$I(v)$ = rate of change of the volume of a particle by vapor condensation, $\mu m^3 s^{-1}$
M = molecular weight of the gas, g mole^{-1}
$n(v)$ = size distribution function μm^{-3} cm^{-3}
$n_0(v)$ = size distribution function of feed aerosol, μm^{-3} cm^{-3}
N = total aerosol number concentration, cm^{-3}
N_0 = total aerosol number concentration in feed, cm^{-3}
q = volumetric flow rate through CSTR, cm^{3}s^{-1}
S_0 = rate of formation of particles by nucleation, cm^{-3} s^{-1}
$U(x)$ = unit step function
v = particle volume, μm^3
v_f = volume of feed aerosol, μm^3
v_0 = volume of particles formed by nucleation, μm^3
V = CSTR volume, cm^3
$\bar{V}$ = total aerosol volume concentration, μm^3cm^{-3}
$\bar{V}_0$ = total aerosol volume concentration in feed, μm^3cm^{-3}
x = dimensionless particle volume, $N_0 v/\bar{V}_0$
x_0 = $N_0 v_0/\bar{V}_0$

Greek Letters

α = $\theta c_0 \sigma_0 N_0/\bar{V}_0$ or $\theta c_0 \sigma_1$
$\beta(v,\tilde{v})$ = coagulation coefficient, cm^{3}s^{-1}
γ = exponent in growth rate expression
$\delta(v)$ = Dirac delta function
$\delta(x)$ = $\bar{V}_0 \delta(v)/N_0$
θ = V/q
κ = $\beta\theta N$
ρ = liquid density of aerosol particles, g cm^{-3}
σ_γ = constant in expression for $f(v)$, $\mu m^{3-3\gamma}$ s^{-1}(g-mole cm^{-3})$^{-1}$
$\psi_i(x)$ = size distribution around i^{th} peak in the size distribution
ω = $\theta S_0/N$
$*$ = convolution operator

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Adsorption of Methane and Several Mixtures of Methane and Carbon Dioxide at Elevated Pressures and Near Ambient Temperatures on 5A and 13X Molecular Sieves by Tracer Perturbation Chromatography

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The principles of tracer perturbation chromatography were applied to measure the sorption of pure methane and several methane-carbon dioxide mixtures on 5A and 13X molecular sieves at near ambient temperatures to pressures in excess of 7 MPa (1 000 lb/in.²abs). The molecular sieves studied were industrial grade zeolite crystals pelleted with 20 wt % clay binder.

The statistical mechanical model of Ruthven was applied to both pure methane and to several mixtures of methane rich, methane-carbon dioxide mixtures from a few MPa (50 lb/in.²abs) to pressures as high as 10.34 MPa (1 500 lb/in.²abs) at near ambient temperature. While the theory appears to correlate the data well even at high pressures, some limitations of the theory begin to appear for the mixtures of higher dioxide concentrations.

SCOPE

The extent, range or scope of the foregoing work covers the competitive adsorption of binary mixtures of dissimilar gases at elevated pressures. Although industrial adsorptive processes usually take place at elevated pressures involving mixtures, high pressure adsorption data of gases on molecular sieves have seldom been reported (Lederman and Williams, 1964). Choosing tracer perturbation chromatography as the technique, Gilmer and Kobayashi (1965) measured the adsorption of methane and several mixtures of methane and carbon dioxide up to 7 MPA (1 000 lb/in.²abs.). Data are taken to allow a clear distinction to be made between Gibbs and absolute adsorption. The study includes the prediction of pure component and mixture adsorption K values by the Ruthven model (1971, 1975, 1976) for methane and carbon dioxide over the range of pressure covered in this work.

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CONCLUSIONS AND SIGNIFICANCE

The principles of radioactive tracer chromatography can be successfully applied to measure the adsorption of methane and selected mixtures of methane and carbon dioxide on 5A and 13X molecular sieves at high pressures. The technique is applicable so long as the peaks are not excessively obliterated as in the case of more strongly adsorbed species, for example, water.

Under most of the conditions of the experiment, it was necessary to distinguish between Gibbs and absolute adsorption. Competitive adsorption of methane and carbon dioxide was appropriately accounted for in most instances by the Ruthven model (1971, 1975, 1976). Slight adjustments to the Henry's constant were, however, needed for the less strongly adsorbed component, methane in this case, in the presence of high concentrations of the more strongly adsorbed component, carbon dioxide. The adsorption K values of the more strongly adsorbed component, carbon dioxide, were properly predicted except at the rather higher concentrations of carbon dioxide in methane.

Contributions of the work (significance) are:

1. The successful extension of tracer perturbation chromatography to study adsorption in gas mixtures at elevated pressures on two molecular sieves, 5A and 13X.

2. The confirmation of the applicability of the Ruthven model to high pressure gas mixtures which more closely approximate conditions encountered in gas processing.

Additional high pressure adsorption data, particularly for mixtures, are needed to evaluate the interactive terms of the Ruthven model under conditions approaching those encountered in industrial practices.

The use of molecular sieves to remove polar from nonpolar molecules is advantageous when near extinction concentrations of the polar species are desired. Such purification processes are usually conducted at elevated pressures and ambient temperatures. It is therefore significant to have experimental measurements and subsequent evaluation of theories for the description of sorption processes under possible application conditions as carried out in this study.

The study of adsorption of gases on molecular sieves by tracer perturbation chromatography impinges on at least three principal areas: the structure and nature of zeolites, the adsorption of gases and gas mixtures on zeolites and tracer perturbation chromatography and its application to adsorption studies.

A review of the literature on zeolites and adsorption is prohibitive. However, the following literature provides a good background for this study: the general treatise by Breck (1974) for the first area, the general review papers by Riekert (1970) and by Ruthven et al. (1973) to cover the second and the review paper by Kobayashi et al. (1967) to cover the third area. Other papers are referred to at appropriate occasions in the text.

Martin and Synge (1941) introduced the original chromatographic equation, which relates the total volume of carrier gas required to elute a sample V_r to the gas and solid phase volumes V_g and V_s and the distribution coefficient H:

$$V_r = V_g + V_s/H \tag{1}$$

This equation can be derived in a number of ways. Originally, it was developed by considering the column to be composed of a large number of equilibrium stages. The equation can also be deduced by setting the total retention time equal to the time spent in the gas phase plus the time spent in the stationary phase (Gilmer and Kobayashi, 1965; Haydel, 1965). This solution is also accessible from the partial differential equations describing the chromatographic process.

