Diffusion Studies of CO_2, NO, NO_2, and SO_2 On Molecular Sieve Zeolites by Gas Chromatography

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Gas chromatographic techniques were used to measure the diffusion coefficients and the isosteric heats of adsorption of CO_2, NO, NO_2, and SO_2 on 5A and 13X molecular sieves, natural mordenites, and synthetic Na- and H-mordenites in the temperature range of 133 to 325°C. Diffusional resistances for all gases studied decrease in the following order: natural mordenites $>$ Na-mordenites $>$ H-mordenites $>$ (13X, 5A) indicating the increased ease of flow in the 3-dimensional network. Isosteric heats of adsorption (range from 3 kcal/mole to 12 kcal/mole) and activation energies (range from 3 kcal/mole to 19 kcal/mole) decrease in the same order. The variations of diffusion coefficients, heats of adsorption, and activation energies are discussed in terms of the interaction between the surface and gas molecules as well as the openings of the pores relative to the size of the diffusing molecules.

An understanding of the diffusional mechanisms and the determination of the effective diffusion coefficients in zeolites are essential for their application to catalysis and adsorption in a scientific manner. Most diffusion studies on zeolites have been done by either a constant-volume or a constant-pressure technique as summarized by Barrer (*2*). The application of the principles of gas-solid chromatography to the measurements of heat of adsorption and effective diffusion coefficient of gases in porous solids has been reported in the literature (*4, 8, 9, 11, 12, 14*). Most recently this technique has been applied to the measurements of heats of adsorption and effective diffusion coefficient of hydrocarbons and inert gases on various zeolitic materials (*6*). No such measurements by gas chromatography have been reported on the diffusion of inorganic gases, such as CO_2, NO, NO_2, and SO_2 in zeolites.

The basic principles involved here are rather simple. A pulse of the gas under study is injected into a carrier gas stream at the entrance of a packed column. The broadening of the peak at the outlet of the column is then analyzed for different carrier gas flow rates. An unsteady state technique measures the effective diffusion coefficient of the continuous pore structure as well as the dead-end pores.

The present study concerns the diffusion of small concentrations of SO_2, NO, NO_2, and CO_2 in 5A and 13X molecular sieves, H-, Na- and natural mordenites between temperatures of 133°C and 325°C. It is hoped that a better understanding of the selective adsorption of molecular sieves in conjunction with the acid stability of mordenites will shed some light on the possible applications of molecular sieves as solid sorbents for the removal of pollutants.

Some investigators prefer to use the techniques of constant volume or constant pressure for the measurements of diffusion coefficients while others select the technique of gas chromatography for its determination. Both types have their shortcomings. It is felt, however, that the gas chromatography approach is most appropriate for the present investigation as the technique is especially suitable for high temperature and low sorbate concentration measurements of diffusion coefficients and estimation of heat of adsorption. Such information is extremely difficult to obtain using conventional vacuum techniques of constant volume or constant pressure. There are several additional advantages of using gas chromatography techniques. The experimental set-up and the interpretation of data are relatively simple if one uses a simple model such as the Van Deemter equation. A large number of solid pellets is normally used, providing a good representative specimen of solids under study.

THEORY

This study is based on the well-known equation developed by Van Deemter, Zuiderweg, and Klinkenberg (*5*) for a gas chromatographic column

$$\text{H.E.T.P.} = A + B/u + Cu \qquad (1)$$

where H.E.T.P. is the height equivalent to a theoretical plate and u is the interstitial carrier gas velocity.

The constants A, B, and C in Equation (1) may be interpreted respectively in any particular system in terms of eddy diffusion, molecular diffusion, and resistance to mass transfer. For the purpose of the present study, it is necessary to obtain the constant C which corresponds to the limiting slope of the curve of H.E.T.P. versus u at high interstitial velocities. C may be related to the molecular diffusion coefficient D_{12} and the effective diffusion coefficient in the porous solid D_{eff} by

$$C = \frac{\dfrac{F_I^2\, d_p^2}{75(1 - F_I)^2 D_{12}} + \dfrac{F_I K d_p^2}{2\pi^2 (1 - F_I) D_{\text{eff}}}}{\left[1 + K \dfrac{F_I}{1 - F_I}\right]^2} \qquad (2)$$

Equations (1) and (2) were obtained by comparison of the Gaussian distribution curves derived separately from the plate and rate theories with the assumption of a linear isotherm.

