

greater improvements in yields. On the basis of the results presented here, it would seem worthwhile to investigate cultivation of mass cultures of algae in open channels exposed to sunlight with a view to efficient utilization of solar energy.

Since photochemical reactions, in general, possess features similar to those of photosynthesis, the methodology presented in this paper would be applicable to these situations also.

#### NOTATION

$C$	= constant in Tamiya rate mechanism
$D$	= eddy dispersion coefficient
$D_1$	= variance in Equation (14)
$E$	= enzyme, also, statistical expectation, efficiency
$g_L$	= Lagrangian correlation coefficient
$h$	= Planck constant
$I$	= light intensity
$k$	= rate constant, also, constant in Equation (28)
$L$	= channel depth
$M_x$	= mean of $x$
$P$	= productivity
$\bar{R}_m$	= mean microscopic rate of photosynthesis
$\bar{R}$	= macroscopic photosynthetic rate
$\bar{S}$	= coefficient of variation of photosynthetic rate
$t$	= time
$U_c$	= mean velocity at the center of channel
$W$	= Wiener process, $W_x$ , second moment of $x$
$Z$	= position of algal cell
$\bar{Z}$	= mean position of cell

#### Greek Letters

$\beta$	= Beer's law coefficient
$\delta$	= Dirac delta function
$\epsilon$	= constant in Tamiya rate mechanism
$\nu$	= frequency of light
$\rho$	= culture density
$\sigma$	= standard deviation
$\tau$	= time increment in autocorrelation function

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# Measurement of Zeolitic Diffusivities and Equilibrium Isotherms by Chromatography

The chromatographic method has been used to study the sorption and diffusion of methane, ethane, propane, and cyclopropane in 5A molecular sieve. Both the equilibrium isotherms and the time constants for zeolitic diffusion, obtained from the chromatographic peaks, agree well with the values obtained previously by the gravimetric method, thus confirming the validity of the experimental technique. The results obtained in several previously reported chromatographic studies are reviewed, and it is shown that the apparent discrepancies between chromatographic and gravimetric data arise mainly from differences in the way in which the micropore diffusivity is defined. The relative advantages and disadvantages of the gravimetric and chromatographic methods are briefly considered.

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#### SCOPE

The chromatographic method has been suggested as an alternative to the conventional gravimetric or volumetric methods for studying the kinetics and equilibrium

of sorption in biporous adsorbents such as molecular sieves. However, there has been no detailed comparison between results obtained, under comparable conditions, by chroma-

tography and by the more conventional gravimetric or volumetric methods. Such a comparison is presented in the present study. In order to obtain reliable values for intracrystalline diffusivities by the chromatographic method, it is necessary to eliminate the effects of other mass transfer resistances such as external film resistance and macropore diffusional resistance. This requires the use of small adsorbent particles, and, under these conditions, the effect of axial dispersion may be significant. Experiments were performed using both a helium carrier and a mixed carrier containing helium and the adsorbable component in known proportions. The first moment of

the chromatographic peak gives the slope of the equilibrium isotherm. The Henry constants are obtained directly from the data obtained with a pure helium carrier, and by integration of the slopes obtained with a range of different carrier compositions, the complete isotherm may be determined. Time constants for zeolitic diffusion are derived from the second moments after due correction for axial dispersion and other mass transfer resistances. Both the equilibrium isotherms and the diffusional time constants derived in this way agree well with the values obtained previously by the gravimetric method using a similar sample of adsorbent.

## CONCLUSIONS AND SIGNIFICANCE

The good agreement which is observed between the gravimetric and chromatographic data confirms the validity of both experimental techniques. While it is possible to obtain reliable diffusion measurements by the chromatographic method, the range of conditions under which this is possible is somewhat restrictive. When diffusion is rapid, as for methane in 5A, the effect of intracrystalline diffusion is masked by axial dispersion, and chromatographic determination of the diffusivity is no longer feasible. The previously reported chromatographic diffusivity data of Sarma and Haynes (argon in 4A) and Hashimoto and Smith (*n*-butane in 5A) appear to differ markedly from

the gravimetric values previously reported for these systems. Detailed examination, however, shows that the differences are due to a difference in the definition of the intracrystalline (micropore) diffusivity. When corrected to the same basis, the chromatographic and gravimetric data agree well. Implicit in the chromatographic method is the assumption that the diffusivity is independent of concentration. For most systems, this is a valid approximation at low sorbate concentrations. However, certain molecular sieve systems exhibit an inverse concentration dependence of diffusivity within the Henry's law region, and, under these conditions, the chromatographic method can yield erroneous results.