For a multicomponent carrier gas whose sorbable components are at equilibrium in the column, the chromatographic differential equation describing the system is:

Continuity

$$\frac{\partial c_i}{\partial t} + \frac{w \partial c_i}{\partial z} - \frac{D_i \partial^2 c_i}{\partial z^2} + \frac{V_s}{V_g}\frac{\partial \bar{c}_i}{\partial t} = 0 \tag{2}$$

Equilibrium established between the gas phase c_i and the adsorbed phase, $\bar{c}_i$

$$\bar{c}_i = \alpha_i c_i \tag{3}$$

No isotropic separation in the column

$$\frac{\bar{c}_i}{c_i} = \frac{\bar{c}_i^*}{c_i^*} \tag{4}$$

Hattaway (1973) solved the chromatographic equations for various boundary conditions between the gas and adsorbed phases using the z moment transform of Horn (1971):

$$M_n = \int_{-\infty}^{\infty} c_i z^n dz \tag{5}$$

In general, to apply the moment transform to a function $c_i(z,t)$, it is necessary that $c_i(z,t)$ be of exponential order and continuously differentiable in $-\infty < z < \infty$ and $0 < t < \infty$. Also, in applying the z moment transform to Equation (2), the following relationships are useful:

$$\frac{dM_n}{dt} = \int_{-\infty}^{\infty} z^n \frac{\partial c_i}{\partial t} dz$$

$$-nM_{n-2} = \int_{-\infty}^{\infty} z^n \frac{\partial c_i}{\partial z} dz$$

and

$$\int_{-\infty}^{\infty} z^n \frac{\partial^2 c_i}{\partial z^2} dz = n(n-1)M_{n-2}$$

The solution for the first chromatographic moment is

$$\bar{z} = M_1/M_0 = \frac{wt^*{}_i}{1 + \alpha_i V_s/V_g} \tag{6}$$

Equation (6) can be rearranged to give a relation in the form of Equation (1) by setting $wV_g/\bar{z} = Q_c$ and $\bar{z} = L$, where the retention time is measured.

The amount of the adsorbed species in the column can be found from Equation (6):

$$N_{Ai} = \text{absolute adsorption} = \bar{c}_i V_s = \left[\frac{wt_i^* V_g - V_g}{\bar{z}}\right] c_i$$

$$= (Q_c t_i^* - V_g) c_i \tag{7}$$

There is another definition of adsorption, besides the absolute adsorption, which arises from a purely thermodynamic analysis of the system—the Gibbs or differential adsorption. The Gibbs adsorption is the excess of the sorbed species in the adsorption volume over that which would be in the adsorption volume if the adsorbent had no adsorption forces. At low pressures, differences in the two definitions of adsorption are not discernable, but at higher pressures the difference is quite significant. The Gibbs adsorption is the type of adsorption value generally measured by traditional volumetric or gravimetric means and is related to the absolute adsorption (Hori and Kobayashi, 1973):

$$N_{Gi} = N_{Ai} - V_s c_i \tag{8}$$

$$= (Q_c t^*_{ri} - V_G)c_i \tag{9}$$

$$V_G = V_g + V_s \tag{10}$$

Both V_G and V_g can be found chromatographically.

All of the chromatographic equations presented so far cover the retention of the injected perturbations in just the column alone. In actual operation, the retention times of the peaks include also the effects of any dead volume between the injector and the column, between the column and the detector element, plus any particular detector response time effects. In order to subtract out these effects, the same injections are made through an empty bypass column under the same conditions as the column injections. The apparatus was designed and built so that the bypass system is exactly the same as the column system without the packed column. Haydel (1965) discussed the advantages of this method over the methods of flow splitting and dead volume calibration. Equation (7) becomes

$$N_{Ai} = [Q_c(t^*_{i,c} - t_{i,BP}) - V_g]\, c_i \tag{11}$$

Normally, the temperature at which the carrier gas is being pumped into the system is different from the actual system temperature; to correct for this

$$Q_c = Q_p \frac{T_c Z_c}{T_p Z_p} \tag{12}$$

Using $c_i = y_i P / Z_c R T_c$, the absolute adsorption of component *i* per gram of adsorbent is

$$\overline{N}_{Ai} = \left[(t^*_{i\ c} - t^*_{i\ BP}) \frac{Q_p T_c Z_c}{T_p Z_p} - V_g\right] \frac{y_i P}{Z_c R T_c m} \tag{13}$$

For the Gibbs adsorption

$$\overline{N}_{Gi} = \left[(t^*_{i\ c} - t^*_{i\ BP}) \frac{Q_p T_c Z_c}{T_p Z_p} - V_G\right] \frac{y_i P}{Z_c R T_c m} \tag{14}$$

The difference between Equations (13) and (14) is the appearance of V_g in the former and V_G in the latter. V_g is the free gas volume which excludes the sorbed phase volume in Equation (13), while V_G represents the sum of V_g and V_s, the volume of the sorbed phase or the intracrystalline volume. For many high pressure systems, the differences in c_iV_g [in Equation (9)] and c_iV_G [in Equation (11)] become appreciable, and hence $\overline{N}_{Ai}$ and $\overline{N}_{Gi}$ become significantly different. One can, in principle, measure the sorbed phase volume V_s as has been done in previous studies (Masukawa and Kobayashi, 1968; Hori and Kobayashi, 1973).

Equations (13) and (14) apply to both pure components and to mixtures, with the condition that the perturbation species, a radioactive analogue of species *i*, be very small, possess identical sorptive properties as its nonradioactive analogue and be practically detectable.

EXPERIMENTAL PROCEDURE

The equilibrium amount of a sorbed species was calculated from Equation (14) for both binary mixtures and pure components. Basically, the procedure was to first characterize a column by finding *m*, V_G and V_g and then to inject radioactive analogs of the sorbable species in a given carrier gas to determine t_i^*c and t_i^*BP. The chromatographic apparatus for obtaining the basic measurements is shown in Figure 1. The apparatus is designed to take full advantage of the stable flow rate characteristic of the tandem proportioning pump. The carrier gas is displaced at a constant rate from the discharge end of the pump through the system and collected in the receiving end of the pump. This pump is designed such that the negative rate of volumetric change of the pumping side is equal to the positive rate of volumetric change of the receiving side, thus generating very stable flow rates.

Prior to any chromatographic work, the activated weight of the molecular sieve in a column was determined. After packing a column was packed with molecular sieve and vibrated, reducing unions were placed on both ends, and glass wool was packed into the dead space between the molecular sieve and the unions. One end of the column was capped and the other end was fitted with a shutoff valve. Then the molecular sieve column was activated by heating to 350° to 400°C and evacuating to less than 10^{-4} Torr for more than 8 hr. After this, the shutoff valve was closed and the column assembly was disconnected and weighed. The weight of the molecular sieve was found by subtracting the weight of the empty column assembly which had been determined prior to packing. Finally, the column was attached to the apparatus and reactivated at the same conditions as before.

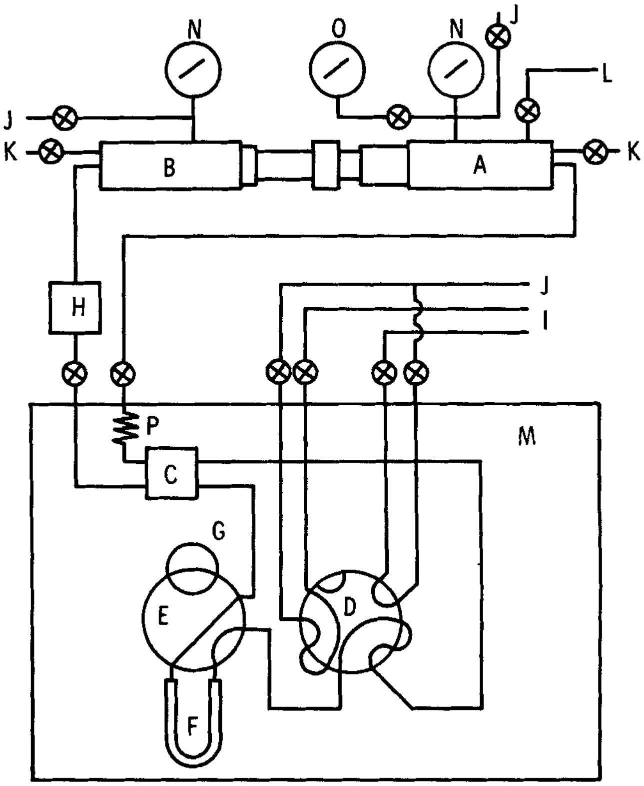

Figure 1. Schematic diagram of apparatus.

