Part III

Adsorption of Oxygen and Nitrogen on Molecular Sieves

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Studies of the simultaneous adsorption of oxygen and nitrogen contaminants on molecular sieves from cryogenic streams have required the investigation of adsorbent capacities under equilibrium and dynamic conditions, and have included the effect of preadsorbed water on capacity. Gas chromatographic techniques have been used to determine the single and 2 component equilibrium capacities of oxygen and nitrogen on Linde 13X molecular sieves at low temperatures and concentrations. A simple model has been used to predict dynamic oxygen adsorption capacity under conditions of simultaneous nitrogen adsorption from a cryogenic stream. The predicted values have been confirmed from experimental breakthrough curves. Oxygen adsorption capacity has been measured in the presence of preadsorbed water to determine the effect of regeneration on adsorbent capacity.

ADSORPTION processes are used extensively in the cryogenic industries for the removal of trace contaminants which may freeze out in process equipment thus causing plugging and safety hazards. Hydrogen processing in particular is subject to a considerable safety problem from the presence of small concentrations of oxygen and nitrogen which may result from air leakage. For example, the deposition of solid oxygen from liquid or gaseous hydrogen at −410° F. occurs at concentrations as low as 0.01 p.p.m. and will result in a considerable explosion hazard.

The present study was carried out to permit the prediction of safe dynamic adsorption capacities for oxygen on molecular sieve beds and the conditions necessary for regeneration. Data are reported for the single and multiple component adsorption of oxygen and nitrogen at −100° to −300° F. and at 10^{-3} to 10 mm. of Hg partial pressures. Data have also been obtained for the adsorption of oxygen in the presence of preadsorbed water. The degree of regeneration is an important factor in determining breakthrough time.

LOW PRESSURE EQUILIBRIUM ADSORPTION OF OXYGEN AND NITROGEN ON 13X MOLECULAR SIEVES

Three experimental techniques were used to obtain equilibrium adsorption capacity data. The first was a rapid but indirect method utilizing the elution time of an injected sample from a chromatograph. The second was a more direct method, in which the adsorbent was equilibrated with a flowing gas stream containing the adsorbate. The amount of adsorbed material was measured by desorption through a gas chromatograph. Thirdly, a volumetric all-glass static adsorption apparatus was used to determine adsorption capacity for pure oxygen and nitrogen at low pressure. This allowed confirmation of the previous techniques by checking the pure component capacities.

Chromatograph Retention Times. The limiting adsorption capacity for a single adsorbed component in a nonadsorbed carrier gas may be determined from its elution time in a chromatograph column. The advantages of this technique are the simplicity of the apparatus (Figure 1) and the rapidity with which results may be obtained.

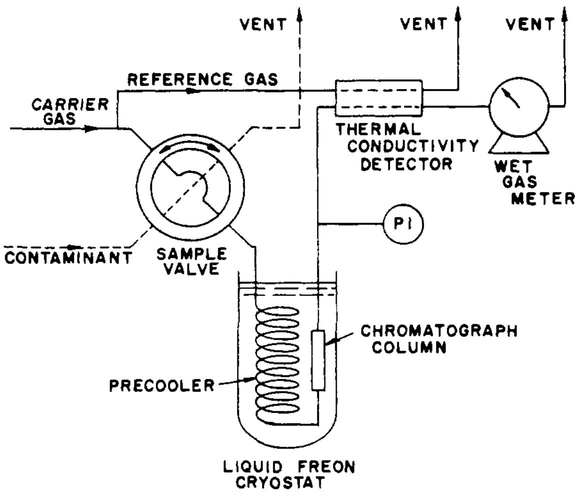

Figure 1. Apparatus to measure adsorption capacity by elution time of injected contaminant

A chromatograph column of 13X molecular sieves ($Na_2O \cdot Al_2O_3 \cdot 2.8SiO_2 \cdot xH_3O$)[2] manufactured by Linde Division, Union Carbide Corp., was immersed in a cryostat capable of operating from ambient to –340° F. Elution of impurity from the column was observed with a thermal conductivity detector. Hydrogen was used as a carrier gas to measure the elution times of injected oxygen and nitrogen samples. Elution time is the time from injection of the sample to appearance of the impurity peak maximum at the thermal conductivity detector. At low adsorbate concentration, elution time is independent of sample size (Appendix). Therefore, the smallest possible sample was used, the minimum size being set by the lowest limit of detection of the thermal conductivity detector. The gas holdup time of the system was determined by injecting samples of helium, which is negligibly absorbed.