Experimental studies of the kinetics and equilibria of sorption in molecular sieves have been carried out mainly by standard gravimetric or volumetric methods. Chromatographic methods offer an alternative approach which has been utilized in several of the more recent studies (Sarma and Haynes, 1974; Hashimoto and Smith, 1973; Macdonald and Habgood, 1972; Ma and Mancel, 1973). Where comparisons between chromatographic and gravimetric data are possible, the agreement is not always good, but the extent to which such discrepancies reflect real differences is uncertain. In order to provide a more reliable comparison, the present chromatographic study was undertaken using a sample of the same adsorbent as had been used in previous gravimetric studies in this laboratory (Loughlin, 1970; Derrah, 1973). The data show good agreement, and a more detailed examination of some of the previously reported chromatographic data reveals the reasons for the apparent discrepancies.

### THEORETICAL

The response of a molecular sieve column, subjected to a pulse injection of sorbate at the inlet at time zero, may be described by the following set of equations:

Zeolitic diffusion:

$$D_c \left( \frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) = \frac{\partial q}{\partial t} \quad (1)$$

$$q(r_c, t) = K_c c(R, t) \quad (2)$$

$$\frac{\partial q}{\partial r}(0, t) = 0 \quad (3)$$

$$\bar{q} = \frac{3}{r_c^3} \int_0^{r_c} r^2 q \, dr \quad (4)$$

Macropore diffusion:

$$\theta D_p \left( \frac{\partial^2 c}{\partial R^2} + \frac{2}{R} \frac{\partial c}{\partial R} \right) = w(1 - \theta) \frac{\partial \bar{q}}{\partial t} + \theta \frac{\partial c}{\partial t} \quad (5)$$

$$\frac{3k}{R_p} [C(z, t) - c(R_p, t)] = \frac{\partial \bar{Q}}{\partial t} \quad (6)$$

$$\frac{\partial c}{\partial t}(0, t) = 0 \quad (7)$$

$$\bar{Q} = \frac{3w(1 - \theta)}{R_p^3} \int_0^{R_p} \bar{q} R^2 \cdot dr + \frac{3\theta}{R_p^3} \int_0^{R_p} c R^2 dR \quad (8)$$

Column:

$$D_L \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \left( \frac{1 - \epsilon}{\epsilon} \right) \frac{\partial \bar{Q}}{\partial t} = \frac{\partial C}{\partial t} \quad (9)$$

$$C(z, 0) = c(R, 0) = q(r, 0) = 0 \quad (\text{or constant}) \quad (10)$$

$$C(0, t) = C_o \cdot \delta(t) \quad (11)$$

$$C(\infty, t) = 0 \quad (12)$$

This set of equations is formally similar to that used by Haynes and Sarma (1973) to describe the chromatographic response of a column packed with a biporous adsorbent. However, in order to maintain consistency with previous gravimetric studies, we have expressed the adsorbed phase concentration ( $q$ ) on a crystal volume basis, we have included a factor ( $\omega$ ) to account for the presence of an inert clay binder, and we have defined both the macropore diffusivity and the axial dispersion coefficient on a free area basis. The relationship between our parameters and those of Haynes and Sarma is thus:  $K_c D_c = D_x$ ,  $w(1 - \theta) = 1 - \theta_y$ ,  $K_c = \theta_x(1 + K_a)$ ,  $\theta D_p = D_y$ ,  $D_L \epsilon = D_z$ . The mean and variance of the response peak are therefore given by

$$\mu = \frac{L}{v} \left\{ 1 + \left( \frac{1 - \epsilon}{\epsilon} \right) K_p \right\} \quad (13)$$

$$\frac{\sigma^2}{2\mu^2} = \frac{D_L}{vL} + \left( \frac{\epsilon}{1 - \epsilon} \right) \cdot \left( \frac{v}{L} \right) \cdot$$

$$\left\{ \frac{R_p}{3k} + \frac{R_p^2}{15\theta D_p} + \frac{r_c^2}{15D_c K_p} \right\} \quad (14)$$

where  $K_p = \theta + w(1 - \theta)K_c$  and we have assumed  $K_p \gg 1$ .