A Discharge side of pump
B Receiving side of pump
C Thermal Conductivity cell
D Double injector valve
E Switching valve
F Molecular sieve column
G Bypass column
H Ionization chamber
I To sample system
J Vent lines
K To vacuum system
L To carrier gas supply cylinder
M Constant temperature bath
N 2000 psia Heise gauges
O 400 psia Heise gauge
P Temperature equilibration coil

In order to calculate the Gibbs sorption, the total gas volume of the column V_G must be known. This was determined by using a helium carrier gas and perturbing with neon, which was found to be negligibly adsorbed at these temperatures.

In order to calculate the absolute sorption, the free gas volume V_g, excluding the sorbed phase volume V_s, was determined also. Molecular sieves are microporous and do not have a free gas volume directly associated with the sorbed molecules. This is because the limited sorption volume is within the surrounding crystalline structure. The intracrystalline volume V_s is constant, thus making the free gas volume associated with the macropores and column void volume constant also. The intracrystalline, V_g, volume was found by using a carbon dioxide carrier gas at 0.14 MPa (20 lb/in.^{2}abs) and perturbing it with helium. Carbon dioxide at 0.14 MPa fills the zeolite intracrystalline structure. Helium is not retained by the zeolite at these temperatures and is blocked from entering the crystals by the carbon dioxide. The intracrystalline volume V_s was obtained by difference.

After V_G and V_g were determined, the column was regenerated to pull off the carbon dioxide. Then, the pure component methane carrier gases were run starting with the highest carbon dioxide percentage gases first. Prior to the first carbon dioxide mixture run, the column was presaturated with carbon dioxide and then brought to equilibrium with the carbon dioxide-methane carrier gas. In filling the system with a carrier gas, the system was evacuated and flushed with the carrier gas several times.

TABLE 1. SORPTION COLUMN CHARACTERISTICS

Type	Sorbent mass, g	Length, in.	I.D., in.	Mesh size	V_G, cm^3	V_g, cm^3	$\bar{V}_s$, cm^3/g
5A	3.100	12	0.182	40-60	4.141	2.529	0.197
13X	2.226	18	0.118	60-80	2.912	2.320	0.267
13X	2.876	12	0.182	40-60	4.130	3.360	0.271

Materials Used

The molecular sieve zeolites were obtained locally. The 5A molecular sieves came in the form of 1/8 in. pellets, and the 13X molecular sieves came in the form of 1/8 in. beads. Both types are composed of approximately 20% inert clay binder. Prior to use in the chromatographic columns, these pellets were crushed, sieved to the proper mesh size and activated.

The methane used for the pure component isotherms was Linde ultra high purity grade (99.97%) methane. The carbon dioxide used in this work was Linde Coleman grade (99.99%) carbon dioxide. The helium used as a carrier gas and for perturbations was high purity grade (99.995%). All three of these gases were further dried by passing them over a bed of activated 13X molecular sieve pellets prior to loading into the pump.

The neon used for free gas perturbations was Matheson research grade (99.998%) neon.

The radioactive carbon dioxide and methane samples were transferred to stainless steel sample bombs and pressurized with their respective nonradioactive analogs.

Three carbon dioxide-methane mixtures (0.77, 1.05 and 1.43% carbon dioxide) were prepared from Coleman grade carbon dioxide and ultra high purity methane and are certified to be within 2% of stated percentages. Another mixture, 5.5% carbon dioxide in methane, was on hand from some previous work. All four were further analyzed by comparison thermal conductivity and found to be within specification. The carbon dioxide-methane mixtures were not dried prior to filling the pump owing to fear of removing any of the carbon dioxide with the drying agent.

The compressibility factors and thermodynamic properties of the gases were computed from an eleven-constant BWRS equation of state. The computer program for this was adapted from one developed by Starling (1973).

Experimental Results

The characteristics of the molecular sieve columns used in this work (m, V_G, V_g) are listed in Table 1. In Table 2, the values of $\bar{V}_s$, the intracrystalline volume per gram, are compared with the limiting carbon dioxide sorption volumes of other investigators. The chromatographic $\bar{V}_s$ values are slightly greater than the limiting sorption volumes; however, good agreement is obtained in all three cases.

Figure 2 gives the absolute and Gibbs sorption of methane on 5A at 298°K up to pressures in the neighborhood of 10 MPa (1 500 lb/in.^{2}abs). Divergence of the two types of adsorption takes place after the pressure exceeds a few MPa. The data of this work are also compared with data determined by a volumetric procedure Lederman and Williams (1964). The agreement is good considering that the temperature of their studies was approximate and the molecular sieve was activated at a lower temperature.

Figure 3 presents the absolute adsorption of methane on 5A molecular sieve at 288°, 298° and 308°K. The same data are presented as Gibbs adsorption in Figure 4 showing characteristic maxima in isotherms at high pressures.

Figure 5 presents similar absolute adsorption data of methane on 13X. Figure 6 compares the absolute adsorption of methane on 5A and 13X at identical temperatures of 298°K. Little difference in the methane adsorption between the two molecular sieves can be seen up to the neighborhood of 5 MPa (750 lb/in.^{2}abs).

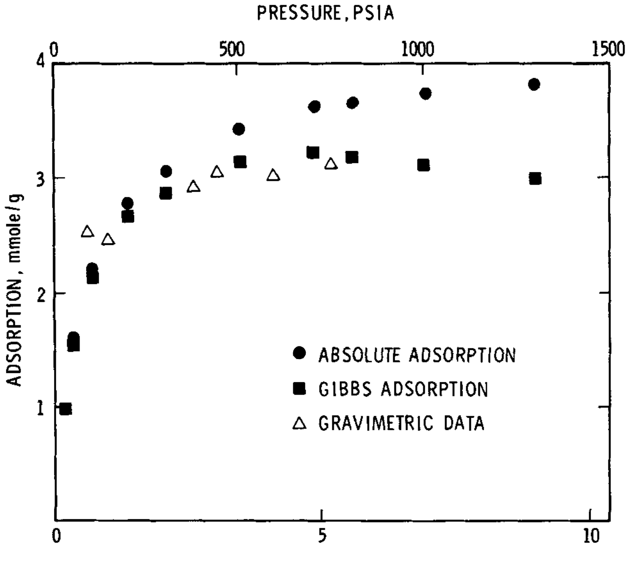

Figure 2. Comparison of gravimetric and chromatographic data for methane adsorption on 5A molecular sieve at 298K.

The apparent sorbed phase densities for pure methane $\bar{N}_A/\bar{V}_S$ are plotted in Figure 7 for 5A and 13X molecular sieves. As expected, the sorbed phase densities of methane in 5A is higher than on 13X, probably because of the more closed structure of the former relative to the latter. Indeed, the sorbed phase density of methane on 5A approached the density of liquid methane at 167°K at adsorption pressures approaching 10 MPa (1 500 lb/in.^{2}abs) adsorption and 298°K. Thus, even the methane molecules are apparently tightly bound to the surface under these conditions. 13X with its more open structure evidently results in greater freedom of motion of the methane molecule in the sorbed state.

