where all the signs are taken into account in defining $\mathbf{v}_k$ and $\mathbf{v}_k^+$. Let the sets of all solutions $\mathbf{v}$ of inequalities (A2) and all solutions $\bar{\mathbf{v}}$ of (A3) be $\mathcal{V}$ and $\overline{\mathcal{V}}$.

Proposition

The set $\mathcal{V}$ is a circumscribing interval of the set $\overline{\mathcal{V}}$.

Proof. By the definition of $\mathbf{v}_k^-$ and $\mathbf{v}_k^+$, it is obvious that $\mathcal{V} \leqq \overline{\mathcal{V}}$. Now, it suffices to show that there are solutions $\mathbf{v}$ of inequalities (2) of the form

$$\mathbf{v} = \begin{bmatrix} v_1 \\ v_2 \\ v_{i-1} \\ V_i^+ \\ v_{i+1} \\ \cdot \\ \cdot \\ \cdot \\ v_m \end{bmatrix}$$

where V_i^+ is the i^{th} element of the vector $\mathbf{V}^+ = \mathbf{v}_k^+ - \overline{\mathbf{G}}_k^{-1}\mathbf{J}_k\mathbf{J}'\mathbf{x}^1$.

Introducing nonnegative slack vectors $\mathbf{y}$ and $\mathbf{z}$ in inequalities (A2), we get

$$\overline{\mathbf{G}}_k\mathbf{v} + \mathbf{I}\mathbf{y} = \mathbf{x}_k^+ - \mathbf{J}_k\mathbf{J}'\mathbf{x}^1 \tag{A4}$$

and

$$\overline{\mathbf{G}}_k\mathbf{v} - \mathbf{I}\mathbf{z} = \mathbf{x}_k^- - \mathbf{J}_k\mathbf{J}'\mathbf{x}^1 \tag{A5}$$

Let the i^{th} row of $\overline{\mathbf{G}}_k^{-1}$ be $\bar{\mathbf{g}}_{i,k}$, and first assume that all the elements of the row vector $\bar{\mathbf{g}}_{i,k}$ are nonnegative. Premultiplying (A4) by $\overline{\mathbf{G}}_k^{-1}$, we get

$$\mathbf{v} + \overline{\mathbf{G}}^{-1}\,\mathbf{y} = \overline{\mathbf{G}}^{-1}\mathbf{x}_k^+ - \mathbf{G}_k^{-1}\mathbf{J}_k\mathbf{J}'\mathbf{x}^1$$

Let $\mathbf{y} = \mathbf{0}$ (nonbasic variables). Then

$$\mathbf{v} = \overline{\mathbf{G}}_k^{-1}\mathbf{x}_k^+ - \mathbf{G}_k^{-1}\mathbf{J}_k\mathbf{J}'\mathbf{x}^1$$

is a solution of (A4), and it is of the form desired; that is

$$\mathbf{v}' = (v_1, v_2, \ldots, v_{i-1}, V_i^+, v_{i+1}, \ldots, v_m)$$

Substitution

$$\mathbf{v} = \overline{\mathbf{G}}^{-1}(\mathbf{x}_k^+ - \mathbf{J}_k\mathbf{J}'\mathbf{x}^1)$$

into (A5) yields

$$\mathbf{x}_k^+ - \mathbf{I}\mathbf{z} = \mathbf{x}_k^-$$

and, since $\mathbf{x}_k^- \leqq \mathbf{x}_k^+$, there is some nonnegative $\mathbf{z}$ satisfying the above equation. Then

$$\mathbf{v} = \overline{\mathbf{G}}_k^{-1}(\mathbf{x}_k^+ - \mathbf{J}_k\mathbf{J}'\mathbf{x}^1)$$

is a solution of (A4) and (A5), hence, of the inequalities (A2). Now, for the general case where the elements of the row vector $\bar{\mathbf{g}}_{i,k}$ are of mixed signs, with no loss of generality, assume

$$\bar{\mathbf{g}}_{i,k} = (-, +, +, \ldots, +)$$

Consider the following systems of equations:

$$\begin{array}{llll} \bar{g}_{11,k}v_1 + g_{12,k}v_2 + \ldots & + \bar{g}_{1m,k}v_m - z_1 & & = x^-_{1,k} - \ldots \\ \bar{g}_{21,k}v_1 + \ldots & + \bar{g}_{2m,k}v_m + y_2 & & = x^+_{2,k} - \ldots \\ \quad \vdots & \qquad\qquad \ddots & & \\ \bar{g}_{m1,k}v_1 + \ldots & + \bar{g}_{mm,k}v_m & + y_m & = x^+_{m,k} - \ldots \end{array} \tag{A6}$$