The equilibrium constant (or the slope of isotherm) may thus be calculated directly from the first moment of the chromatographic response peak. In order to obtain the time constant for zeolitic diffusion from the second moment, it is necessary to estimate the contributions arising from axial dispersion, external film, and macropore diffusional resistance. The latter can be minimized by the use of small adsorbent particles. At low Reynolds numbers, the external film coefficient is given, approximately, by  $kR_p/D_m \approx 1.0$  ( $N_{Sh} \rightarrow 2.0$ ), and the axial dispersion coefficient is given by  $D_L \approx 0.7 D_m + vR_p$ . The macropores of Linde 5A sieve are relatively large so that transport occurs predominantly by molecular diffusion, with the macropore diffusivity given by  $D_p \approx D_m/\tau$ . Reported values of  $\tau$  show some variation. We have taken a value of 2.0 in accordance with the data of Roberts and York (1967), Sargent and Whitford (1971), and Lee and Ruthven (1977). Somewhat higher values (3 to 4) were obtained by Hashimoto and Smith (1973). However, since in the present systems the correction for macropore resistance is minor, the precise value of  $\tau$  is not important.

With these approximations, Equation (14) may be written as

$$\frac{\sigma^2}{2\mu^2} \left( \frac{L}{V} \right) = \frac{D_L}{v^2} + \left( \frac{\epsilon}{1 - \epsilon} \right) \left( \frac{1}{3} + \frac{\tau}{15\theta} \right) \frac{R_p^2}{D_m} + \left( \frac{\epsilon}{1 - \epsilon} \right) \frac{r_c^2}{15K_p D_c} \quad (15)$$

in which the terms on the right-hand side represent the respective contributions of axial dispersion, film, and macropore resistance, and zeolitic diffusional resistance. Since the values of  $D_m$ ,  $v$ ,  $\epsilon$ ,  $\theta$ ,  $R_p$ , and  $\tau$  are known, the first two terms may be estimated, thus allowing the time

TABLE 1. DETAILS OF COLUMN AND ADSORBENT

Column: packed length = 33 cm  $\times$  0.95 cm I.D.

Bed voidage:  $\epsilon = 0.37$

Adsorbent: Linde 5A 30-40 mesh pelleted sieve (Lot MX 1582-Matheson, Coleman, Bell)

$R_p = 0.025$  cm

$\theta = 0.32$

$\tau = 2.0$

$r_c \approx 1.8 \times 10^{-4}$  cm

TABLE 2. COMPARISON OF CHROMATOGRAPHIC AND GRAVIMETRIC HENRY CONSTANTS

Sorbate	Temperature ( $^{\circ}$ K)	$K_c$ (gravimetric)	$K_c$ (chromatographic)
CH <sub>4</sub>	348	16	12.7
C <sub>2</sub> H <sub>6</sub>	298	860	735-816
	348	177	146
C <sub>3</sub> H <sub>8</sub>	398	720	360
cyclo-C <sub>3</sub> H <sub>8</sub>	398	1 555	1 550-1 830

Gravimetric values are calculated from data of Loughlin (1970) and Derrah (1973).

