NOTATION

D = molecular diffusivity
k = mass transfer coefficient
k^+ = dimensionless mass transfer coefficient, k/u^*
N_{Sc} = Schmidt number
t = eddy contact time
U_∞ = free stream velocity
u = velocity in axial direction
u^+ = u/u^*
u^* = shear velocity
x = length in axial direction
y = radial distance from wall
y^+ = yu^*/ν

Greek Letters

ϵ = eddy diffusivity
ν = kinematic viscosity

Subscripts

ET = eddy, transition region
EW = eddy, wall region
H = heat
m = mass
M = momentum

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Manuscript received April 23, 1973, and accepted May 14, 1973.

Multicomponent Rates of Sorption of SO_2 and CO_2 in Sodium Mordenite

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Recently diffusion in binary sorbate systems has been considered. However, in almost all the cases considered, either one of the components was assumed to be inert or counter diffusion was assumed (Roberts and York, 1967; Satterfield and Katzer, 1970, 1971; Kondis and Dranoff, 1970, 1971).

Kokoszka (1970) studied the rate of sorption of propane and butane mixtures from helium by 5A molecular sieves. He reported that the rates of sorption of a tertiary system of propane and butane in helium were lower than the respective rates of sorption as pure components. Riekert (1971) studied the rate of exchange between CO_2 and C_2H_6 in hydrogen and sodium mordenites. He found that a countercurrent migration was possible in both zeolites.

Habgood (1958) studied the diffusion of mixtures of nitrogen and methane in 4A molecular sieves. He observed that nitrogen diffused faster than methane and was preferentially sorbed at the beginning. However, it was later displaced by methane, resulting in the observation of a maximum in the amount of nitrogen sorbed. Based on the chemical potential as the driving force for diffusion, Round et al. (1966) presented a numerical solution to the equations describing the sorption of a binary mixture.

EXPERIMENTAL APPARATUS AND PROCEDURE

Sorption rates were measured in a well-stirred constant volume sorption chamber consisting of a cylindrical aluminum vessel of 3-liter capacity. The agitator shaft with a steel bar attached to its bottom end was magnetically driven by a one-half horsepower D.C. motor at a controlled and measured speed. The impeller was constructed of stainless steel with two equally-spaced adjustable baskets around the shaft in which the sorbent pellets could be placed, a design similar to that used by Carberry (1961) and Ma (1967). An aluminum propeller was also attached to the shaft to ensure adequate mixing. Three equally-spaced half-inch stainless steel rods were employed as baffles with clearance between the baffles and the chamber wall. Details of the apparatus were described by Kokoszka (1970) and Roux (1972). A schematic diagram of the sorption system is shown in Figure 1.

The pellets were placed in the baskets and regenerated under a vacuum of about 25 μm Hg and at a temperature of

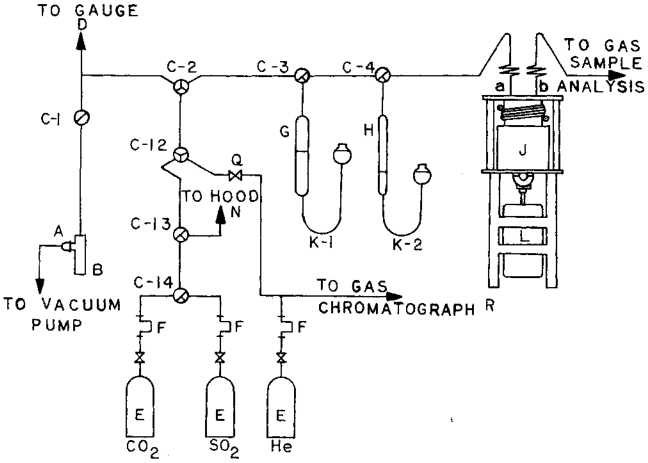

Fig. 1. Schematic diagram of the sorption apparatus.

250°C for 12 hrs. The chamber was filled with helium and kept at atmospheric pressure by adjusting the mercury leveling bulb. A measured amount of gas was introduced to the vessel through a gas-injection burette. The gas phase concentration of the sorbate as a function of time was measured by taking the sample through the sampling loop and analyzed by a gas chromatograph. Twelve to fifteen samples were taken and the system was left running for about four hours to obtain the equilibrium data. The speed of rotation was set at 1,100 rev./min. as it was shown that the sorption rate was constant for a speed of rotation above 600 rev./min.