The adsorption capacity was determined from the elution time and other experimental parameters by the formula: (Appendix)

$$\frac{C}{Py} = \frac{Mf(t - t_o)}{W_sRTZ} \qquad (1)$$

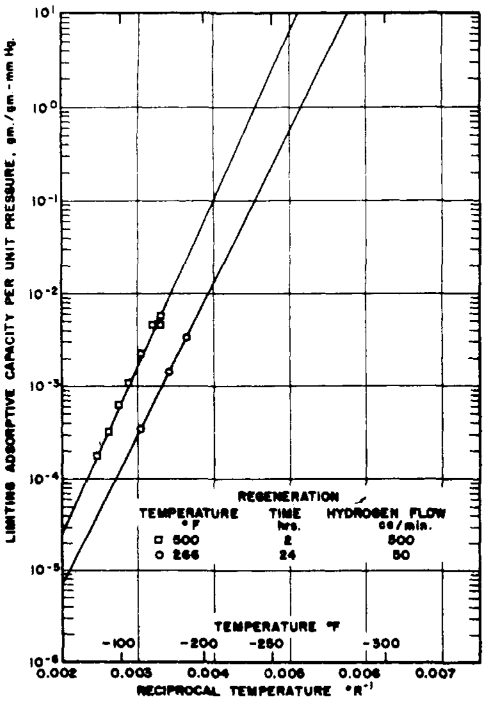

Figure 2. Adsorptive capacity of nitrogen on 13X molecular sieves

Data from elution time measurements are necessarily obtained at an unknown contaminant concentration, and are therefore only significant in the linear isotherm region where elution time is independent of concentration. The data obtained from elution time studies are thus only useful at low concentrations, and must be presented as C/Py (the limiting slope of the capacity *vs.* partial pressure curve at low contaminant partial pressure). Values of C/Py were calculated from Equation 1 using experimental data. The results for the adsorption of oxygen and nitrogen on 13X molecular sieves are plotted in Figures 2 and 3 as a function of the reciprocal temperature. A linear plot was found for the temperature region between –80° and –250° F. in which data were measured. Comparison of the data indicates the limiting capacity of 13X sieves for nitrogen to be about 40 times greater than for oxygen.

Dynamic Saturation. Direct measurements for the single and multicomponent adsorption capacities for oxygen and nitrogen were made by dynamic saturation of a test adsorber. A flow diagram of the apparatus is shown in Figure 4. Gas mixtures containing known concentrations of oxygen and nitrogen were prepared by static blending of the pure constituents. The appropriate gas mixture was then blended continuously with a purified helium carrier gas by metering through a stainless steel capillary.

Molecular sieve capacities were studied at liquid oxygen temperature and atmospheric pressure. Because of the very high capacities under these conditions, small samples of adsorbent and high gas flow rates were used. The test adsorbers contained 50 mg. samples of adsorbent in 0.25-inch diameter copper tubes.

The carrier gas, containing a known contaminant concentration, was passed over the adsorbent until equilibrium was obtained. At high concentrations of impurity, saturation was determined by observing the return of the effluent contaminant concentration to the level of the inlet stream. At low concentration levels, the adsorbent was exposed to the contaminant for various periods of time. If saturation were achieved, a longer period would not increase the amount of contaminants adsorbed.