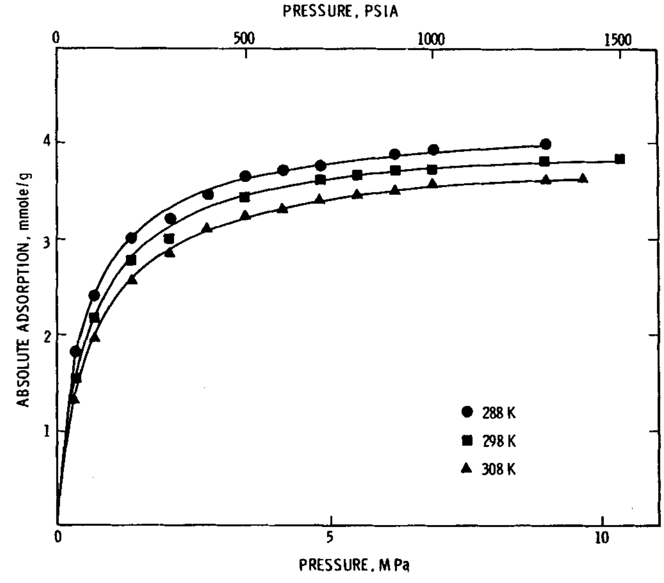

Figure 3. Absolute adsorption isotherms for methane on 5A molecular sieve.

TABLE 2. COMPARISON OF $\bar{V}_s$ WITH LIMITING ZEOLITIC CARBON DIOXIDE SORPTION VOLUME OF OTHER INVESTIGATORS

Type	Source	Limiting CO$_2$ volume, cm^3/g	Limiting CO$_2$ volume corrected for binder (× 0.80), cm/g	$\bar{V}_s$ this work, cm^3/g
13X	Breck and Grose (1973)	0.33	0.264	0.267-0.271
13X	Cruchaudaet et al. (1973)	0.32	0.256	0.267-0.271
5A	Cruchaudaet et al. (1973)	0.242	0.1936	0.197

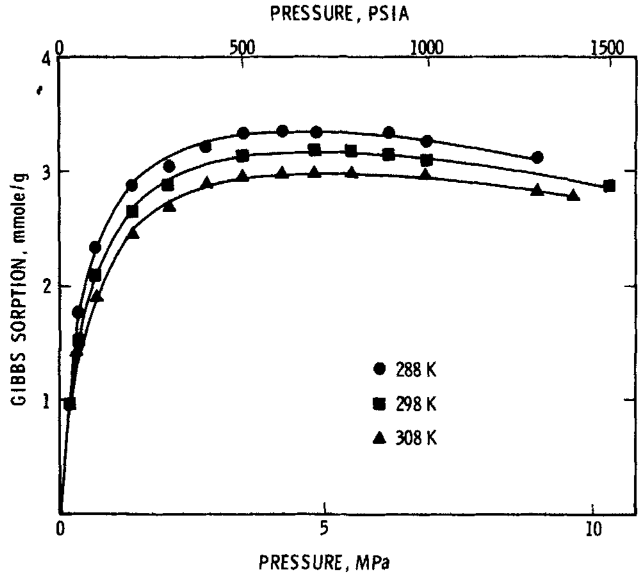

Figure 4. Gibbs adsorption isotherms for methane of 5A molecular sieve.

Figures 8 and 9 give the total sorption as well as the carbon dioxide sorption from various carbon dioxide-methane mixtures on 5A and 13X, respectively. The pure carbon dioxide sorption data (Cruchaudaet, 1973; Avgul et al., 1968; Barrer and Gibbons, 1965; Garg and Ruthven, 1975) on the two molecular sieves are also plotted on the same figures.

Figure 10 gives a comparison of the sorption capacities of 5A and 13X for methane and carbon dioxide for a fixed gas composition. Simultaneous carbon dioxide sorption capacity of 5A is higher compared to that of the 13X, while the simultaneous methane sorption capacities lie in reverse order. Figure 11 compares the sorption selectivity of carbon dioxide from a mixture of methane and carbon dioxide (y = 0.0143 mole% carbon dioxide in the gas phase), demonstrating the greater selectivity of carbon dioxide over methane on 5A rather than on 13X. Selectivity is defined as the ratio of the K value for methane sorption defined by the K value for carbon dioxide sorption, or

$$S = \frac{y_{CH_4} x_{CO_2}}{x_{CH_4} y_{CO_2}} \tag{15}$$

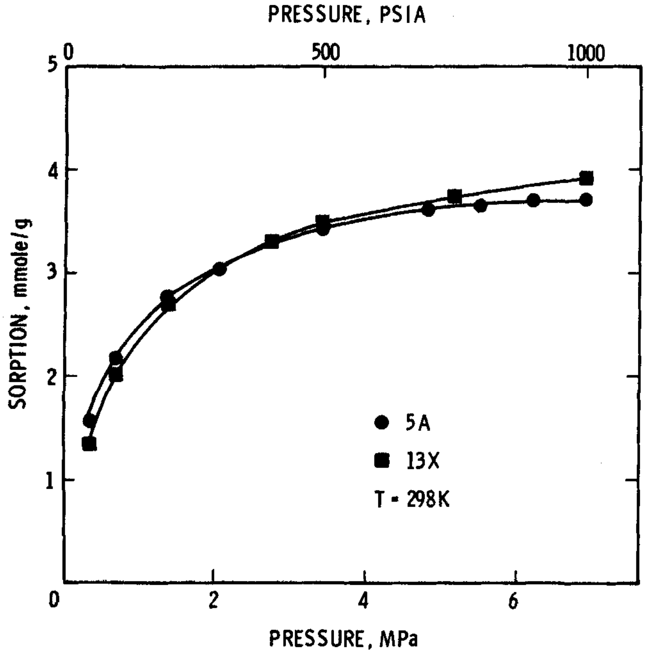

Figure 6. Comparison of methane absolute adsorption isotherms on 5A and 13X molecular sieve.

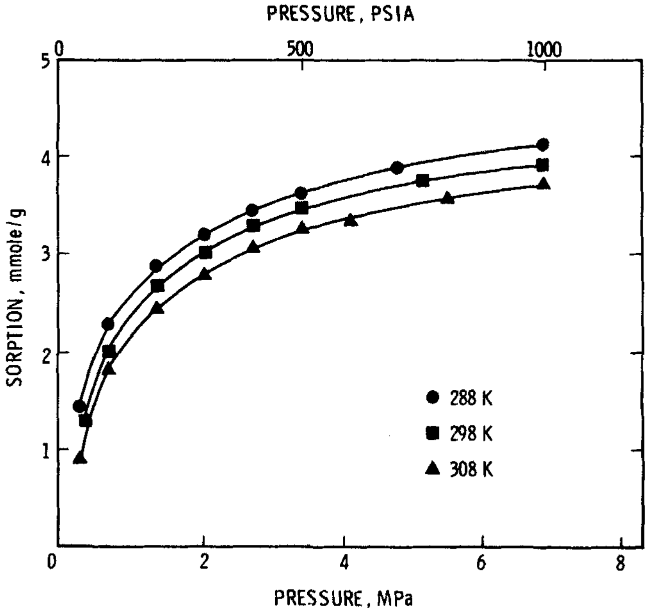

Figure 5. Absolute sorption isotherms of methane on 13X molecular sieve.