$$\begin{array}{llll} \bar{g}_{11,k}v_1 + \ldots & + \bar{g}_{1m,k}v_m + y_1 & & = x^+_{1,k} - \ldots \\ \bar{g}_{21,k}v_1 + \ldots & + \bar{g}_{2m,k}v_m - z_2 & & = x^+_{1,k} - \ldots \\ \quad \vdots & \qquad\qquad \ddots & & \\ \bar{g}_{m1,k}v_1 + \ldots & + \bar{g}_{mm,k}v_m & - z_m & = x^-_{m,k} - \ldots \end{array} \tag{A7}$$

Again, premultiplying (A6) by $\overline{\mathbf{G}}_k^{-1}$ and letting $(z_1, y_2, y_3, \ldots, y_m) = \mathbf{0}$, we get a basic feasible solution $\mathbf{v}$ of (A6) in the form desired, that is, $(v_1, v_2, \ldots, V_i^+, \ldots, v_m)'$, and it is easily verified to be a solution also of (A7). Hence, there exists a solution $\mathbf{v}$ of (A2) of the form $(v_1, v_2, \ldots, V_i^+, \ldots, v_m)'$ for any i. Therefore, $\overline{\mathcal{V}}$ is a circumscribing interval of $\mathcal{V}$.

The Purification of Helium Gas by Physical Adsorption at 76°K.

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The physical adsorption isotherms for three methane-helium mixtures, two nitrogen-helium mixtures, and one methane-nitrogen-helium mixture were measured at 76°K. and pressures of 2 to 65 atm. on a coconut shell charcoal. The adsorption isotherms of the pure components (nitrogen, methane, and helium) were also determined over the appropriate pressure ranges.

Methods for predicting the mixture adsorption isotherms by using only the pure component isotherms are discussed and are shown to be adequate for these systems.

The concentration vs. time or breakthrough curves were also measured for both the binary and ternary mixtures at a number of different flow rates. Mass transfer coefficients for both the gas phase and the adsorbed phase were obtained from these breakthrough curves.

Helium, once a laboratory curiosity, is now an important industrial gas. Helium usage was 948 million cu. ft. in 1966, and commercial consumption is expected to grow at about 15%/yr. in the future (*1*).

The facilities that produce high purity helium use a physical adsorption process at liquid nitrogen temperature for removal of the last quantities of nitrogen or hydrocarbon impurities. However, there are no published data on either the equilibrium adsorption capacities of commercial adsorbents for nitrogen or hydrocarbon impurities, or on the kinetic processes taking place in the adsorption beds. The work reported here was undertaken in order to obtain some of these key design data.

EQUIPMENT AND PROCEDURE

The principal features of the equipment for measuring the mixture adsorption isotherms and the concentration-time curves are shown in Figure 1. Detailed descriptions of the equipment have been published (*2* to *4*); thus only a brief outline of the experimental procedure will be given here.

Helium gas containing a known concentration of impurity is introduced into the system at the desired operating pressure, cooled to 76°K., and passed through a packed bed of adsorbent where the impurity is adsorbed. The purified helium then passes through a heat exchanger, a throttling valve, and a gas meter before going to storage. A small sample of the gas from the outlet of the adsorbent bed is passed through a thermal conductivity detector (for nitrogen) or a hydrogen flame ionization detector (for methane) to provide a continuous analysis of the concentration-time (breakthrough) curve for the effluent stream. When the adsorbent is saturated with impurity, the flow is stopped and the adsorption cell is isolated and then heated to desorb all gases. These desorbed gases are then flushed from the cell into the sample gas holder by using argon as the flush gas. The amount of desorbed gas is measured with a calibrated wet test meter, and the composition is determined with a gas chromatograph.

The dead space volume of the adsorption cell and connected capillary tubing was determined by the standard helium expansion method. An adjustment was made for the change in volume of the cell between room temperature and liquid nitrogen temperature, but the correction for volume change due to pressure was negligible. At equilibrium, the amount of unadsorbed nitrogen or methane is very small, since the gas phase is almost pure helium. The amount of helium in the gas phase, however, is very large, and to correct properly for the unadsorbed helium, the dead space volume must be adjusted to account for the volume occupied by the adsorbed nitrogen or methane. For this correction, the density of the adsorbed phase was assumed to be the same as that of the normal liquid or solid at the temperature of the experiment.

The pure component isotherms were determined by using standard volumetric techniques. The equipment and procedures are described elsewhere (*2*, *5*).