Residence time distribution experiments showed that the gas in the chamber is practically well-mixed (Roux, 1972). A uniform concentration in the bulk gas phase was observed within 20 sec after the injection of the gas into the chamber.

The heating units and the cooling coil were around the outer wall of the sorption chamber. The temperature was controlled by a proportional controller with variations not exceeding 0.5°C during an experiment and 3°C during the activation of the sorbent.

Helium, carbon dioxide, and sulfur dioxide were research grade. Sodium mordenite was provided by Norton Company. All experiments were made on 0.316 cm diameter, 0.632 cm long self-bonded pellets.

RESULTS AND DISCUSSION

Sorption Rate

Experiments were carried out with mixtures of dilute CO_2 and SO_2 in helium. The total pressure of the system was maintained at approximately one atmosphere pressure. The partial pressure of SO_2 and CO_2 was either 21 or 42 mm Hg and helium was used as an inert to keep the system at atmospheric pressure.

Rates of sorption were measured under the following four sets of conditions which provided different kinds of interactions between molecules. These four types of injections will be referred to as Types 1, 2, 3, and 4 injections in the following discussion.

Type 1: The sorbent was exposed to a pressure of about one atmosphere of helium and CO_2 was then injected into the system. After the equilibrium between CO_2 and the sorbent was established, SO_2 was introduced.

Type 2: Same as Type 1 except the order of injection was reversed.

Type 3: CO_2 and SO_2 were premixed and then injected into the system which had previously been exposed to one atmosphere of helium.

Type 4: The sorbent was exposed to a pressure of about one atmosphere of CO_2. SO_2 was then injected.

In order to be sure that the diffusion process was controlled by intracrystalline diffusion, a run was made on pellets of one-fourth of the original size. The rate of sorption was found to be essentially identical to that of the larger pellets of 0.632 cm in length. This indicated that the resistances in the macropores were small compared to those in micropores. Thus it was concluded that the process was controlled by intracrystalline diffusion. Kondis and Dranoff (1970 and 1971) also demonstrated that the rate controlling step is intracrystalline diffusion in their study.

Fick's law has been widely used in the calculation of diffusivities in intracrystalline diffusion although it is generally felt that the agreement between experimental data and the law is more of an exception than a rule. The situation is even more complicated in the present study due to the introduction of the second component in the system. However, under the present circumstances, it was felt that calculations of the reduced diffusivities (D/a^2) would provide valuable information for the purpose of comparison. The values of D/a^2 tabulated in Tables 1 and 2 were calculated at $M_t/M_\infty = 0.5$. An elaborate mathematical model would be needed for detailed quantitative analysis of the data. However, the model presented later provides a simple qualitative description of the process. It fails to predict quantitatively the experimental results due to its simplifying assumptions. A more realistic model is currently under investigation.

Figures 2 to 5 show the rate curves obtained for partial pressures of CO_2 and SO_2 of 42 mm Hg. The diffusive flux of SO_2 was hindered by the presence of CO_2 to a smaller extent than that of CO_2 hindered by SO_2. The reduced diffusivity of SO_2 decreased in the following

Table 1. Diffusivities in Ternary Mixtures

	SO_2			CO_2			
T, °C	$\frac{D \times 10^4}{a^2}$, s^{-1}	Initial press., mm Hg	Equil. in mixture, mg/g	$\frac{D \times 10^4}{a^2}$, s^{-1}	Initial press., mm Hg	Equil. in mixture, mg/g	Type
45	0.540	21.7	150	3.75	21.6	8	1
45	0.723	22.4	158	—	22.4	6	2
45	0.628	21.8	157	—	22.1	8	3
45	0.484	22.3	142	—	760	—	4
25	0.495	21.7	177	2.18	21.5	18	1
25	0.544	21.8	183	—	21.6	5	2
25	0.516	21.5	181	—	22.0	22	3
25	0.432	21.3	158	—	760	—	4
5	0.375	21.3	214	1.65	20.3	21	1
5	0.434	22.2	217	—	21.0	9	2
5	0.402	21.3	214	—	21.0	17	3
5	0.302	21.5	192	—	760	—	4