CORRELATION OF HIGH PRESSURE ADSORPTION DATA

Ruthven developed expressions for the adsorption of molecules in adsorbates consisting of discrete cavities (Ruthven, 1971). The theory may be applied to the adsorption of relatively simple molecules in zeolites if the zeolite crystal is idealized as a collection of discrete cavities with uniform potentials inside cavities with a potential barrier between cavities. Further assumptions of the model are:

1. Random independent movement of adsorbate molecules in a cavity.
2. Potential field between the cavity and the molecule that is independent of the number of molecules in a cavity.
3. The interaction between the adsorbate molecules within a cavity may be represented by a Sutherland potential.

From the configuration integral, the resulting relation for the average number of molecules per cavity for a pure component

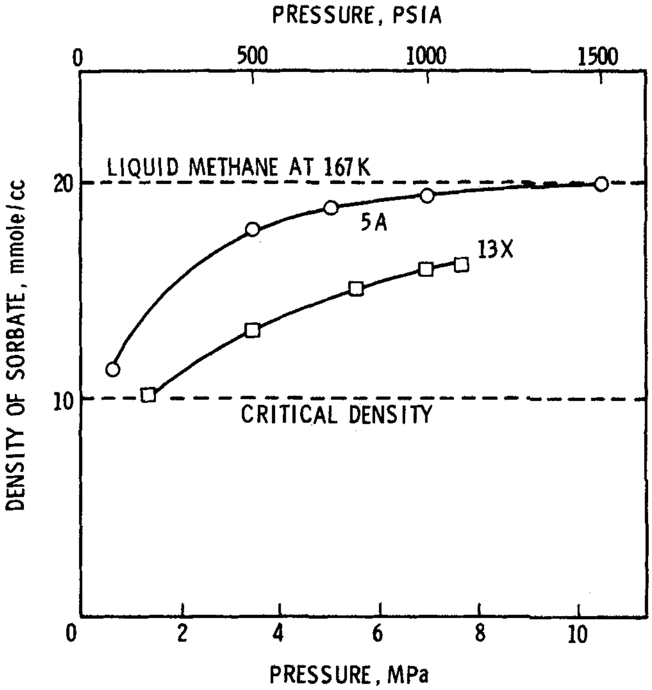

Figure 7. Calculated adsorbed phase densities for methane on 5A and 13X molecular sieves.

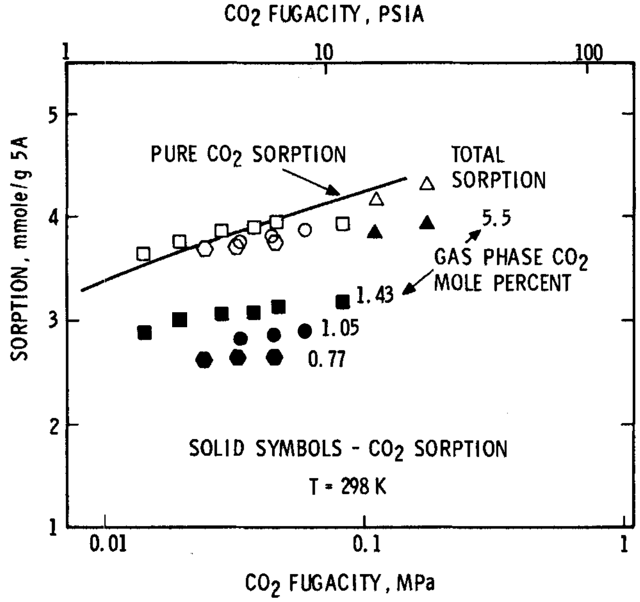

Figure 8. Total adsorption and carbon dioxide adsorption from carbon dioxide-methane mixtures on 13X molecular sieve at 298K.

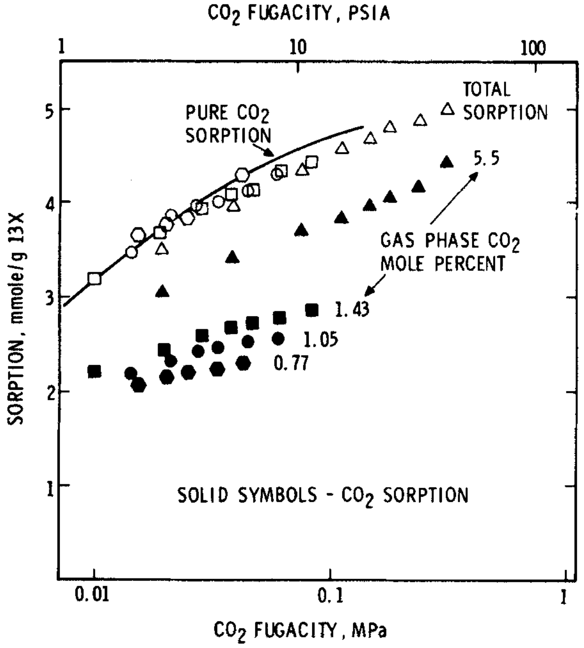

Figure 9. Total adsorption and carbon dioxide adsorption from carbon dioxide-methane mixtures on 13X molecular sieve at 298K.

was obtained:

$$\bar{c}' = \frac{K'f + \sum_{n=2}^{m}\left[\frac{(K'f)^n\left(1-\frac{nb}{v}\right)^n \exp\frac{nb\epsilon}{vkT}}{(n-1)\,!}\right]}{1 + K'f + \sum_{n=2}^{m}\left[\frac{(K'f)^n\left(1-\frac{nb}{v}\right)^n \exp\frac{nb\epsilon}{vkT}}{n!}\right]} \tag{16}$$

For a binary mixture of species 1 and 2, the expression for the average occupancy becomes (Ruthven et al., 1973)

$$\bar{c}' = \frac{k_1'f_1 + \sum_j \sum_i \frac{(K_1'f_1)^i\ (K_2'f_2)^j(1-ib_1/v-jb_2/v)^{i+j}}{(i-1)\,!j!}\exp\left(\frac{ib_1\epsilon_1+jb_2\epsilon_2}{vkT}\right)}{1+K_1'f_1+K_2'f_2\sum_j \sum_i \frac{(K_1'f_k)^i(K_2'f_2)^j(1-ib_1/v-jb_2/v)^{i+j}}{i!j!}\exp\left(\frac{ib_1\epsilon_1+jb_2\epsilon_2}{vkT}\right)} \tag{17}$$

with the constraint that $i + j > z$ and $ib_2 + jb_2 \leq v$.

In applying the above relations, it is necessary to know the characteristics of the specific zeolite, for example, v, the volume

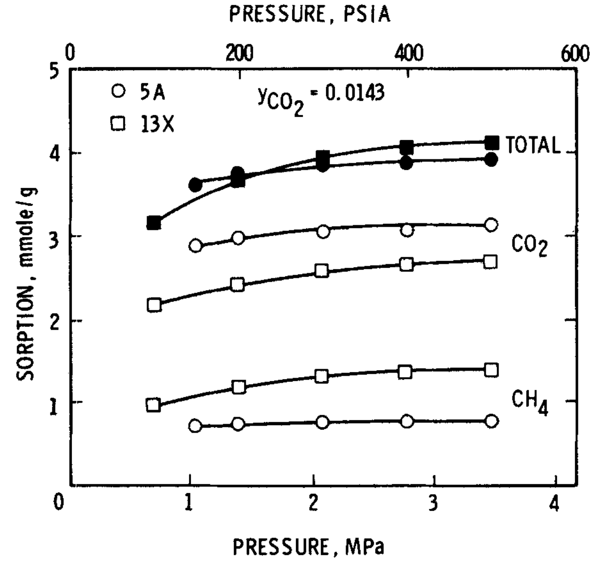

Figure 10. Comparison of selectivity of carbon dioxide from carbon dioxide-methane mixture on 5A and 13X molecular sieves at 298K for 1.43 mole % carbon dioxide.