The adsorbent used in all of the experimental work was an activated coconut shell charcoal* with nitrogen B. E. T. surface area of 904 sq. m./g. Before each run, the adsorbent was reactivated for 12 to 18 hr. by heating to 200°C. and flushing with dry pure helium gas. The gas mixtures were prepared and analyzed in this laboratory.

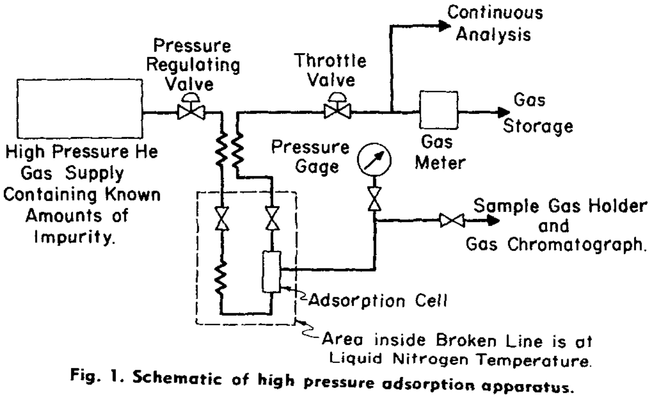

Fig. 1. Schematic of high pressure adsorption apparatus.

ADSORPTION ISOTHERMS

Pure Component Isotherms

The adsorption isotherms of nitrogen, methane, and helium are shown in Figures 2 and 3.*

The two values, V_E and V_T, shown in Figure 3 illustrate a problem peculiar to high pressure adsorption measurements, that is, the appropriate definition of the amount adsorbed. Coolidge (*6*) presents several definitions. The first, V_E, is the classical or Gibbs definition, in which the amount adsorbed is defined as the excess material present in the pores over that which would be present under the normal density at the equilibrium pressure. A second definition, V_T, places the amount adsorbed just equal to the total amount contained in the pore volume (that is, all matter under the influence of the adsorption forces). At

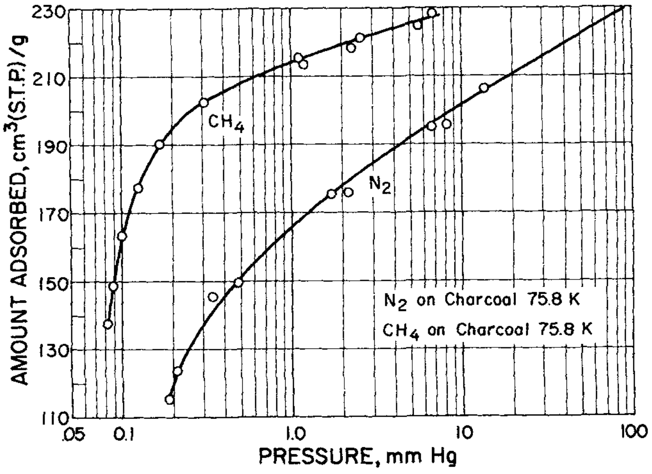

Fig. 2. Adsorption isotherms of methane and nitrogen.

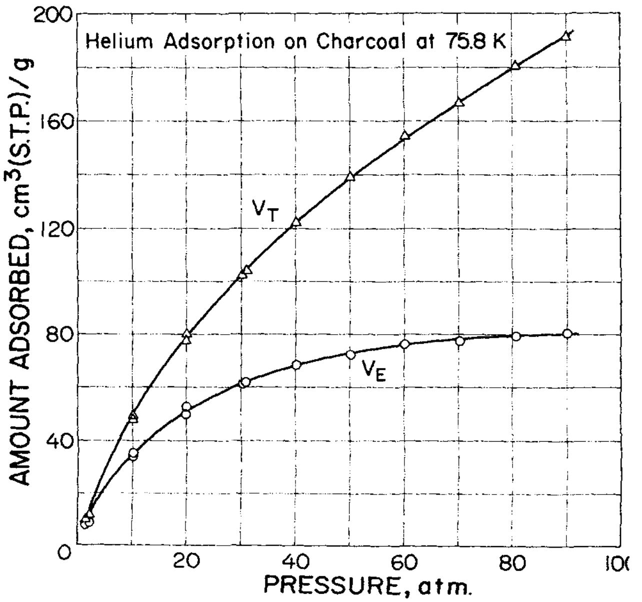

Fig. 3. Adsorption isotherms of helium.

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* Barnebey-Cheney Company, type IG-1, 8 to 10 mesh. Precise specification in this paper of the charcoal employed has been necessary to make the results of this work sufficiently meaningful. Identification of the charcoal or its manufacturer by the National Bureau of Standards in no way implies a recommendation or an endorsement by the Bureau.