After saturation of the adsorbent, the total gas flow was reduced, and the amount of gas adsorbed was determined by warming the adsorbent to room temperature. The desorbed contaminants generated peaks on the chromato-

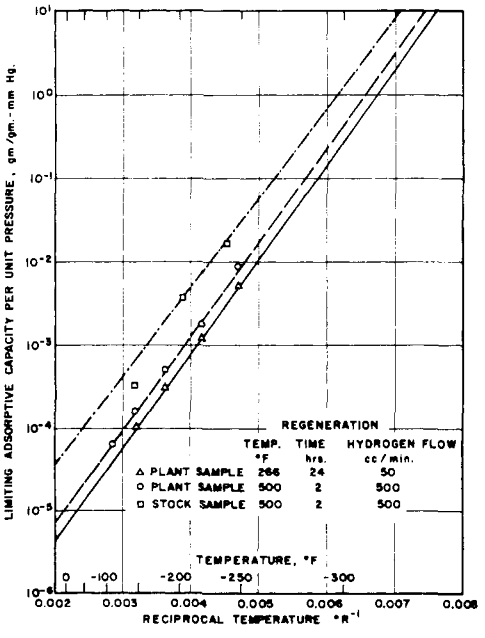

Figure 3. Adsorptive capacity of oxygen on 13X molecular sieves

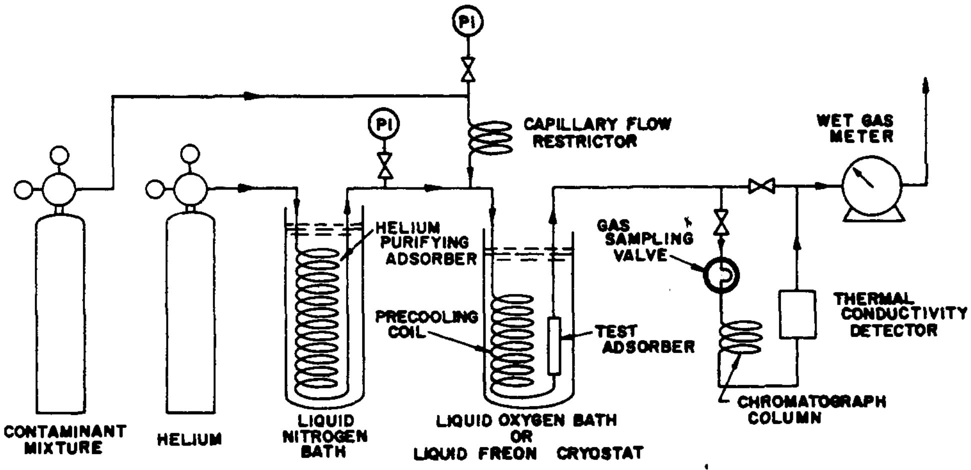

Figure 4. Direct measurement of adsorptive capacity by saturation/desorption method

graph which were compared with peaks generated by standard samples.

Single Component Oxygen Capacity. The capacity of 13X molecular sieves for oxygen, obtained from these measurements, is shown in Figure 5 as a function of partial pressure. The full line is drawn through the directly measured capacity data, and the broken line represents the limiting capacity extrapolated from measurements using the elution technique. The measured data should approach this latter line asymptotically at low pressures. Figure 5 thus presents a comparison of the data obtained from the measurement of chromatograph elution time with the directly measured capacities.

Oxygen Adsorption in the Presence of Nitrogen. The adsorption of oxygen and nitrogen on materials other than molecular sieves generally exhibits a higher capacity for oxygen than nitrogen, and a higher relative concentration of oxygen in the adsorbed phase for mixed systems. Molecular sieves possess abnormal properties in that the nitrogen exhibits a higher adsorption capacity (as much as 40 times greater at low partial pressures). Adsorption of oxygen-nitrogen mixtures demonstrates this anomaly in that nitrogen displaces oxygen from the adsorbed phase. The reasons for this phenomenon are as yet unclear.

The capacity of 13X molecular sieves for the simultaneous adsorption of oxygen and nitrogen was measured at −297° F. and with partial pressures of 0.03 mm. of Hg for oxygen and 0.12 mm. of Hg for nitrogen. (Assuming the contaminants in a process stream would be air.) The measured capacity data are shown in Table I.