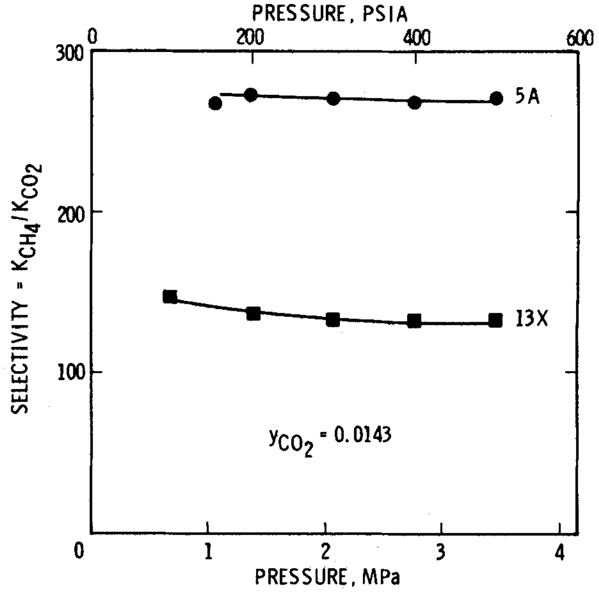

Figure 11. Comparison of selectivity of carbon dioxide from carbon dioxide-methane mixture on 5A and 13X molecular sieves at 298K and 1.43 mole % carbon dioxide.

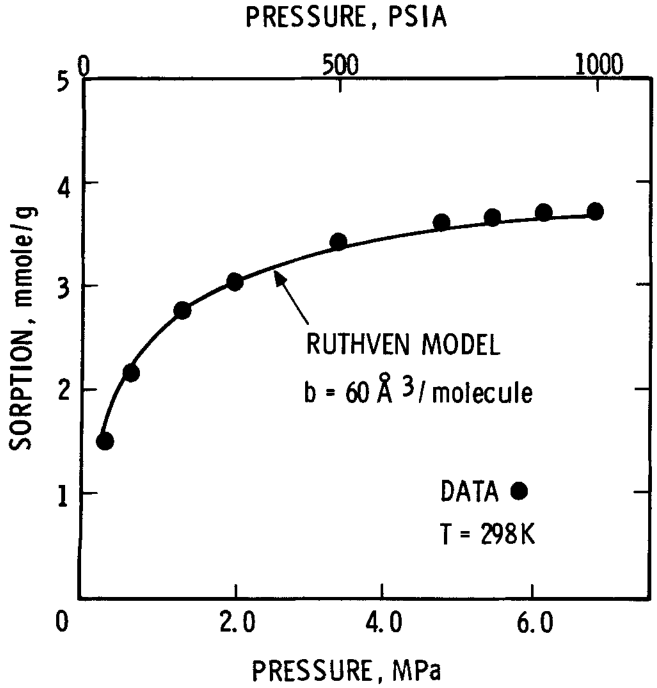

Figure 12. Prediction of methane adsorption on 5A molecular sieve by the Ruthven model.

TABLE 3. CONSTANTS OF THE RUTVEN MODEL FOR PREDICTING PURE COMPONENT METHANE SORPTION

5A molecular sieve

v = 776 A^3	ϵ/k = 148°K	
T K	b A^3/molecule	K_{CH4} molecule/cavity MPa
288	58-60	3.37
289	60-62	24.75
308	60-64	18.70

Conversion factor = 0.45 mmole-cavity/molecule-g.

13X molecular sieve

v = 822 A^3	ϵ/k = 148°K	
T K	b A^3/molecule	K_{CH4} Molecule/cavity MPa
288	58-60	15.68
298	58-60	12.05
308	60-62	9.41

Conversion factor = 0.517 mmole-cavity/molecule-g.

of a zeolite cage K', the Henry's law constant for adsorption b, the effective adsorbate molecular volume and ϵ the Sutherland constant for attraction as well as the number of cages per unit mass of adsorbent. The Henry's law constant for sorption can best be evaluated from precise low pressure sorption data, for example, by plotting $\ln(P/\bar{c})$ vs. $\bar{c}$ and determining its intercept.

The model has been successfully applied to the adsorption of methane, oxygen, nitrogen and carbon monoxide and binary mixtures of these gases on 5A zeolite at low pressures. Ruthven et al. (1976) and Loughlin et al. (1974) found the effective Henry constants for cyclopropane-ethylene-5A sorption to be quite different from their pure component values.

In the case of methane, the pure component model of Ruthven, Equation (16), has been found to predict pure component methane-5A data in the 10 to 1 000 Torr range at 273°K. The effective molecular volume used in the prediction, 77 Å^3/molecule, is slightly higher than the critical volume for methane, 71.5 Å^3/molecule. If we use effective adsorbed molecular volumes calculated from the high pressure data of this work, 58 to 62 Å^3/molecule for 5A and 59 to 60 Å^3/molecule for 13X, and Henry constants from the literature (Ruthven, 1976); Barrer and Sutherland, 1956), all of the pure component methane data of this work could be predicted within 1 to 5%. Figures 12 and 13 are examples of the predictions. Values for the constants used in the predictions are given in Table 3. The decrease in effective molecular volume with increasing pressure is not surprising at these temperatures and has been suggested by Ruthven (1976).

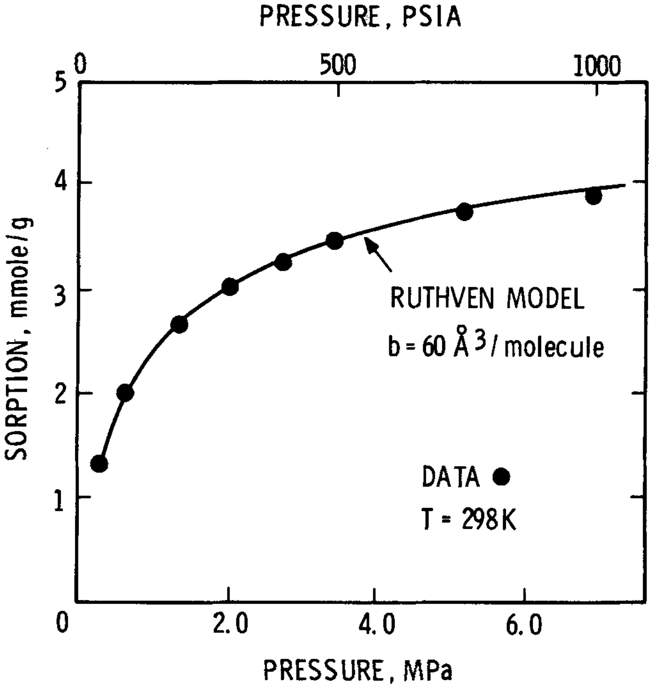

Figure 13. Prediction of methane adsorption on a 13X molecular sieve by the Ruthven model.