* Tabular values for these isotherms are available from the Cryogenic Data Center, National Bureau of Standards, Boulder, Colorado 80302. (S.T.P.) refers to 0°C. and 1 atm.

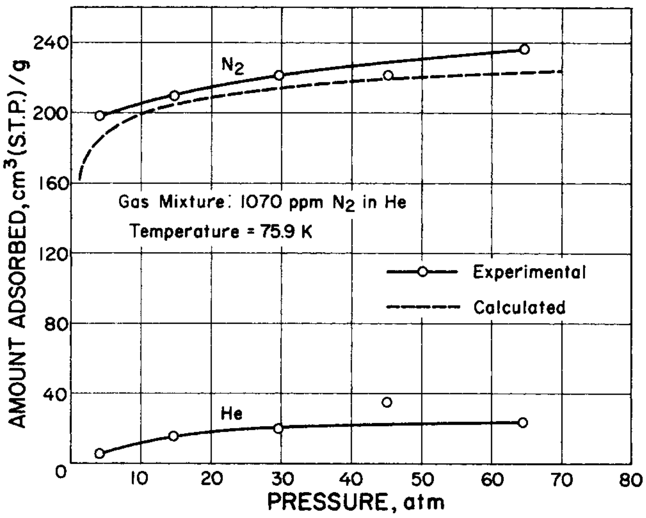

Fig. 4. Adsorption of a nitrogen-helium mixture.

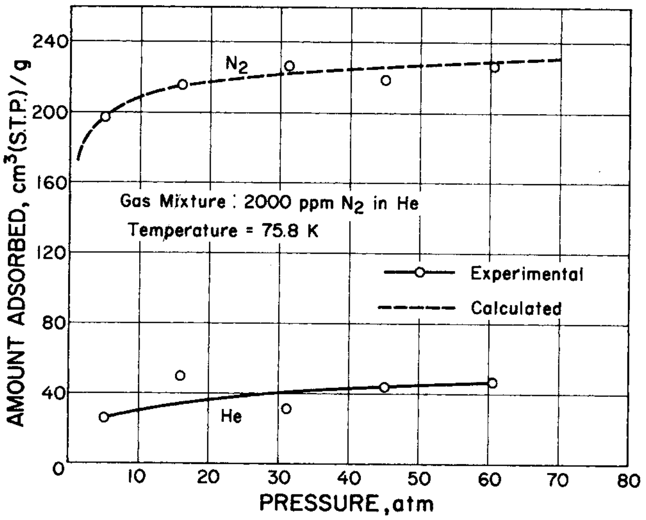

Fig. 5. Adsorption of a nitrogen-helium mixture.

moderate temperatures and pressures below 1 atm., the difference between V_E and V_T is generally insignificant.

Binary Isotherms

The adsorption isotherms for three binary mixtures are presented in Figures 4 to 6 and in Table 1. Table 1 also contains four additional points, for mixtures of 930 and 150 p.p.m. methane, not shown graphically.

The capacity values for all of the binary and ternary isotherms (Figures 4 to 7 and Tables 1 and 2) correspond to the classical or Gibbs definition of adsorption. The nitrogen and methane isotherms in these figures show a significant increase in capacity with pressure; this is the reverse of the effect observed with nitrogen-hydrogen and methane-hydrogen systems on charcoal (4), where both the nitrogen and the methane isotherms showed a significant decrease in capacity with increase in pressure. This result is not surprising, since the hydrogen systems are highly nonideal, while the helium systems in some instances may closely approximate ideal behavior in the gas phase.

The calculated curves shown in Figures 4 to 6 were obtained by assuming ideal gas behavior; that is, the partial pressure of the gas was calculated and used in conjunction with the appropriate pure component isotherm of Figure 2 to obtain the capacity. The assumption of ideal gas behavior is reasonable in this case, since the solid-vapor phase equilibrium data of Hiza and Kidnay (7) for the helium-methane system indicate a maximum deviation of 7% from ideal behavior at 76°K. and pressures of 1 to 20 atm. The disagreement between the calculated and experimental curves is less than 10% in all cases. It would, of course, be possible to use the partial

Table 1. Principal Experimental and Calculated Variables for Binary Mixtures

Average temperature = 75.8°K.
D_p = 0.193 cm.; S = 26.2 sq.cm./g.
Bed length = 6.4 cm.; Bed diameter = 1.91 cm.