These results showed that the equilibrium oxygen capacity in the presence of nitrogen may be reduced by a factor of approximately 7.5, whereas the nitrogen capacity is only reduced by 16%. However, in a dynamic system, the reduction of oxygen capacity is much less and may only amount to approximately 50% of the pure component capacity.

Static Saturation. As a check on the previously measured data, some single component capacity measurements were made by static equilibrium. An all-glass static adsorption apparatus of the volumetric type was available for the measurement of adsorption isotherms at pressures from 10^{-5} to 10^{+3} mm. of Hg and at temperatures from ambient to −340° F.

Adsorption isotherms of 13X molecular sieves for oxygen and nitrogen were developed at −297° F. using the static apparatus. Regeneration of the sieves was carried out at 500° F. to a pressure below 10^{-6} mm. of Hg. Adsorption isotherms were developed between 10^{-3} mm. of Hg and atmospheric pressure. The results are shown in Figure 6.

Table I. Simultaneous Adsorption of Oxygen and Nitrogen

(Adsorbent, 13X molecular sieves; temp., −297° F.; carrier gas, helium)

Partial Pressure, Mm. of Hg		Capacity, Gram/Gram	
Oxygen	Nitrogen	Oxygen	Nitrogen
0.03	0.12	0.0036	0.117
0.03	0.00	0.027	0.00
0.00	0.12	0.00	0.14

THE BREAKTHROUGH CAPACITY OF A DYNAMIC ADSORBER

The breakthrough time of an adsorber bed may be defined as the time elapsing from first entry of adsorbate into the bed until the appearance of a predetermined concentration of adsorbate in the effluent gas. An exact prediction of the

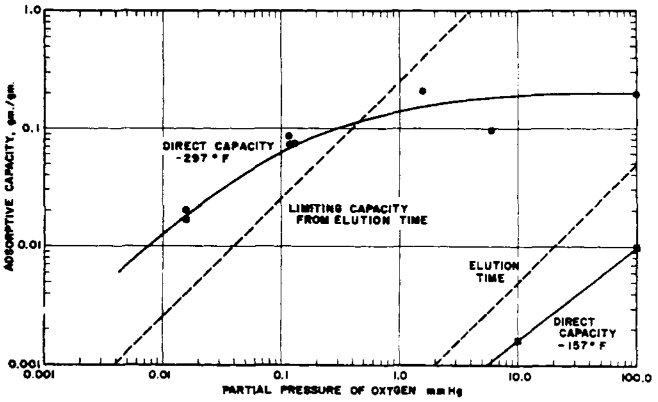

Figure 5. Adsorptive capacity of 13X molecular sieves for oxygen by dynamic saturation

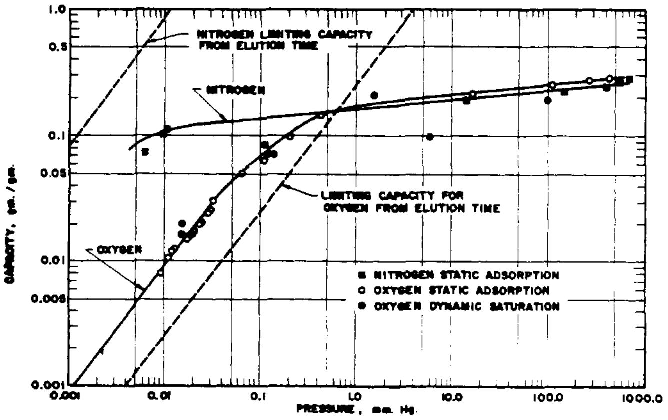

Figure 6. Adsorption on 13X molecular sieves at −297° F.