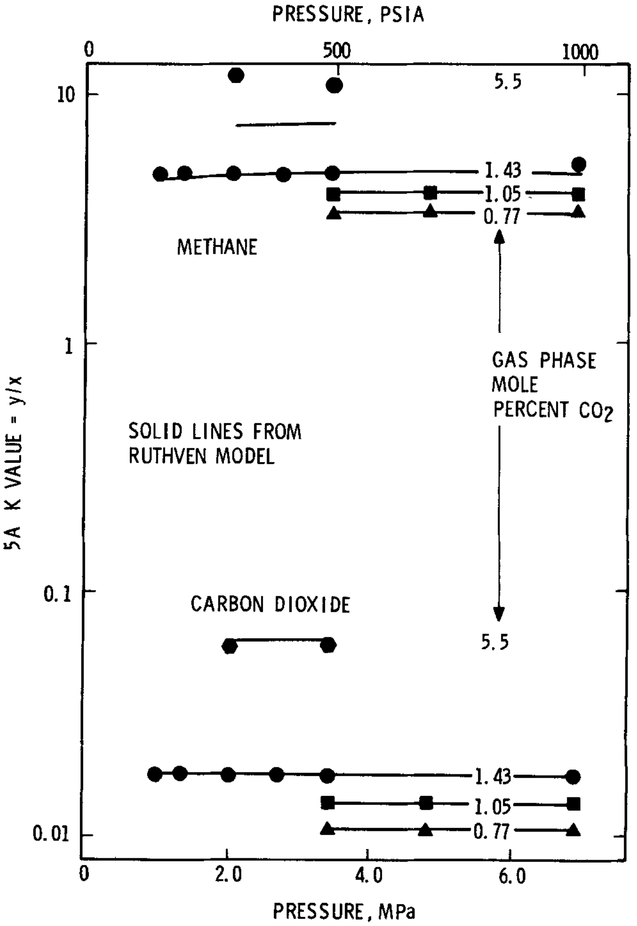

Figure 14. Carbon dioxide-methane K values vs. pressure for 5A molecular sieve at 298K.

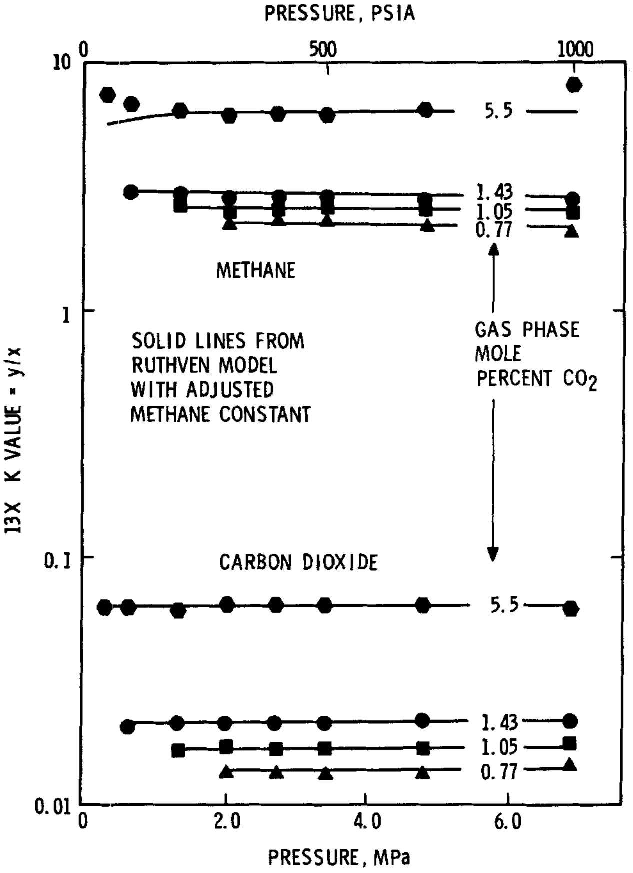

Figure 15. Carbon dioxide-methane K values vs. pressure for 13X molecular sieve at 298K.

One feature of the Ruthven model for binary sorption is that it predicts that K values (y_i/x_i) for given mixture will remain relatively constant as the pressure increases. The K values for the 5A and 13X systems exhibit this behavior (Figures 14 and 15). From Henry constants derived from the pure carbon dioxide sorption data of Linde (1959) and the pure methane Henry constants used previously, K values were predicted using Equation (17). The predicted K values also are plotted in Figures 14 and 15. The values for the constants used are given in Table 4. As before, liquid like effective molecular volumes were used for both carbon dioxide and methane.

TABLE 4. CONSTANTS FOR RUTHVEN BINARY MODEL TO PREDICT CARBON DIOXIDE-METHANE SORPTION AT 298°K

5A molecular sieve

K_{CO_2} = 7 600 molecule/cavity-MPa
K_{CH_4} = 24.75 molecule/cavity-MPa
b_{CO_2} = 60 A/molecule
b_{CH_4} = 60 A/molecule
$\epsilon/k(CO_2)$ = 195°K $\epsilon/k(CH_4)$ = 148°K
Conversion factor = 0.45 mmole-cavity/molecule-g.

13X molecular sieve

K_{CO_2} = 5 043 molecule/cavity-MPa
K_{CH_4} = 30.93 molecule/cavity-MPa
b_{CO_2} = 62 A^3/molecule
b_{CH_4} = 64 A^3/molecule
Conversion factor = 0.517 mmole-cavity/molecule-g.

In Figures 16 and 17, the K values for carbon dioxide are plotted against its mole fraction in the gas phase for 5A and 13X. For the 13X, the prediction from the pure component Henry constants is below the experimental points, indicating more methane in the intracrystalline volume than predicted. 13X has a very open structure, and the cavities are not quite as discrete as in the A type of zeolites. The line through the experimental points was found by increasing the methane Henry constant. For the 5A, the prediction from the pure component Henry constants appears to be quite good for y_{CO_2} less than 2%. Because it was suspected that the data in the higher region lies below the prediction, the point at $y_{CO_2} = 0.0389$ was taken with a carbon dioxide mixture made in the tandem proportioning pump. With large concentrations of carbon dioxide in the zeolite, the methane Henry constant is undoubtedly a poor indication of the interaction between methane and the zeolite. However, the agreement of the theory with the data is remarkable.

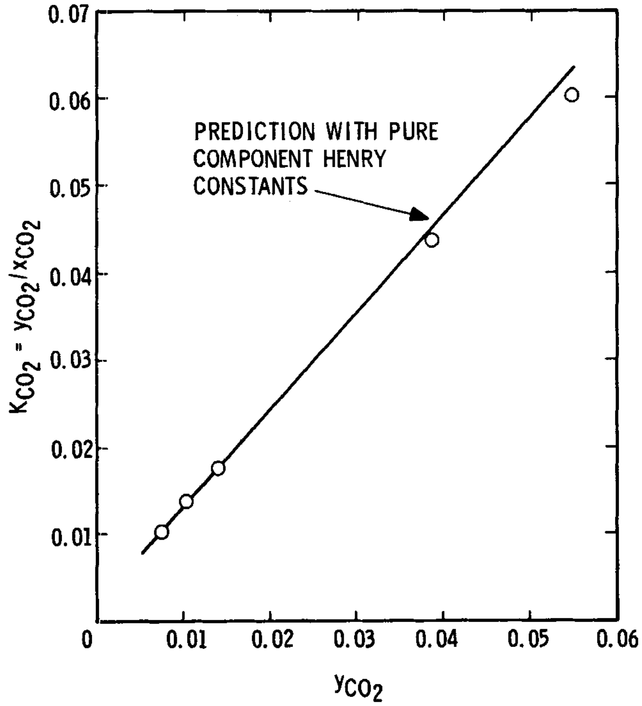

Figure 16. Prediction of carbon dioxide K value from Ruthven model for 5A molecular sieve at 298K (binary carbon dioxide-methane mixtures).