Table 2. Diffusivities in Ternary Mixtures

	SO$_2$			CO$_2$			
T, °C	$\frac{D \times 10^4}{a^2}$, s^{-1}	Initial press., mm Hg	Equil. in mixture, mg/g	$\frac{D \times 10^4}{a^2}$, s^{-1}	Initial press., mm Hg	Equil. in mixture, mg/g	Type
45	0.95	42.2	163	4.95	41.6	4	1
45	1.18	42.3	166	—	42.4	1	2
45	1.16	43.1	165	—	41.8	2.5	3
45	0.85	42.9	157	—	760	—	4
25	0.62	41.7	185	2.60	38.7	15	1
25	0.75	41.5	189	—	40.0	8	2
25	0.67	42.5	188	—	41.2	7	3
25	0.48	41.7	164	—	760	—	4
5	0.40	45.1	214	2.03	41.6	19.5	1
5	0.53	43.7	216	—	41.1	7	2
5	0.48	43.3	214	—	40.7	13.5	3
5	0.30	44.1	192	—	760	—	4

order according to the types of injection: Type 2 > Type 3 > Type 1 > Type 4. This is to be expected as there was no CO$_2$ present for the Type 2 case while at the other extreme (Type 4) SO$_2$ was injected into a system containing one atmosphere of CO$_2$. Although the accuracy of the equilibrium capacity of CO$_2$ was not very high as it represented the difference between two large numbers, a general trend in the equilibrium capacity of CO$_2$ could be observed. Due to the hindrance of SO$_2$ molecules, the amount of CO$_2$ sorbed under equilibrium conditions was smallest for a Type 2 injection. This indicated that either the system was under a nonequilibrium condition or there was a slight hysteresis for CO$_2$ under these conditions.

The reduced diffusivities of CO$_2$ were calculated only for Type 1 injections. This was due to the fact that the amount of CO$_2$ sorbed for Type 2 was too small to permit a meaningful calculation. As for a Type 3 injection, the amount of CO$_2$ sorbed reached values larger than the final equilibrium capacity of mordenite. This rules out the use of the simple Fick's law to calculate the diffusivities. Assuming that the Fick's law was valid, the reduced diffusivities of CO$_2$ for the desorption portion of a Type 1 injection were estimated. They were roughly two orders of magnitude smaller than those of pure CO$_2$ in helium. This might be due to the combined effects of SO$_2$ interference and partial chemisorption of CO$_2$. As shown in Figures 2 to 5, CO$_2$ was almost completely displaced by SO$_2$. Such a phenomenon was also observed by Riekert (1971) in a system of CO$_2$ and C$_2$H$_6$. Only very little CO$_2$ was sorbed when SO$_2$ was present as compared to approximately 8 wt. % of CO$_2$ for CO$_2$ in helium.

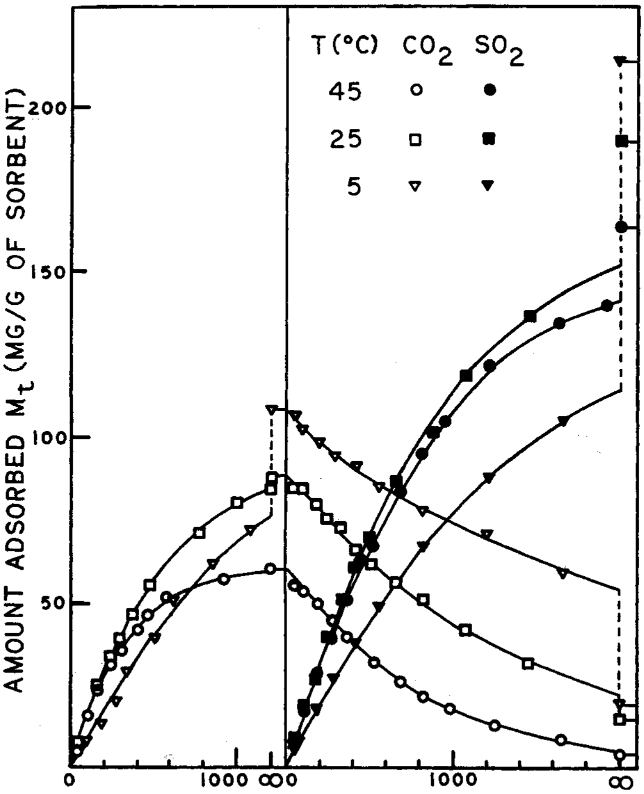

Fig. 2. Diffusion of a ternary mixture Type 1; Initial partial pressure $P_{SO_2} = P_{CO_2} = 42$ mm Hg.