TABLE 3. COMPARISON OF THE RELATIVE CONTRIBUTIONS OF AXIAL DISPERSION, FILM PLUS MACROPORE DIFFUSIONAL RESISTANCE AND CRYSTAL DIFFUSIONAL RESISTANCE [EQUATION (15)]

$x$	$v$ (cm $\cdot$ s $^{-1}$ )	$\sigma^2 L / 2\mu^2 v$ (s)	$D_L / v^2$ (s)	$2.77 \times 10^{-4} / D_m$ (s)	$D_c / r_c^2 \times 10^3$ (s $^{-1}$ )
CH <sub>4</sub> -5A at 348 $^{\circ}$ K					
0	2.17	0.141	0.143	$3.1 \times 10^{-4}$	—
0.183	2.66	0.086	0.096	$3.1 \times 10^{-4}$	—
0.326	3.22	0.071	0.068	$3.1 \times 10^{-4}$	—
0.374	2.81	0.084	0.087	$3.1 \times 10^{-4}$	—
0.413	2.54	0.105	0.105	$3.1 \times 10^{-4}$	—
C <sub>2</sub> H <sub>6</sub> at 298 $^{\circ}$ K					
0	4.6	0.025	0.022	$5.5 \times 10^{-4}$	—
0	9.1	0.012	0.007	$5.5 \times 10^{-4}$	—
0.30	9.0	0.149	0.007	$5.5 \times 10^{-4}$	13.3
0.46	4.2	0.146	0.026	$5.5 \times 10^{-4}$	9.4
0.48	4.6	0.157	0.023	$5.5 \times 10^{-4}$	11.6
0.54	4.0	0.30	0.028	$5.5 \times 10^{-4}$	6.7
0.63	4.6	0.31	0.023	$5.5 \times 10^{-4}$	7.1
0.66	4.4	0.28	0.024	$5.5 \times 10^{-4}$	9.2
C <sub>3</sub> H <sub>8</sub> at 398 $^{\circ}$ K					
0	5.9	0.04	0.018	$3.9 \times 10^{-4}$	9.6
0.09	5.1	0.09	0.023	$3.9 \times 10^{-4}$	8.4
0.10	4.6	0.085	0.029	$3.9 \times 10^{-4}$	7.5
0.10	4.6	0.07	0.029	$3.9 \times 10^{-4}$	10.6
0.33	4.4	0.16	0.031	$3.9 \times 10^{-4}$	13.1
0.41	3.9	0.27	0.039	$3.9 \times 10^{-4}$	12.3
cyclo-C <sub>3</sub> H <sub>8</sub> at 398 $^{\circ}$ K					
0	6.2	0.134	0.018	$3.6 \times 10^{-4}$	0.34
0	4.0	0.171	0.040	$3.6 \times 10^{-4}$	0.36
0.086	6.3	0.20	0.018	$3.6 \times 10^{-4}$	3.6

$2.77 \times 10^{-4}$  cm $^2$  is the value of the factor  $(\epsilon/1 - \epsilon)(1/3 + \tau/15\theta)R_p^2$  in equation 15.

constant for zeolitic diffusion to be obtained by difference. It is evident that reliable values for the latter quantity can be obtained only when this term represents the major contribution to the overall dispersion.

## EXPERIMENTAL

Response peaks were measured using a standard gas chromatograph (Perin Elmer 880) fitted with a thermal conductivity detector. Details of the column and adsorbent are given in Table 1. Gas velocities were sufficiently low that the pressure drop through the column was small. Helium was used as the carrier gas, and measurements were made by injecting a small pulse of the adsorbable component either into a pure helium carrier or into a mixed carrier (helium plus adsorbable component) of known composition. The linearity of the system was checked by varying the pulse size.

The conditions under which it is possible to obtain reliable diffusivity data from chromatographic measurements have been considered in some detail by Sarma and Haynes (1974). If one is interested primarily in the intracrystalline diffusivity, it is essential to choose experimental conditions such that this term is the major resistance to mass transfer. Under these conditions, the chromatographic peak generally shows appreciable tailing, and this can make it difficult to evaluate the moments accurately. The relative importance of external film and macropore resistance may be reduced by using small adsorbent particles, but under these conditions, axial dispersion may become significant. The effect of axial dispersion can, in principle, be reduced by the use of a high gas velocity, but this may introduce an unacceptably large pressure drop across the column. The final choice of conditions is therefore a compromise, and some correction for axial dispersion and film and macropore resistance may be necessary. The problem of finding acceptable conditions becomes more severe when the intracrystalline diffusivity is high, and, in the case of methane, it was not possible to achieve satisfactory conditions for reliable determination of the intracrystalline diffusivity, since the effect of axial dispersion was always dominant over the entire range of operating conditions.