Concentration of impurity in the inlet helium stream	Pressure, atm.	Impurity adsorbed, cc. (STP)/g.	Helium adsorbed, cc. (STP)/g.	G, g./(hr.) (sq. cm.)	D_pG/μ	k_g	k_s
2,000 p.p.m. N_2	60.50	227	47	87	57	6.0	0.69
2,000 p.p.m. N_2	45.00	218	44	52	34	5.2	0.38
2,000 p.p.m. N_2	31.15	226	31	42	27	4.6	0.41
2,000 p.p.m. N_2	15.80	215	50	24	16	3.8	0.19
2,000 p.p.m. N_2	5.00	197	26	17	11	2.2	0.27
1,070 p.p.m. N_2	64.45	237	24	105	68	8.5	0.46
1,070 p.p.m. N_2	45.05	221	35	80	52	7.6	0.51
1,070 p.p.m. N_2	29.45	222	20	61	40	6.4	0.35
1,070 p.p.m. N_2	14.70	210	15	45	29	4.7	0.33
1,070 p.p.m. N_2	4.05	199	6	29	19	3.7	0.19
930 p.p.m. CH_4	6.80	243	9	75	49	5.9	0.19
930 p.p.m. CH_4	4.55	227	17	54	35	4.6	0.15
930 p.p.m. CH_4	2.65	239	3	60	39	4.8	0.17
480 p.p.m. CH_4	16.70	236	16	62	40	6.5	0.14
480 p.p.m. CH_4	13.00	241	8	89	58	6.9	0.16
480 p.p.m. CH_4	6.00	234	13	132	85	9.0	0.22
480 p.p.m. CH_4	2.70	225	10	62	40	5.1	0.14
150 p.p.m. CH_4	36.45	231	7	203	132	13.7	0.10

Table 2. Principal Experimental and Calculated Variables for Ternary Mixtures

Average temperature = 75.6°K.
$D_p = 0.193$ cm.
$S = 26.2$ sq.cm./g.
Gas composition: 690 p.p.m. CH_4 + 1,460 p.p.m. N_2

Pressure, atm.	G, g./(hr.) (sq.cm.)	D_pG/μ	N_2 adsorbed, cc. (STP)/g.	CH_4 adsorbed, cc. (STP)/g.	He adsorbed, cc. (STP)/g.	$[k_g]_{CH_4}$	$[k_s]_{CH_4}$
10.90	76	49	22	200	45	7.5	0.054
8.90	55	35	17	207	37	5.1	0.052
5.40	134	87	19	201	35	9.7	0.062
2.30	50	33	15	195	43	5.3	0.077

fugacity of the methane or nitrogen in the calculation instead of the partial pressure, as was done previously for the hydrogen systems (*4*). However, for the systems considered here this procedure will not improve the agreement between calculated and experimental values, since the use of the fugacity will result in a lower calculated curve. The fact that the experimental curves for two of the isotherms lie above the calculated curves is surprising, because it seems to indicate that the helium enhances the adsorption of the nitrogen and methane. In the hydrogen systems studied previously (*4*), the presence of the hydrogen strongly inhibited the methane and nitrogen adsorption. Considerable care was taken to check all calibrations in order to avoid any consistent errors in measurement; so it is unlikely that the observed enhancement is due to experimental error.

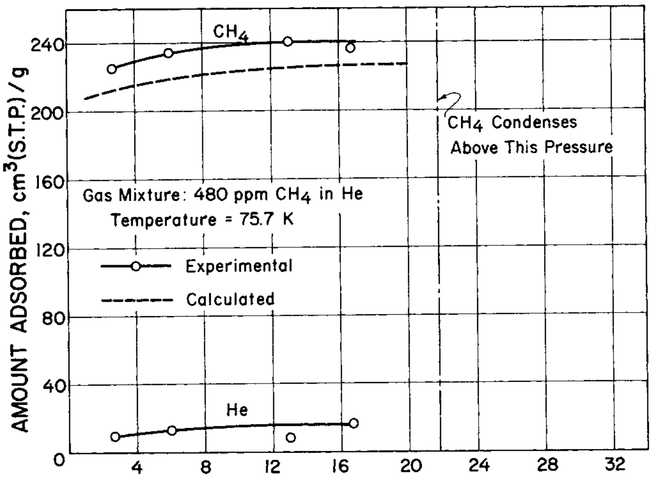

Fig. 6. Adsorption of a methane-helium mixture.