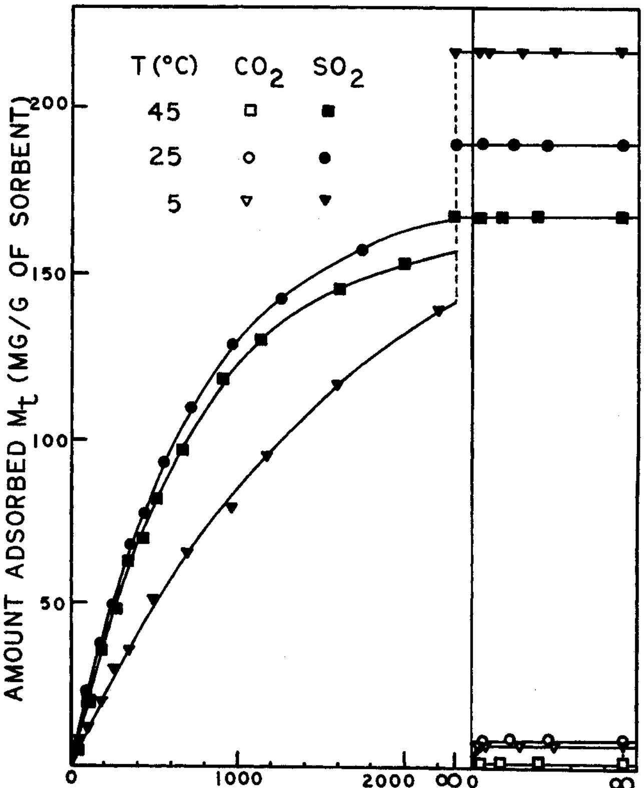

Fig. 3. Diffusion of a ternary mixture Type 2; Initial partial pressure $P_{SO_2} = P_{CO_2} = 42$ mm Hg.

One very interesting phenomenon observed in this study was the maximum of the CO_2 rate curve for a Type 3 injection as shown in Figure 4. As far as we know, there was only one similar observation reported in the literature (Habgood, 1958).

The phenomenon of the maximum may be explained in the following manner. Just after the injection of the mixture into the chamber, the coverage of the sorbent with sorbates was small. The diffusion of both CO_2 and SO_2 resulted mainly from the large gradients in concentrations, with CO_2 penetrating more rapidly because of its larger diffusivity. As the SO_2 coverage of the sorbent increased, the capacity of CO_2 decreased because SO_2 had a much greater affinity for the sorbent. In the meantime CO_2 continued to diffuse and be sorbed in the sorbent. When enough molecules of CO_2 and SO_2 were sorbed to attain a certain degree of coverage of the surface, SO_2 continued to be sorbed on less active sites. At the same time, SO_2 also started to compete with CO_2 on sites which were originally occupied by CO_2. As SO_2 had a larger affinity for the surface, this competition resulted in the desorption of CO_2. Thus, the rate curve of CO_2 exhibited a maximum.

TEMPERATURE DEPENDENCE

The activation energies calculated from the slopes of the straight lines of an Arrhenius type of plot of the reduced diffusivity versus $1/T$ are summarized in Table 3.

The activation energy of diffusion for CO_2 was independent of the initial pressure. However, the activation energy of diffusion for SO_2 increased with the initial pressure. This may be due to the fact that SO_2 is a polar molecule which was very strongly adsorbed on the ionic surface of the zeolite. At high pressure, the coverage of the wall of the pore was close to saturation. Thus the molecules diffused through the pores with more difficulty, resulting in a higher activation energy. When the sorbent was saturated under one atmosphere of CO_2 (Type 4), the molecules had even more difficulty to diffuse and thus the activation energy was higher.