## RESULTS AND DISCUSSION

The experimental results are summarized in Tables 2 and 3 and in Figures 1 and 2. With the exception of the data for propane, the Henry constants calculated from the chromatographic response, according to Equation (13), agree well with the previously reported gravimetric values. If we neglect the adsorption of helium, the first moment (mean residence time) for a pulse of hydrocarbon injected into a mixed carrier stream (mole fraction  $x$ ) is given by (Stalkup and Deans, 1963)

$$\mu = \frac{L}{v} \left\{ 1 + \left( \frac{1-\epsilon}{\epsilon} \right) (1-x)K'_p \right\} \quad (16)$$

where  $K'_p$  is the slope of the isotherm at that particular composition. Measurements were made for a range of different carrier gas compositions, and the equilibrium isotherm was then obtained by graphical integration [ $K'_p = \theta + w(1-\theta)(dq/dc)$ ]. Chromatographic isotherms determined in this way are compared with the gravimetric isotherms in Figure 1. It is evident that the agreement is quite satisfactory, particularly in view of the cumulative error inherent in the integration of the chromatographically determined slopes.

From the data given in Table 3, it may be seen that the dispersion for methane is quantitatively accounted for by the axial dispersion term, and it follows that no information concerning the zeolitic diffusivity can be obtained from the response peaks. This is true also of the low concentration runs with ethane. By contrast, for the higher concentration ethane data as well as for propane and cyclopropane, the major contribution to the dispersion arises from zeolitic diffusion and values of the time constant  $r^2_c/D_c$  may there-

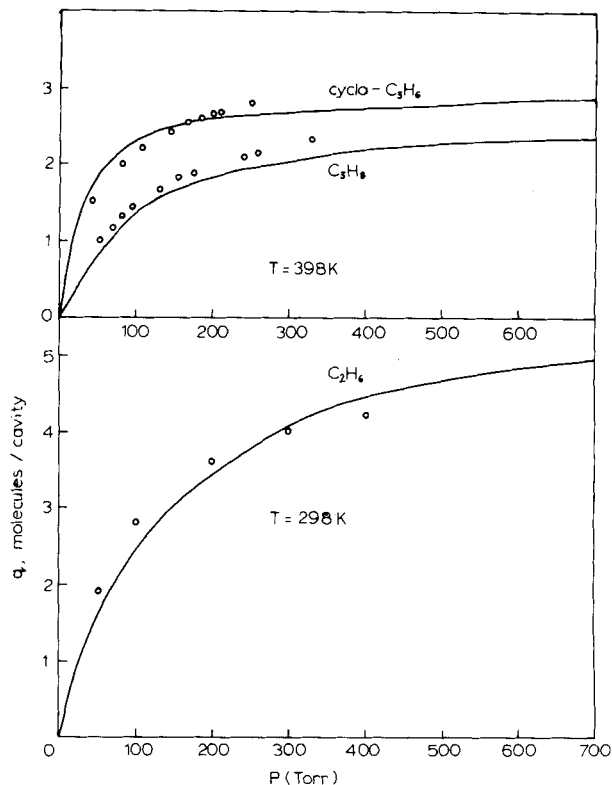


Fig. 1. Comparison of chromatographic and gravimetrically determined equilibrium isotherms. (Gravimetric point data are from Loughlin, 1970, and Derrah, 1973).