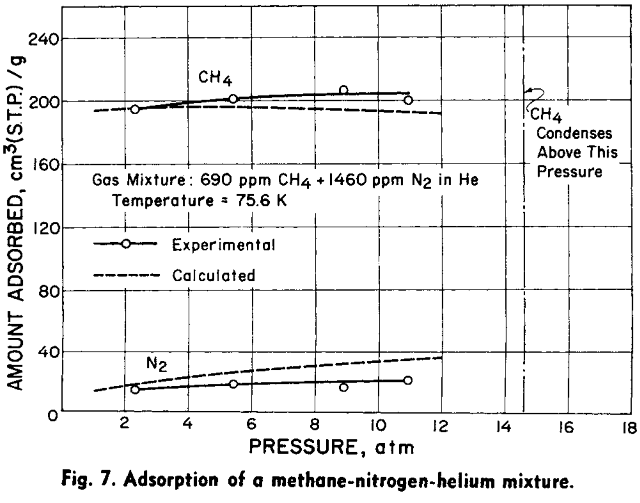

Fig. 7. Adsorption of a methane-nitrogen-helium mixture.

Ternary Isotherms

The adsorption isotherm for a ternary mixture of methane, nitrogen, and helium is presented in Figure 7 and Table 2. The calculated curves were obtained by using the method proposed by Kidnay and Myers (*8*). Briefly, this method uses the pure component isotherms of nitrogen and methane (Figure 2) and a relationship similar in form to Raoult's law to predict the mixture adsorption. Two assumptions were employed in making the calculations: first, the helium was assumed to act solely as a carrier gas for the nitrogen and methane and not to influence their adsorption by the charcoal, and, second, ideal behavior was assumed for both the gas phase and the adsorbed phase. Thus the ternary mixture of nitrogen, methane, and helium was treated as an ideal binary mixture of nitrogen and methane.

A difficulty encountered in applying the Kidnay-Myers method to the data is that the pure component isotherms of nitrogen and methane (Figure 2) are not parallel, as required by the theory. However, it has been shown (*8*) that in most cases the method works quite well even for nonparallel isotherms.

The agreement shown between the experimental and calculated values in Figure 7 is excellent, and it seems that this procedure for predicting adsorption equilibrium for dilute gas mixtures will prove very useful.

BREAKTHROUGH CURVES

Adsorption purifiers are generally fixed bed units in which the carrier gas containing the impurity to be adsorbed is passed through a packed bed of adsorbent. In this type of operation there are two distinct mass transfer processes: the diffusion of the impurity through the gas phase to the surface of the adsorbent, and diffusion into the particle. If both of these processes were extremely rapid, equilibrium would exist at all points in the adsorbent bed, and a plot of the adsorber outlet concentration as a function of time would be a step function. Usually, however, one or both of the mass transfer processes

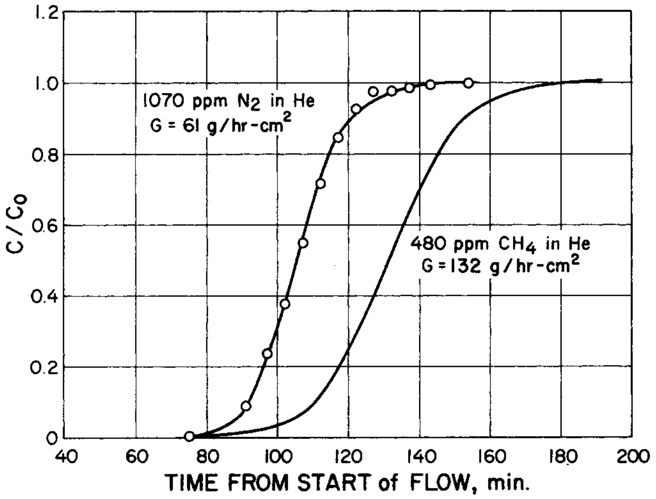

Fig. 8. Typical breakthrough curves for binary mixtures.

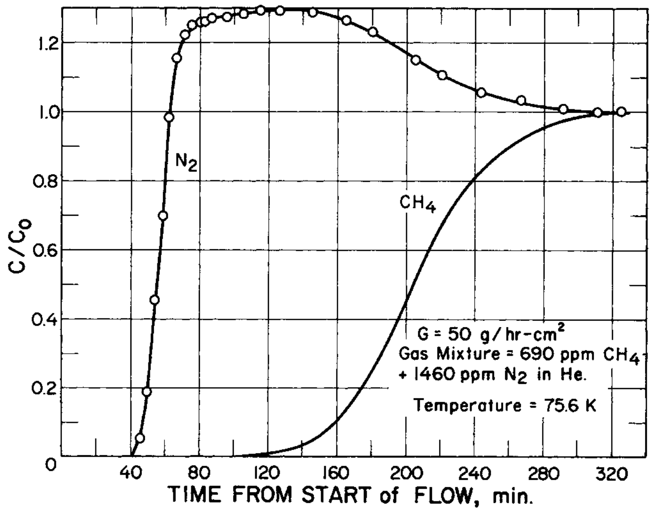

Fig. 9. Typical breakthrough curve for a ternary mixture.

are relatively slow, with the result that the concentration time (breakthrough) curve assumes an S shape. The prediction of breakthrough curves is of some practical importance, since the determination of the amount of adsorbent that is unsaturated when the first trace of impurity appears at the outlet of the adsorbent bed requires a knowledge of the breakthrough curve for the system under consideration.