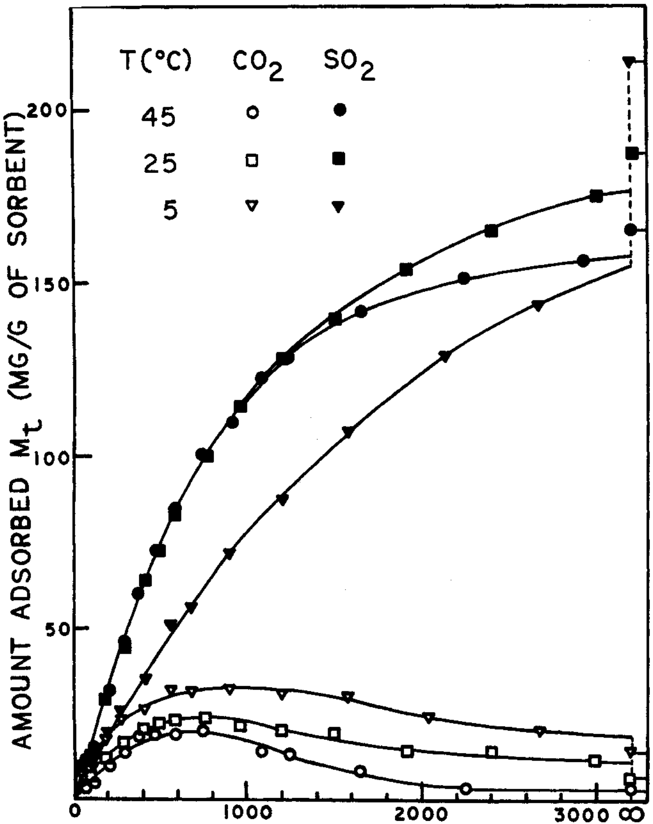

Fig. 4. Diffusion of a ternary mixture Type 3; Initial partial pressure $P_{SO_2} = P_{CO_2} = 42$ mm Hg.

TABLE 3. ACTIVATION ENERGIES OF DIFFUSION

Activation energies (kcal/g-mole)

Pressure, mm Hg	CO_2 (type 1, 2, 3, 4)	SO_2 (type 1, 2, 3)	SO_2 (type 4)
21	4.0	2.0	2.0
42	4.0	3.7	4.6

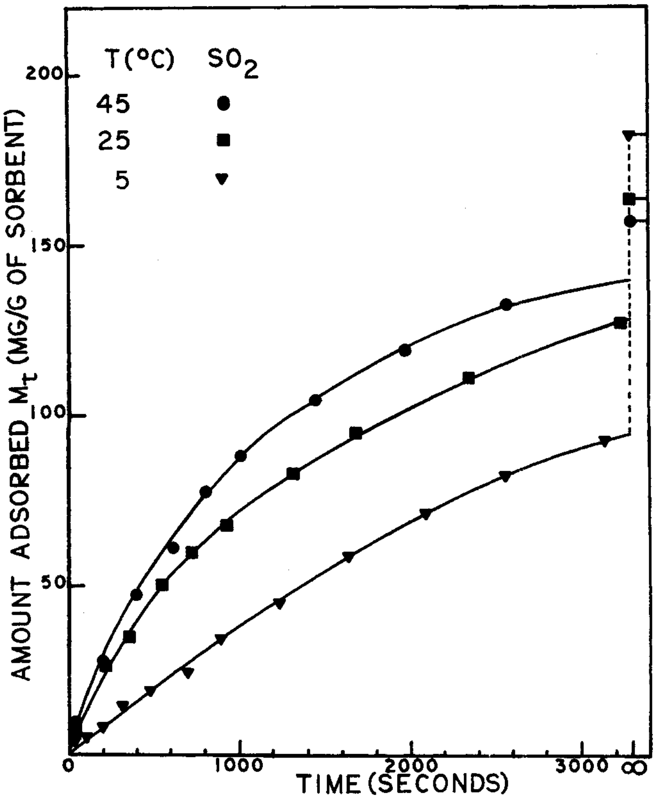

Fig. 5. Diffusion of a ternary mixture Type 4; Initial partial pressure $P_{SO_2} = 42$ mm Hg.

MATHEMATICAL MODEL

In view of the complexity of the actual process which is occurring in the crystal structure of zeolites, it is rather difficult to describe the process by a simple model. However, in an attempt to describe qualitatively the experimentally observed rate phenomena, a simple model was considered with the following simplifying assumptions:

1. The pores of mordenite may be treated as a simple geometry of a slab.
2. The diffusivities D_1 and D_2 for CO_2 and SO_2 in the mixture were constant.
3. A fraction of the CO_2 or SO_2 molecules was immobilized in the pores (chemisorption) while the rest remained mobile under a lesser influence of the surfaces.
4. The fraction of CO_2 being immobilized for pure CO_2-sorbent system was the same as that of SO_2 for pure SO_2-sorbent system.
5. The number of molecules being immobilized was directly proportional to the total number of mobile mole-