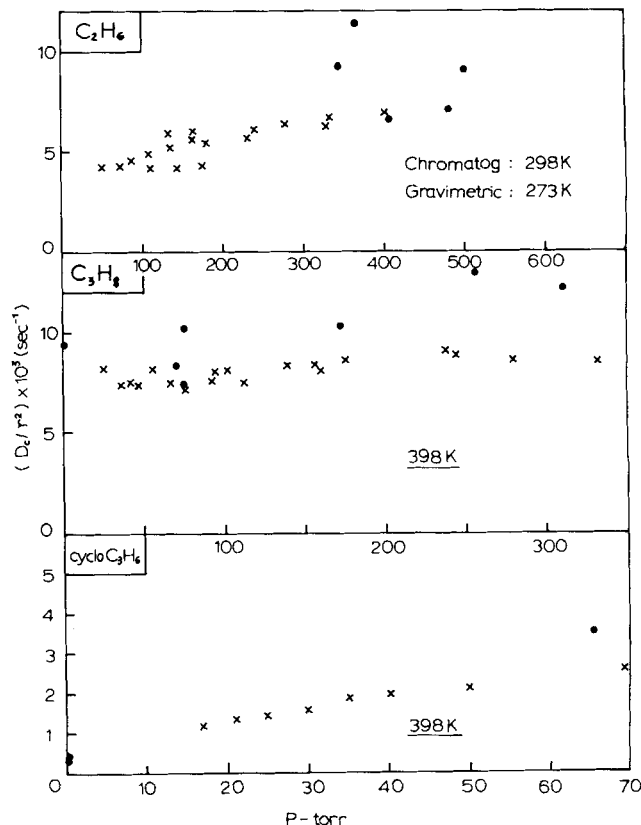


Fig. 2. Comparison of chromatographic and gravimetric time constants for zeolitic diffusion in 5A molecular sieve. (Chromatographic values from present study,  $\bullet$ ; gravimetric values from Loughlin, 1970, and Derrah, 1973,  $\times$ ).

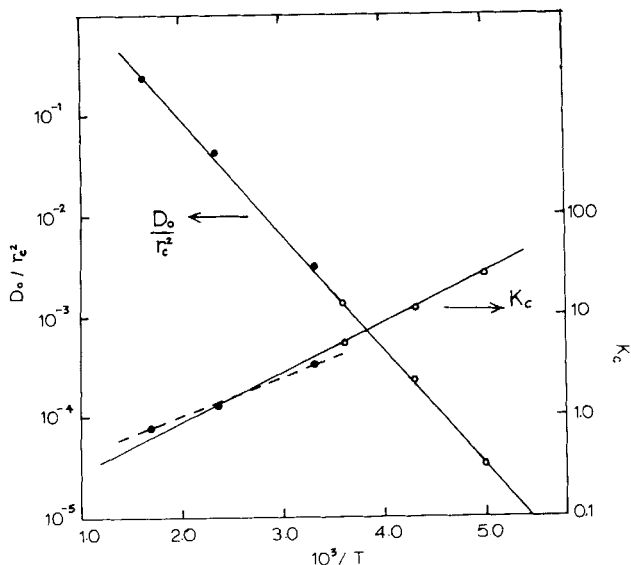


Fig. 3. Comparison of chromatographic and gravimetric diffusional time constants and equilibrium constants for diffusion of argon in 4A sieve (Chromatographic data of Sarma and Haynes, 1973, ●; gravimetric data of Ruthven and Derrah, 1975, ○).

fore be estimated with some confidence. This difference in behavior reflects the expected increase in zeolitic diffusional resistance with increasing molecular size in the sequence  $\text{CH}_4 < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8 < \text{cyclo-C}_3\text{H}_8$  (Ruthven, Derrah, and Loughlin, 1973).

Figure 2 shows a comparison of the chromatographic values of  $D_c/r_c^2$ , with the gravimetric values obtained previously by Loughlin (1970) and Derrah (1973). For propane and cyclopropane, for which systems comparative data are available at 398°K, the agreement is well within the margin of error of the experimental measurements. The data for ethane are somewhat more scattered, probably as a result of the relatively larger contributions from axial dispersion, but it is evident that the average of the chromatographic values at 298°K lies, as expected, somewhat above the gravimetric data for 273°K.

