
CHKERD = (XID * BA) + (XJD * BB)
IF(CHKERD.GT.V) GO TO 700
PFACID = 1.
IF(ID) 9999,918,933
933 DO800 K=1,ID
KD = K
PFACID = PFACID * KD
800    CONTINUE
918    MD = JD + ID
      C4 = (XKAPA**ID) * (XKBPP**JD)
      XMAJ2 = C4 * (1.00 - (XID*BA)/V - ((XJD*BB)/V)**MD)
      CD = (XMAJ2 / PFACID) * (1.00 / PFACJD)
      XDEN = XDEN + CD
700    CONTINUE
500    CONTINUE
      IF(ICHECK) 9999,920,921
C
C CALCULATION OF ADSORBED CONCENTRATIONS:
C
920    CO2(III) = XNUM / XDEN
      ICHECK = ICHECK + 1
      GO TO 2222
921    CN2(III) = XNUM / XDEN
100    CONTINUE
      DO333 LL=1,NDATA
      CO2(LL) = CO2(LL) * 11.2111D00
      CN2(LL) = CN2(LL) * 11.2111D00
333    CONTINUE
C
C OUTPUT:
C
922    DO1100 N=1,NDATA
      WRITE(9,14) XP02(N),C02(N)
1100   CONTINUE
      14 FORMAT(1X,F7.1,3X,F9.4)
      DO1200 N=1,NDATA
      WRITE(7,15) XPN2(N),CN2(N)
1200   CONTINUE
      15 FORMAT(1X,F7.1,3X,F9.4)
9999   STOP
END

******************************************************************************
C IAST24.FOR
C THIS PROGRAM CALCULATES xo2,qT,q02, and qN2
C AT 297.15 K USING THE IAST THEORY OF MYERS AND
C PRAUSNITZ.
C
C IMPLICIT REAL * 8 (A-H,O-Z)
DIMENSION XP02(30),XPN2(30),PT(30),YO2(30),YN2(30)
DIMENSION X02(30),XN2(30),PO2PU(30),PN2PU(30),XNO2PU(30)
DIMENSION XNN2PU(30),XNT(30),XNO2(30),XNN2(30)
OPEN(UNIT=7,NAME='IASO24.DAT',TYPE='NEW',DISPOSE='SAVE')
OPEN(UNIT=8,NAME='IASN24.DAT',TYPE='NEW',DISPOSE='SAVE')
289
OPEN(UNIT=9,NAME='IAST24.RES',TYPE='NEW',DISPOSE='SAVE')

INPUT:

XPO2(1) = 65.1D00
XPO2(2) = 75.2D00
XPO2(3) = 135.8D00
XPO2(4) = 207.7D00
XPO2(5) = 299.0D00
XPO2(6) = 403.2D00
XPO2(7) = 415.5D00
XPO2(8) = 578.3D00
XPO2(9) = 619.1D00
XPO2(10) = 728.9D00
XPO2(11) = 755.6D00
XPO2(12) = 829.9D00
XPO2(13) = 847.0D00
XPO2(14) = 887.0D00

XPN2(1) = 100.9D00
XPN2(2) = 115.3D00
XPN2(3) = 229.9D00
XPN2(4) = 367.9D00
XPN2(5) = 569.8D00
XPN2(6) = 747.2D00
XPN2(7) = 817.2D00
XPN2(8) = 1230.9D00
XPN2(9) = 1261.2D00
XPN2(10) = 1642.9D00
XPN2(11) = 1676.7D00
XPN2(12) = 1935.7D00
XPN2(13) = 1944.1D00
XPN2(14) = 2124.2D00

NDATA = 14

PARAMETERS FOR CALC. OF THE SPREADING PRESS. OF O2.
SOP1 = .0045521D00
SOP2 = 2.2479D-05
SOP3 = 1.00323D00

PARAMETERS FOR CALC. OF THE SPREADING PRESS. OF N2.
SNP1 = .054163D00
SNP2 = 2.2830D-04
SNP3 = 0.83329D00

PARAMETERS FOR CALC. OF THE N2 ISOTHERM.
QOP1 = 0.00466905D00
QOP2 = .0000462853

290
PARAMETERS FOR CALC. OF THE O2 ISOTHERM.
QNP1 = 0.0475481
QNP2 = 5.16372D-04
QNP3 = .8263D00

CALCULATIONS:

DO100 I=1,NDATA
PT(I) = XPO2(I) + XPN2(I)
100 CONTINUE
DO200 I=1,NDATA
Y02(I) = XPO2(I) / PT(I)
YN2(I) = XPN2(I) / PT(I)
200 CONTINUE
DO888 I=1,NDATA
ICHECK = 0
XXPN2 = XPN2(I) + 1.D00
500 T1 = ((XPO2(I) * XXPN2) / (XXPN2 - XPN2(I)))**SOP3
T2 = (T1 * SOP1) / (1.D00 + (SOP2 * T1 ))
T3 = XXPN2**SNP3
T4 = (T3 * SNP1) / (1.D00 + (SNP2 * T3))
T5 = T4 - T2
GO TO(600,601,602) ICHECK
600 IF(T5) 501,555,502
501 XXPN2 = XXPN2 + 1.D00
GO TO 500
502 XXPN2 = XXPN2 - 1.D00
ICHECK = ICHECK + 1
GO TO 500
601 IF(T5) 650,555,651
650 XXPN2 = XXPN2 + .1D00
GO TO 500
651 XXPN2 = XXPN2 - .1D00
ICHECK = ICHECK + 1
GO TO 500
602 IF(T5) 660,555,555
660 XXPN2 = XXPN2 + .01D00
GO TO 500
555 PN2PU(I) = XXPN2
888 CONTINUE

DO700 I=1,NDATA
C1 = PN2PU(I) - XPN2(I)
PO2PU(I) = (XPO2(I) * PN2PU(I)) / C1
700 CONTINUE
DO800 I=1,NDATA
X02(I) = XPO2(I) / PO2PU(I)
XN2(I) = 1.D00 - X02(I)
CONTINUE

DO 900 I = 1, NDATA
   C2 = 1.000 + (QOP2 * P02PU(I))
   XNO2PU(I) = (QOP1 * P02PU(I)) / C2
   C3 = PN2PU(I)**QNP3
   C4 = 1.000 + (QNP2 * C3)
   XNN2PU(I) = (QNP1 * C3) / C4
   CONTINUE

DO 1000 I = 1, NDATA
   RNT = (X02(I) / XNO2PU(I)) + (XN2(I) / XNN2PU(I))
   XNT(I) = 1.000 / RNT
   XNO2(I) = XNT(I) * X02(I)
   XNN2(I) = XNT(I) * XN2(I)
   CONTINUE

DO 1100 I = 1, NDATA
   WRITE(9, 930) I
   WRITE(9, 901) XPO2(I), XPN2(I), PT(I), PO2PU(I), PN2PU(I)
   WRITE(9, 902) Y02(I), YN2(I), X02(I), XN2(I)
   WRITE(9, 903) XNO2(I), XNN2(I), XNO2PU(I), XNN2PU(I), XNT(I)
   CONTINUE

930 FORMAT(//, 1X, 'POINT NO.:', I3)
901 FORMAT(1X, 'PO2=', F8.2, ' PN2=', F8.2, ' P=', F8.2, ' PO2*', F8.2)
902 FORMAT(1X, 'Y02=', F6.4, ' YN2=', F6.4, ' X02=', F6.4, ' XN2=', F6.4)
903 FORMAT(1X, 'Q02=', F8.3, ' QN2=', F8.3, ' Q02*=', F8.3, ' QN2*=', F8.3)
   CONTINUE

DO 1200 I = 1, NDATA
   WRITE(7, 904) XPO2(I), XNO2(I)
   WRITE(8, 904) XPN2(I), XNN2(I)
   CONTINUE

904 FORMAT(1X, F8.2, 3X, F8.3)
STOP
END
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