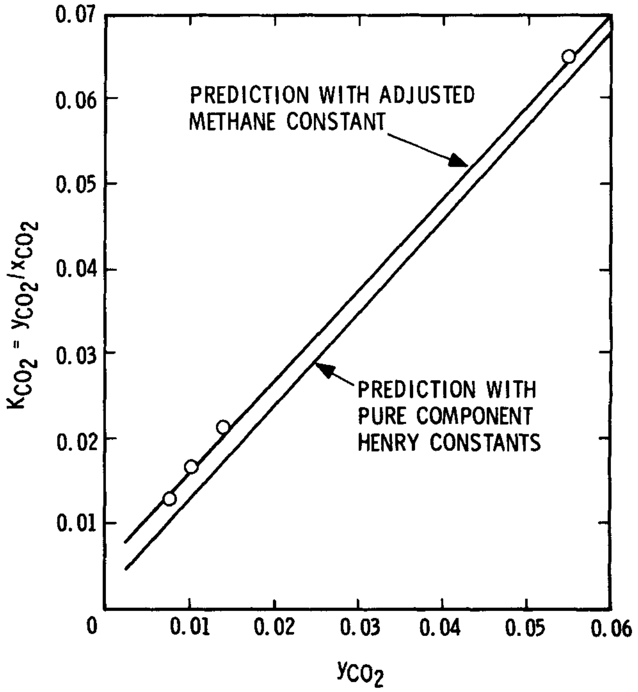

Figure 17. Prediction of carbon dioxide K value from Ruthven model for 13X molecular sieve at 298K (binary carbon dioxide-methane mixtures).

Predicting the carbon dioxide K values from Equation (17) is fairly easy because the carbon dioxide K value is relatively insensitive to changes in the methane Henry constant. The actual sorption quantities are much harder to predict because they depend heavily on knowing the exact effective molecular volumes involved and the effect of pressure.

ERROR ANALYSIS

All evaluations of the uncertainty in experimental data are based upon estimates of the errors in the measurements. A reasonable method for calculating the propagation of the uncertainties into the final results must follow from these estimates. An uncertainty is the possible value that an error can take; an error is the difference between the true value and the calculated results. The basic results of this work are calculated from Equation (13). The form of Equation (13) is such that as the column retention volume approaches the sum of the volume corrections for the bypass and V_g, the amount of the error increases. This happens at high pressures as the sorption saturation level is reached. In addition, it should be noted that uncertainties in the retention volumes arise not only from the inability to measure time accurately but also from the uncertainty in the location of the peak mean.

Using the method of Kline and McClintock (1953), the uncertainty of the *p e* component methane adsorption data was estimated to be 2 to 3% between 0.34 and 6.89 MPa. For the carbon dioxide K values, the uncertainty was 10 to 15% at 3.44 MPa. For the methane measurements, most of the error arises from uncertainty in the residence time measurements. For the carbon dioxide, the major portion of the error comes from the uncertainty in the gas phase mole fraction; that is, the retention volume is much larger than the column gas phase or bypass corrections.

CONCLUSION

The principles of radioactive tracer chromatography have been applied to pure component methane and binary methane-carbon dioxide adsorption on 5A and 13X molecular sieves. By using an assumption of constant intracrystalline adsorption volume, the technique yielded data which agreed well with those taken by a volumetric method. Furthermore, the technique yields information on the effective molecular adsorption volumes at high pressures. For methane, the effective molecular adsorption volume was found to be liquidlike at the conditions studied.

If we use effective molecular adsorption volumes calculated from the data, and pure component parameters from the literature, the pure component methane data and the behavior of the mixture K values can be predicted using the statistical thermodynamic model of Ruthven. Some deviation from the theory can be seen at high carbon dioxide loadings.

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The authors wish to acknowledge the donation of samples of 5A and 13X by the Linde Division of the Union Carbide Corporation. The National Science Foundation provided generous financial support for the study. Also, the interest and general contributions of many colleagues and associates are acknowledged.

NOTATION

b = effective molecular volume of sorbate species in a zeolite cavity
c = column free gas phase concentration
$\bar{c}$ = intercrystalline phase concentration
$\bar{c}'$ = sorbate molecular concentration per zeolite cavity
$\bar{D}$ = gas Phase diffusivity corrected for tortuosity
F = fugacity
H = distribution coefficient of Equation (1), $c/\bar{c}$
K = y_i/x_i
K = Henry's law constants, Equations (17) and (18)
k = Boltzmann constant
L = length of packed chromatographic bed in a column
m = mass of sorbent in column
M_n = n^{th} order z moment tranform
N_A = absolute sorption per gram sorbent, mmole/g
N_G = Gibbs or differential sorption, mmole
$\bar{N}_A$ = absolute sorption per gram sorbent, mmole/g
$\bar{N}_G$ = Gibbs sorption per gram sorbent, mmole/g
P = sorbed phase pressure
Q = initial concentration of injected species
R = universal gas constant
S = selectivity
T = system temperature
t = time
T_c = temperature in the column
T_p = temperature at the pump
$t_{r\,i}^{*}$ = retention time of radioactive pulse of component i
v = volume of a zeolite cage
V = total volume
V_g = free gas volume excluding the sorbed phase volume; intercrystalline volume
v_g = molar volume of gas phase, cm^3/mmole
V_s = volume of sorbed phase in column; intracrystalline volume
v_s = molar volume of sorbed phase, cm^3/mole
w = gas phase interstitial velocity
z = column axial direction
Z_c = compressibility factor for gas in the column
Z_p = compressibility factor for gas in the pump
α = alpha cavity
α_i = distribution coefficient, $\bar{c}_i/c_i$
ϵ = molecular constant of attraction in Sutherland potential function

Superscripts

A = absolute sorption
BP = bypass
c,col = column
G = Gibbs
g = free gas phase
i = sorbate species
p = pump
s = sorbed phase
tot = total
1,2 = sorbate species

Superscripts

* = radioactive pulse
—— = per gram of sorbent

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Throughflow Drying and Conditioning of Beds of Moist Porous Solids: A Simple Method for the Quantitative Prediction of Moisture and Temperature Fronts

A simple procedure previously developed for the prediction of fixed bed adiabatic sorption operations (Basmadjian, 1980*b*) has been extended to the throughflow drying and conditioning of beds of moist porous solids. The method eliminates time consuming numerical solutions of the model PDE's and yields satisfactory agreement with reported experimental data.

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SCOPE

The simulation of moisture and temperature fronts which arise in throughflow drying and ventilating of fixed beds of moist porous solids has previously required the numerical solution of coupled partial differential equations together with analytical expressions for the complex moisture isotherms. Even for persons experienced in numerical work, the task can easily occupy several days of fairly laborious work. These drawbacks are overcome here by means of a simple two-step procedure. The rigorous equilibrium mass and energy balances are combined with plots of moisture isotherms to carry out a graphical construction of the adiabatic, or effective equilibrium curves. Tabulated solutions for isothermal sorption are then applied along these curves to derive nonequilibrium moisture and temperature profiles or breakthrough curves. The procedure requires less than an hour's unskilled work once the relevant thermal, kinetic and equilibrium data are known.

In the absence of kinetic data, step 1 also provides an easy means of deriving equilibrium bed profiles, establishing the nature of the moisture fronts (stable or expanding) and estimating the length of the plateau zone. These procedures can be used for a rapid analysis of bed behavior over the entire domain of operations and are useful in estimating drying times as well as material and energy consumption.

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