In Figure 3, the chromatographic diffusivities obtained by Sarma and Haynes (1974) for argon in pelleted 4A sieve at low concentrations are compared with the limiting diffusivities from gravimetric data obtained by Ruthven and Derrah (1975) for the same system but with a sample of unaggregated crystals. In order to express the diffusivities on the same basis, the values given by Sarma and Haynes have been divided by the equilibrium constant [ $K_c$  or  $\theta_x(1 + K_a)$ ]. It is evident that the agreement is excellent, thus providing further confirmation of the experimental methods and indicating that the intrinsic zeolitic diffusivities are not significantly affected by pelletization. A similar conclusion was reached previously from a comparison of the diffusivity data for ethane and butane in 5A crystals and pellets (Ruthven and Loughlin, 1971). The gravimetric and chromatographic equilibrium constants, which are also shown in Figure 3, show equally good agreement. There is some evidence that the heat of sorption decreases with temperature. The difference between the diffusional activation energy given by Ruthven and Derrah (1975) (5.8 kcal) and that of Sarma and Hayes (1974) (3.4 kcal) arises entirely from the difference in the way in which the diffusivities are defined.

A basic assumption of the chromatographic method is that the diffusivity is independent of sorbate concentration. For most systems this is a valid approximation within the Henry's law (low concentration) region. However, for

TABLE 4. COMPARISON OF VALUES OF  $E - \Delta H$  WITH APPARENT ACTIVATION ENERGIES (KCAL) FROM CHROMATOGRAPHIC DATA

System	$-\Delta H^*$	$E^\dagger$	$E - \Delta H$	$E_a^*$
Ar-5A	3.3	<1.0	3.4	3.5
Kr-5A	3.6	2.0	5.6	5.9
SF <sub>6</sub> -13X	5.0	2.8	7.8	7.5

\* Values from chromatographic data of Eberly (1969).

† Values of  $E$  from gravimetric data (Ruthven and Derrah, 1975; Ruthven and Doetsch, 1976).

certain systems, including those studied by Eberly (1969) (argon-5A, krypton-5A, SF<sub>6</sub>-13X), gravimetric data show that within the Henry's law region, the diffusivity is inversely proportional to sorbate concentration (Ruthven and Derrah, 1975; Ruthven and Doetsch, 1976):

$$D_o = D'_o/q; \quad D'_o = D'_o e^{-E/RT} \quad (17)$$

Since  $q = K_c c$  and  $K_c$  varies with temperature according to a vant Hoff equation ( $K_c = K_o e^{-\Delta H/RT}$ ), then

$$D_o = (D'_o/K_o c) \exp[-(E - \Delta H)/RT] \quad (18)$$

Under these conditions, the precise value of the apparent crystal diffusivity determined in a chromatographic experiment will depend on the pulse size. However, it is clear from Equation (18) that if the pulse size is kept constant and the temperature varied, the apparent activation energy ( $E_a$ ) will be given by  $E_a = E - \Delta H$ . It may be seen from Table 4 that the chromatographic values of  $E_a$  reported by Eberly agree well with the values of  $E - \Delta H$  from the gravimetric data. The apparent discrepancy arises simply from the assumption of a constant diffusivity in the chromatographic analysis.

Hashimoto and Smith (1973) reported chromatographic diffusivities of order  $10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$  for *n*-butane in 5A sieve at 225°C. This is much larger than the gravimetric values previously obtained in this laboratory ( $3 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ ). However, examination of the defining equations shows that Hashimoto and Smith define their crystal diffusivities in the same way as Sarma and Haynes (that is, on a gas phase concentration basis) so that division by the equilibrium constant  $K_c$  is required for comparison with the gravimetric data. The corrected values are about  $10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$ , which is very much closer to the gravimetric data. The remaining discrepancy (a factor of about 3 to 4) is probably due to the fact that under the conditions of Hashimoto and Smith's study, crystal diffusional resistance was small in comparison with the macropore resistance, thus leading to difficulties in accurate evaluation of the crystal diffusivity.

## CONCLUSION

The chromatographic method offers a practicable alternative to the conventional gravimetric or volumetric methods of measuring equilibrium isotherms and diffusional time constants for sorption in molecular sieves. The agreement which is observed between the recent chromatographic data and the earlier gravimetric data provides useful confirmation of the earlier work. The apparent discrepancies between chromatographic and gravimetric data from different laboratories appear to be attributable mainly to differences in the way in which the zeolitic diffusion coefficients are defined.