In Equation (2) the diffusion coefficient appears under the form of D_{eff}/d_p^2, consequently the choice of the characteristic length of diffusion is of prime importance. One may use the size of the crystal, the equivalent physical dimension of the pellet or define a reduced diffusion coefficient $D^* = D_{eff}/d_p^2$. This last possibility was not used as d_p also appears explicitly in the first term of the numerator of Equation (2). As the physical dimensions of commercial pellets were readily available and D_{eff} represents an overall transfer resistance through the pellet it is felt that the appropriate characteristic length to use is the equivalent physical dimension of the pellet. However, it should be pointed out that in the case where intracrystalline diffusion is known to be the controlling step the dimension of the crystallites should be used as the characteristic length.

The first term in the numerator of Equation (2) allows for the gas phase mass transfer resistance and is based on Ergun's description of film resistance in laminar flow (*10*). It therefore would be significant only at low values of the interstitial carrier gas velocity and may be determined when D_{12} is known. Normally, it is much smaller than the second term in the numerator of Equation (2). Calculations of the second term may be done by making the assumption that the equilibrium isotherm is linear. The distribution coefficient K can then be defined as

$$K = \frac{C_I}{C_{II}} \tag{3}$$

and may be calculated by the following expression

$$\frac{1}{K} = \epsilon + \frac{\beta'}{1 - F_I} \tag{4}$$

where β' is the adsorption equilibrium constant expressed as the moles adsorbed per unit volume of column divided by the moles in the gas per unit volume of gas.

It has been shown that (*7, 13*)

$$\beta' = \frac{t_m u F_I}{L} \tag{5}$$

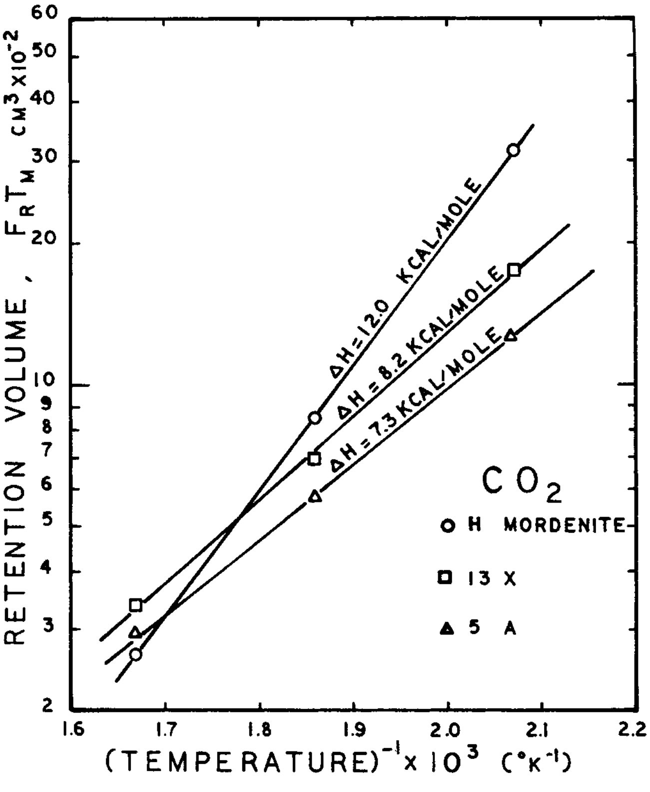

Fig. 1. Pulse flow retention volume as a function of temperature.

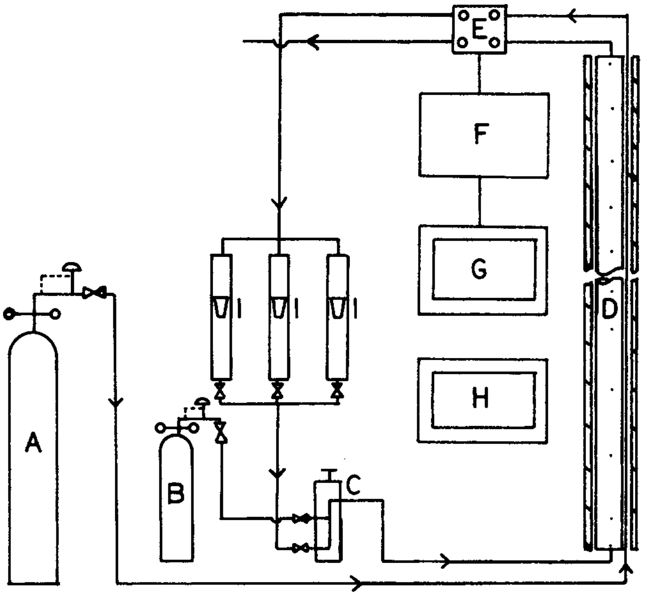

Fig. 2. Schematic diagram of the equipment.