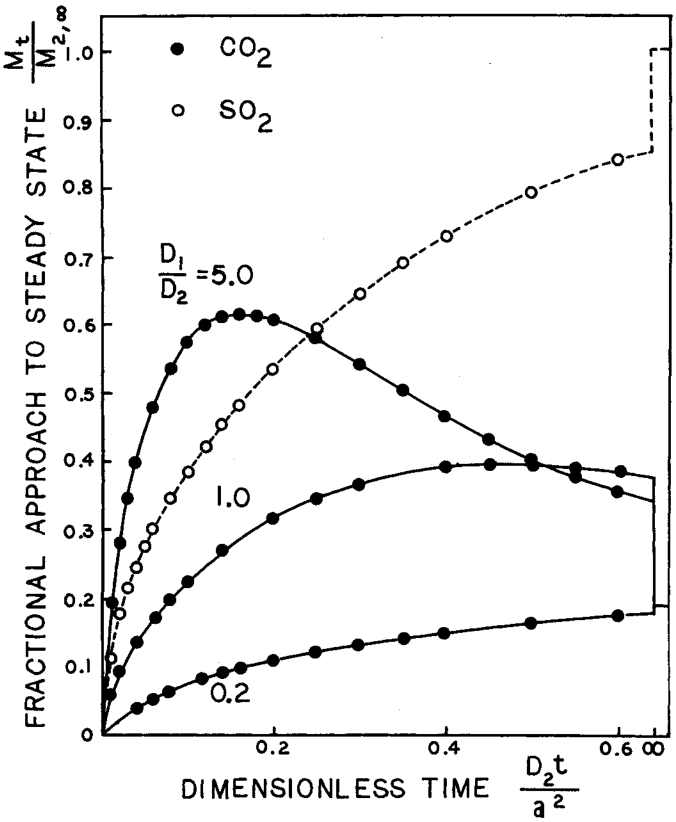

Fig. 6. Theoretical curves for the diffusion of a gas mixture.

cules (linear mixture isotherms) and was attained instantaneously (equilibrium) at any given depth of penetration into the pore.

6 The presence of CO_2 did not affect the fraction of SO_2 being immobilized.

7. A simple linear form could be used to express the reduction of the fraction of CO_2 molecules being immobilized due to the presence of SO_2.

The immobilization of SO_2 was partially borne out by the fact that high temperature regeneration was needed for its removal. Although CO_2 was less immobilized, high vacuum regeneration with some heating also was required for its ultimate removal.

With the above assumptions, the following equations can be derived for a simple geometry of a slab:

$$\frac{\partial n_1}{\partial t} = D_1 \frac{\partial^2 n_1}{\partial x^2} - \frac{\partial s_1}{\partial t} \qquad (1)$$

$$\frac{\partial n_2}{\partial t} = D_2 \frac{\partial^2 n_2}{\partial x^2} - \frac{\partial s_2}{\partial t} \qquad (2)$$

where component 1 refers to CO_2 and component 2 SO_2.

Details of the boundary conditions, the method of solution and the expressions which give the fractions of materials sorbed as a function of time can be found in Roux (1972). The calculated results were plotted in Figure 6 which shows three curves of $M_{t1}/M_{2\infty}$ for the values of $D_1/D_2 = 0.2$, 1, and 5.0. When possible, the parameters used in the calculations of these curves were obtained from the experimental portion of the present study.

When $D_1/D_2 = 5.0$ which is approximately the experimentally observed ratio of diffusivity of CO_2 to that of SO_2, the uptake curve in Figure 6 shows a maximum similar to those observed experimentally. No attempt was made to fit quantitatively the theoretical curve with experimental results because of the over-simplifying assumptions. However, the qualitative agreement was quite encouraging as it would provide a real potential for further development of a more realistic equilibrium relation.

ACKNOWLEDGMENT

The financial support for this investigation was from the National Science Foundation under Grants GK-5556 and GK-33351. The sodium mordenite was provided by Norton Company.

NOTATION

D = diffusivity, $cm^2\ s^{-1}$
$\frac{D}{a^2}$ = reduced diffusivity, s^{-1}
M = amount of material sorbed, mg/g of sorbent
n = number of mobile molecules per unit volume, cm^{-3}
s = number of immobile molecules per unit volume, cm^{-3}
t = time, second
x = coordinate along the pore axis

Subscripts

0 = initial value
1 = carbon dioxide
2 = sulfur dioxide
∞ = equilibrium (infinite time)
t = value at time t

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Manuscript received April 9 and accepted April 18, 1973.