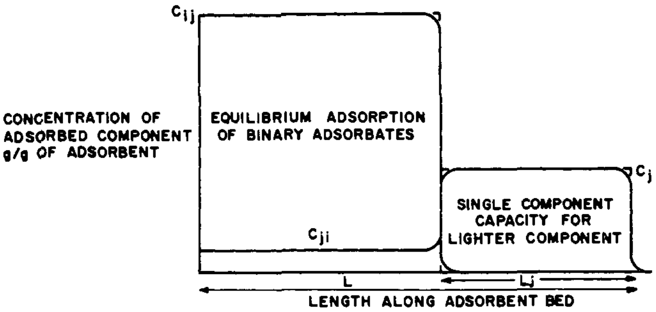

Figure 7. Profile of an adsorber with two adsorptives in the process stream

breakthrough time requires a knowledge of both the dynamic and equilibrium parameters influencing adsorption which does not at present exist. However, an approximate breakthrough time may be predicted by assuming a stepwise concentration profile to travel through the adsorber.

In this case, the breakthrough time for a single adsorbed component is given by (Appendix):

$$t_s = \frac{CW_s}{yMG} \tag{2}$$

Two Component Adsorption. When more than one component is being adsorbed from a gas mixture, the breakthrough time for the less strongly adsorbed components will be reduced. The distribution of binary adsorbates—e.g., nitrogen and oxygen—in an adsorber at the instant before breakthrough may be represented as in Figure 7. The ratio of the amounts of each component on the bed will be equal to the ratio of components in the feed gas. This may be written approximately:

$$\frac{y_i}{y_j} = \frac{C_{ij}\,(L - L_j)}{C_jL_j + C_{ji}\,(L - L_j)} \tag{3}$$

The fractional length of the adsorber occupied by the less strongly absorbed component is then given by:

$$\frac{L_j}{L} = \frac{(y_j/y_i)\,C_{ij} - C_{ji}}{(y_j/y_i)\,C_{ij} - C_{ji} + C_j} \tag{4}$$

The less strongly adsorbed component will break through the bed first. The breakthrough time for the component will be less than for single component adsorption by the ratio of the available adsorption capacities at breakthrough in each case—i.e.,

$$\frac{t_m}{t_s} = \frac{L_jC_j + (L - L_j)\,C_{ji}}{LC_j} \tag{5}$$

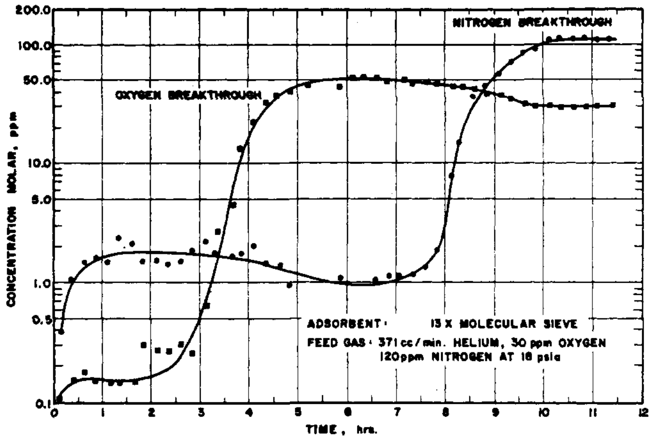

Figure 9. Adsorber effluent concentration for adsorption of oxygen and nitrogen from helium

In the event that C_{ji} is small, then

$$\frac{t_m}{t_s} \approx \frac{L_j}{L} \tag{6}$$

Equation 6 is equivalent to the commonly adopted design procedure of allocating a length of bed to the adsorption of each component and obtaining the total required adsorber length from the sum of the respective parts.

Experimental Measurement of Multicomponent Breakthrough Curves. The particular problem encountered in the experimental determination of breakthrough curves was their measurement at low impurity concentration levels. A technique was developed with which concentrations to a level of less than 0.5 p.p.m. could be determined in the adsorber effluent using a standard laboratory gas chromatograph. The impurities in the effluent were collected on an adsorber and periodically desorbed through the chromatograph. By a suitable combination of flow rates, collecting adsorbent column, chromatograph column, and collection period, any desired number of components in the effluent stream may be determined.