The main advantages of the chromatographic method are the simplicity of the apparatus and the relative ease

with which an experiment may be performed. However, strict attention to details of particle size, column length, gas velocity, pulse size, etc., is necessary if accurate results are to be obtained. The requirement that the pulse be sufficiently small to ensure approximate linearity of the system can be difficult to fulfil for systems in which the isotherm is highly nonlinear and the zeolitic diffusivity low. In such cases, the maximum permissible pulse may be so small that when the pulse is spread out by diffusional resistance, it becomes difficult to measure.

The range of intracrystalline diffusional time constants which may be measured chromatographically is bounded by both upper and lower limits. The upper limit (of  $D_c/r_z^2$ ) arises because if intracrystalline diffusion is rapid, dispersion of the chromatographic peak will be controlled mainly by axial dispersion and the other resistances to mass transfer (as is the case for methane in the present study). The lower limit arises because if intracrystalline diffusion is very slow, the peak will not equilibrate during passage through the column, and the retention time will correspond only to the small macropore capacity of the adsorbent, as observed by Sarma and Haynes for argon in 3A sieve. The latter condition has been considered in greater detail by Habgood and MacDonald (1970). For detailed studies of zeolitic diffusion, conventional gravimetric or volumetric methods have the advantage of simplicity and directness. They are at their best for relatively slow diffusion processes and at moderate pressures and temperatures. The chromatographic technique is more easily extended to the extreme conditions of temperature and pressure often encountered in catalytic systems, and it offers the further possibility of extension to multicomponent systems. Furthermore, for many purposes it is necessary to determine only the overall mass transfer resistance, under specified flow conditions, and this may be accomplished rather easily by the chromatographic method.

## NOTATION

$c$	= sorbate concentration in macropores
$C$	= sorbate concentration in bulk phase
$D_c$	= zeolite diffusivity
$D_L$	= axial dispersion coefficient
$D_m$	= molecular diffusivity
$D_o$	= limiting zeolitic diffusivity at zero sorbate concentration
$D'_o$	= $D'_o e^{-E/RT}$ , temperature dependent constant
$D'_o$	= constant defined above
$D_p$	= macropore diffusivity (based on free pore area)
$D_x, D_y, D_z$	= micropore diffusion coefficient, macropore diffusion coefficient and axial dispersion coefficient as defined by Sarma and Haynes
$E$	= diffusional activation energy
$E_a$	= $E - \Delta H$ , apparent activation energy
$-\Delta H$	= limiting heat of adsorption
$k$	= external film mass transfer coefficient
$K_a$	= sorption equilibrium constant as defined by Sarma and Haynes
$K_c$	= $K_o e^{-\Delta H/RT}$ , sorption equilibrium constant based on sorbate concentration in a zeolite crystal (dimensionless)
$K_p$	= equilibrium constant based on sorbate concentration in a pellet of sieve (dimensionless)
$L$	= length of chromatographic column
$q$	= local sorbate concentration in a zeolite crystal
$\bar{q}$	= average sorbate concentration for a crystal
$\bar{Q}$	= sorbate concentration averaged over a pellet
$r$	= radial coordinate for zeolite crystal
$r_c$	= radius of zeolite crystal

$R$	= radial coordinate for pellet
$R_p$	= pellet radius
$t$	= time
$v$	= interstitial fluid velocity
$w$	= volume fraction of zeolite crystals to total solid material in a pellet
$x$	= mole fraction of sorbate in carrier gas
$z$	= distance measured from bed inlet

## Greek Letters

$\theta$	= void fraction of pellet
$\theta_x$	= void fraction of crystal as defined by Sarma and Haynes
$\theta_y$	= void fraction of pellet as defined by Sarma and Haynes
$\epsilon$	= void fraction of bed
$\delta(t)$	= pulse function
$\mu$	= first moment of response peak
$\sigma^2$	= second moment of response peak
$\tau$	= tortuosity factor

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