Typical breakthrough curves for two binary mixtures and a ternary mixture are shown in Figures 8 and 9.[*] Individual points are shown for the nitrogen curves, since the nitrogen analysis was made on a gas chromatograph equipped with a thermal conductivity detector, and consequently the analysis was done on a sample by sample basis rather than continuously. The methane concentrations, however, were measured continuously, and thus no individual points are shown. In the ternary mixture (Figure 9), the methane is more strongly adsorbed than the nitrogen; thus, the methane displaces the nitrogen from the adsorbent, with the result that the nitrogen appears at the bed outlet first and shows the characteristic desorption curve above $C/C_0 = 1.0$.

The mathematical treatment of the breakthrough curve to evaluate mass transfer coefficients is a subject that has received considerable attention, but the problem is so complex that no general solution has yet been attained. Klotz (*9*), Vermeulen (*10*), and Hall, Eagleton, Acrivos, and Vermeulen (*11*) review the subject thoroughly.

From the engineering point of view, the method of Eagleton and Bliss (*12*) is probably the best method proposed so far, since it allows for transfer resistances in both phases, treats gas adsorption in a manner analogous to gas absorption, and does not require curve matching or numerical integration in order to evaluate the coefficients. Both gas phase and adsorbed phase mass transfer coefficients have been evaluated with the method of Eagleton and Bliss and are tabulated for all of the runs in Tables 1 and 2. The gas phase coefficient k_g is plotted as a function of the mass flow rate G in Figure 10.

The values for the adsorbed phase transfer coefficient k_s are independent of the inlet concentration C_0 for the binary helium systems studied here. This is in contrast to the behavior of the hydrogen-nitrogen and hydrogen-methane systems studied on the same sample of charcoal (*17*), where a pronounced concentration dependence was noted. The k_s values for the helium systems also show a dependence on flow rate G, again in marked contrast to the hydrogen systems. This dependence of k_s on the mass flow rate could be caused by axial mixing, channeling, or by the failure of the breakthrough curves to reach their steady state shape before emerging from the bed.

On the other hand, the k_gS values for the helium system are in perfect agreement with those obtained for the hydrogen systems (*17*).

These results suggest that there is a fundamental difference in the adsorbed phase transport processes between the helium-nitrogen, helium-methane systems, and the hydrogen-nitrogen, hydrogen-methane systems.

The experimental data for the binary mixtures may be

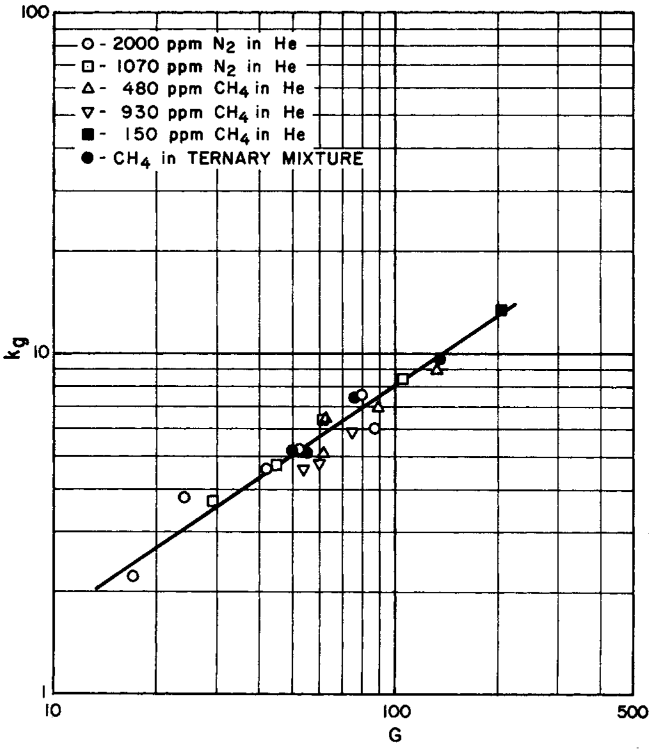

Fig. 10. Correlation of gas phase mass transfer coefficient.