A flow sheet of the apparatus is shown in Figure 8. Breakthrough curves were determined for a 13X molecular sieve column adsorbing oxygen and nitrogen from helium at 0.03 and 0.12 mm. of Hg partial pressure, respectively, and at −298° F. The adsorbent test column was 0.38-cm. in diameter by 5-cm. long, and it was regenerated initially for 30 minutes at 500° F. A second 13X molecular sieve column 0.38-cm. diameter by 15-cm. long at −320° F., was used to collect the oxygen and nitrogen breaking through. This

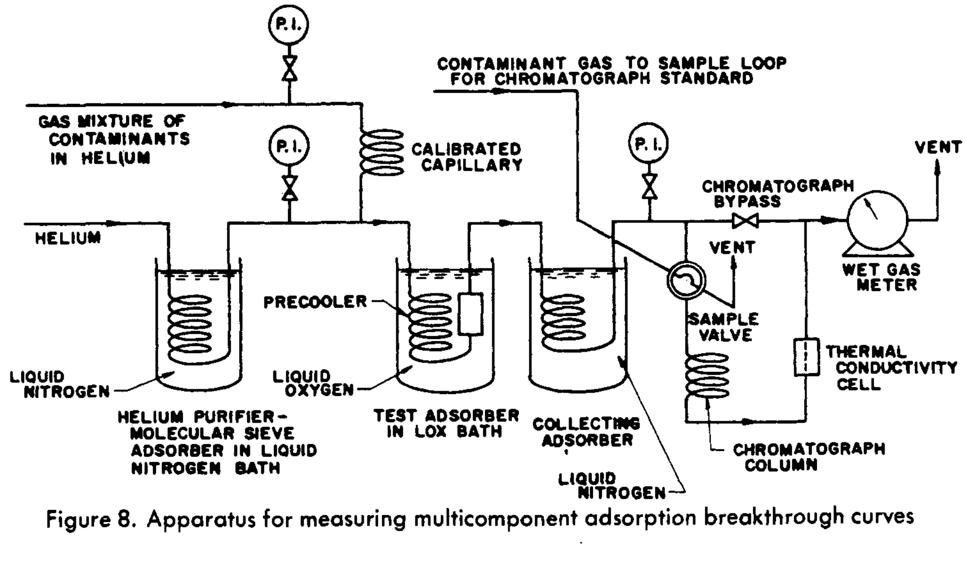

Figure 8. Apparatus for measuring multicomponent adsorption breakthrough curves

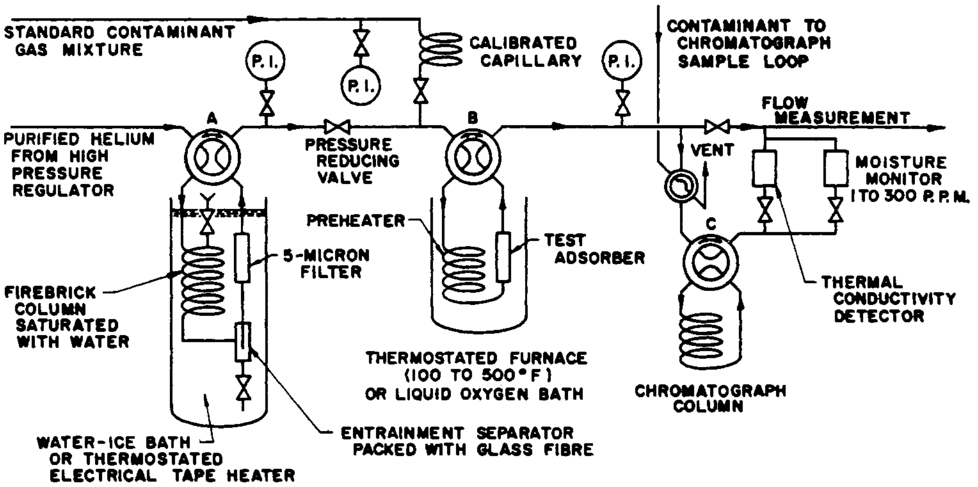

Figure 10. Measurement of adsorbent capacity in presence of adsorbed water

column was desorbed at 15-minute intervals by warming to ambient temperature. The oxygen and nitrogen peaks were separated with an ambient temperature 5A molecular sieve chromatograph column, and they were detected with a thermal conductivity cell. At the completion of the breakthrough experiments, when the test column was saturated with the adsorbates, the equilibrium capacities were measured by desorption of the test column through the chromatograph. The measured values confirmed those determined previously.

A breakthrough curve measured at a flow rate of 370 cm.^{3} per minute is shown in Figure 9. The observed breakthrough time to an oxygen concentration of 15 p.p.m. (one half of the feed concentration) was 3.9 hours. The breakthrough time predicted by Equations 4 and 5 was 4.0 hours. This was considered to be satisfactory confirmation of the adsorption model.

The breakthrough time to a concentration of 1 p.p.m., 3.2 hours, was considerably less than for 30 p.p.m. It is apparent from this that dynamic factors which determine the concentration profiles within the adsorber have a significant influence upon the initial adsorber breakthrough.

THE INFLUENCE OF PREADSORBED WATER ON THE CAPACITY OF MOLECULAR SIEVES

All of the previous data were obtained with completely regenerated molecular sieves. Attention was given in particular to the complete removal of any preadsorbed water which would cause a serious reduction of capacity. The complete regeneration of a large adsorber bed requires a large volume of purge gas at a high temperature, conditions which are not readily achieved in practice. It is of considerable interest, therefore, to know exactly the extent to which regeneration must be carried, and the influence of residual water content on adsorbent capacity.

A method was devised by which the adsorbent capacity may be measured in the presence of a directly determined amount of water vapor. The technique used was to observe the breakthrough curve for water vapor being adsorbed from a stream of known water vapor content. This gives a direct measurement of water vapor capacity at a known partial pressure. The wet adsorbent was then exposed to a carrier gas containing known concentrations of impurity, and its capacity measured at saturation as described previously.

Pure helium was passed through the apparatus (Figure 10) at the required pressures and flow rate with isolation valves *A*, *B*, and *C* set to the bypass positions. A base line was established on the analyzer at zero water concentration. The saturator was then switched into the stream and the corresponding span reading observed on the analyzer. When steady operating conditions had been obtained, the test adsorber was switched into the stream, and the concentration of water in the effluent was monitored until the reading was re-established at the inlet level. The amount of water adsorbed was then determined from a knowledge of the gas flow rate, concentration, and breakthrough time. After saturation of the test adsorber with water, it was isolated and cooled to the oxygen-nitrogen adsorption temperature of −297° F. in a liquid oxygen bath. Oxygen or nitrogen capacity measurements were then made by the dynamic saturation technique. Sharp breakthrough curves for water vapor could be measured in the effluent gas using test columns as small as 50 mg. (0.6-cm. long × 0.38-cm. diameter) at carrier gas flow rates of 500 cm.^{3} per minute at 20 p.s.i.g.

Capacity data were obtained for the adsorption of oxygen from helium at a partial pressure of 0.03 mm. of Hg and −297° F. The results are shown in Figure 11. At high water capacities, a very great reduction of oxygen capacity was observed. However, for a water capacity of 0.01 gram/gram, the reduction of oxygen capacity was less than 30%.

APPENDIX

Numerous treatments have been made of the problem of pulse flow through packed beds. The particular model of pulse flow with longitudinal diffusion and negligible mass

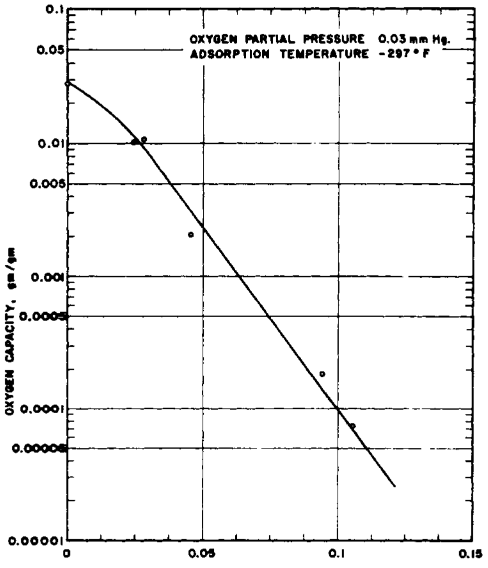

Figure 11. Influence of preadsorbed water on oxygen capacity of 13X molecular sieves

transfer resistance to adsorption which has been assumed for the present case has been solved by Lapidus and Amundson (*3*). The simplified solution presented here is due to Buffham (*1*).