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[*] Tabular values of the breakthrough curves for all of the runs listed in Tables 1 and 2 are available from the Cryogenic Data Center, National Bureau of Standards, Boulder, Colorado 80302.

represented by the relations

$$k_g = 0.35G^{0.68} \text{ for all runs}$$

$$k_s = 0.38 \text{ for helium-nitrogen}$$

$$k_s = 0.16 \text{ for helium-methane}$$

Breakthrough curves for binary mixtures calculated with these relations should be useful for design purposes, provided that the flow rates and the concentrations do not differ too greatly from those reported here.

For the ternary mixture of nitrogen-methane-helium, the problem is more complex; no previous attempts have been made to analyze data of this type. As a matter of fact, experimental breakthrough curves of this type have appeared only in two publications, that of Vander Arend and Chelton (*13*) and that of Needham, Campbell and McLoed (*14*), and in both cases the data are limited to one figure. Since the methane and nitrogen are interacting in the adsorbent bed, the breakthrough curves for the ternary mixture are not independent, and thus these curves cannot be rigorously treated by using the Eagleton and Bliss relations, which were derived for a binary system. However, if it is assumed that the effect of the nitrogen on the methane breakthrough curve is slight, then the methane curve may be analyzed independently of the nitrogen curve by using the method of Eagleton and Bliss. The nitrogen data cannot be treated in this fashion, since the presence of the methane has an obvious pronounced effect on the nitrogen breakthrough curve. As shown in Figure 10, the methane values for k_gs in the ternary mixture are in excellent agreement with those for the binary mixture. The methane values for k_s in the ternary mixture, however, differ markedly from those for the binary mixtures. These results are to be expected; the gas phase is so dilute that the presence of the nitrogen has little effect on the methane, but in the adsorbed phase the nitrogen and methane interact strongly.

Mass transfer coefficients are often plotted as j vs. Reynolds number to allow easy comparison with other data. For the systems presented here, $j = \frac{k_g}{G}\left(\frac{\mu}{\rho D_{AB}}\right)^{2/3}$, and the Reynolds number is defined as D_pG/μ. The values for the gas phase transfer coefficients k_g were converted to j values and compared with the correlation proposed by De Acetis and Thodos (*15*). In all cases, the j values obtained from the breakthrough curves were lower than those of the general correlation; a similar result was found by Eagleton and Bliss (*12*).

DEGREE OF PURIFICATION

The hydrogen flame ionization detector used for the methane analysis was quite sensitive; a change in the methane concentration of 0.2 p.p.m. produced a significant change in the instrument reading. Thus through the continuous analysis of the effluent stream, it was possible to show that the methane concentration in the effluent before the appearance of the breakthrough curve was less than 0.2 p.p.m. No such statement can be made regarding the nitrogen concentration, since the thermistor detectors used for this analysis did not have sufficient sensitivity. However, Brilliantov and Fradkov (*16*) have shown that the nitrogen impurity level in hydrogen can be reduced to less than 2×10^{-4} p.p.m. with activated carbon at 80°K.

CONCLUSIONS

1. For binary mixtures of methane or nitrogen with helium, the equilibrium adsorption capacity of the adsorbent for the impurity can be adequately predicted by assuming that the helium acts only as a carrier gas and diluent for the impurity and does not hinder its adsorption.
2. The adsorption isotherms of methane and nitrogen in a ternary mixture with helium can be predicted by again assuming that the helium acts only as a carrier gas and diluent, and by using the Kidnay-Myers method (*8*) to calculate the isotherms.
3. The method of Eagleton and Bliss (*12*) is satisfactory for evaluating and correlating the mass transfer coefficients for the systems studied.

NOTATION

C = gas phase concentration of impurity at the adsorber outlet
C_0 = gas phase concentration of impurity at the adsorber inlet
D_{AB} = diffusion coefficient
D_p = particle diameter, cm.
G = mass flow rate, g./(hr.)(sq.cm.)
j = mass transfer factor, dimensionless
k_g = gas film mass transfer coefficient, $\frac{\text{g. adsorbed}}{\text{hr.-sq.cm.}} \Big/ \frac{(\text{g. impurity})}{(\text{g. gas})}$
k_s = solid phase mass transfer coefficient, $\frac{\text{g. adsorbed}}{\text{hr.-sq.cm.}} \Big/ \frac{(\text{g. impurity})}{(\text{g. gas})}$
S = surface area of the adsorbent for mass transfer, sq.cm./g.
μ = viscosity
ρ = fluid density

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