Consider a small segment of an adsorbent column. The following assumptions are made: The column is at transverse equilibrium, and adsorption equilibria may be represented by a linear isotherm

$$c_s = kc \tag{7}$$

Then, the material balance on the segment may be written

$$eD \frac{\partial^2 c}{\partial z^2} - u \frac{\partial c}{\partial z} = e \frac{\partial c}{\partial t} + (1 - e) \frac{\partial c_s}{\partial t} \tag{8}$$

Equation 8 may be written

$$eD \frac{\partial^2 c}{\partial z^2} - u \frac{\partial c}{\partial z} = \{ e + k (1 - e) \} \frac{\partial c}{\partial t} = K \frac{\partial c}{\partial t} \tag{9}$$

A change of variables may be made such that

$$X = z - \alpha t \tag{10}$$

$$T = t \tag{11}$$

and

$$eD \frac{\partial^2 c}{\partial X^2} - u \frac{\partial c}{\partial X} = K \left(\frac{\partial c}{\partial T} - \alpha \frac{\partial c}{\partial X} \right) \tag{12}$$

$$\alpha = u/K \tag{13}$$

then

$$eD \frac{\partial^2 c}{\partial X^2} = K \frac{\partial c}{\partial T} \tag{14}$$

For an initial composition profile $c\ (z, 0) = c\ (X, 0)$ such that c is a first order function of X exhibiting a single maximum at $X = 0$ and having the boundary conditions

$$\lim_{z \to -\infty} c = \lim_{z \to \infty} c = 0$$

Then the one dimensional diffusion equation with spatial coordinate X implies that the peak maximum is located at $X = 0$ for all t.

Thus at time t' the peak is located at

$$z = \alpha t' = \frac{ut}{e + k\,(1 - e)} \tag{15}$$

or for an adsorber of length z' the elution time is

$$t = \frac{z'\,[e + k\,(1 - e)]}{u} \tag{16}$$

For a negligibly adsorbed gas $k = 0$

and

$$t_o = \frac{z'e}{u} \tag{17}$$

and

$$t - t_o = \frac{z'k\,(1 - e)}{u} \tag{18}$$

But

$$c_s = \frac{CW_s u}{Fz'} \tag{19}$$

and

$$c = \frac{PyM}{RTZ} \tag{20}$$

Hence by substitution of Equations 19 and 20, Equation 18 reduces to

$$\frac{C}{Py} = \frac{Mf\,(t - t_o)}{W_s RTZ} \tag{21}$$

NOMENCLATURE

c = gas phase adsorbate concentration, grams per cm.^{3}
c_s = solid phase adsorbate concentration, grams per cm.^{3}
e = gas void fraction in adsorber column
f = volumetric flow rate, cm.^{3} per sec.
k = equilibrium constant
t = elution time of adsorbate, sec.
t_o = gas holdup time, sec.
t_m = multicomponent adsorption breakthrough time, sec.
t_s = single component adsorption breakthrough time, sec.
u = gas velocity in empty adsorber column, cm. per sec.
y = mole fraction of adsorbate in gas phase
z = length parameter for adsorption column, cm.
C = adsorption capacity, grams adsorbate/grams adsorbent
D = diffusion constant, cm.^{2} per sec.
G = gas flow rate, gram moles per sec.
L = length of adsorber bed, cm.
M = molecular weight
P = total pressure, mm. of Hg
R = universal gas constant
T = temperature, ° F. or ° R.
W_s = weight of adsorbent, grams
Z = compressibility factor

Subscripts

i, j = denote component i, j, respectively (j less strongly adsorbed than i)
ij = i in presence of j
ji = j in presence of i

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