and thus

$$K = \frac{1}{\epsilon + \dfrac{t_m u F_I}{(1 - F_I)L}} \tag{6}$$

From Equations (2) and (6), it is possible to calculate the effective diffusion coefficient from experimental data which give the value of C.

It is also possible to calculate the isosteric heat of adsorption ΔH by obtaining the retention time of the adsorbate at different temperatures (*14*). If one assumes that the average surface concentration of the adsorbed gas in the column is low and the adsorption equilibrium may be described by the Henry's law type isotherm, then

$$\lim_{\theta \to 0} \Delta H = R \, d\,[\log(F_r t_m)]/d\left(\frac{1}{T}\right) \tag{7}$$

where θ is the fraction of the surface coverage and F_r is the flow rate of the carrier gas measured at room temperature. Thus, a plot of $\log(F_r t_m)$ versus $1/T$ should yield a straight line with a slope equal to $\Delta H/R$. A typical plot of this kind is shown in Figure 1.

The temperature dependence of the diffusion coefficient in zeolites normally is expressed by an Arrhenius type equation

$$D_{eff} = D_0 e^{-E/RT} \tag{8}$$

If one assumes that E is constant over a range of temperature, then a semi-log plot of D_{eff} versus $1/T$ for that range should yield a straight line and the activation energy E may be calculated from its slope.

EXPERIMENT

The equipment for this study was a classical gas chromatography set-up as schematically shown in Figure 2. A 1.0 cm I.D. stainless steel column 213 cm long was packed with cylindrical sorbent pellets. The column was fitted tightly through hollow cylindrical bronze bars to insure good heat transfer. The column was heated by insulated cylindrical heating units whose temperature was controlled by five variacs. The temperature distribution in the column was checked by ten thermocouples located at regular intervals inside the bronze bars. The variation of the ten thermocouples was less than ± 2°C. Injection

Table 1. Characteristics of Columns
Internal cross section area = 0.82 cm²
Column length = 213.3 cm

Description	d_p, cm	ϵ	Bulk density, g/cm³	Pellet density, g/cm³	F_I
5A Mol. Sieves 1/8 in. × 1/8 in. pellets Linde Lot 594 3490243	0.3636	0.40	0.373	1.15	0.676
13X Mol. Sieves 1/8 in. × 1/8 in. pellets Linde Lot 13 945490005	0.3636	0.40	0.687	1.15	0.401
H Mordenite 1/8 in. × 1/8 in. extrudate Norton DM 122 Lot 2982297	0.3636	0.42	0.724	1.32	0.440
Na Mordenite 1/8 in. × 1/8 in. extrudate Norton—SM 112 Lot 00095 G	0.3636	0.53	0.816	1.45	0.626
Natural Mordenite 1/16 in. × 1/16 in. extrudate Linde AW 300 Lot 38017	0.1817	0.40	0.909	1.59	0.428

of the gas sample was done by a Hewlett Packard sampling valve which has a dual sample loop for quick injection. A Gow-Mac thermoconductivity cell with gold-tungsten filaments was used as a detector. Helium was the carrier gas. The pressure drop in the column was measured by a manometer and found to be negligible (normally less than 10 mm Hg).

Samples of 13X and 5A molecular sieves and natural mordenite were obtained from Linde Division, Union Carbide Corporation. Samples of Na- and H-mordenites were obtained from Norton Company. The characteristics of the different zeolites are summarized in Table 1.

The catalyst was regenerated before the start of the run by heating to 400°C for 15 hours under helium atmosphere. The equivalent diameter of the pellets d_p was calculated for spheres of equal volumes. The molecular diffusion coefficient D_{12} was determined by using the well-known formulas derived from the kinetic theories of gases (*3, 16*). The porosity of the column F_I was determined by the bulk density of the pellets (total mass/volume of the column) and the pellet density (mass of a pellet/volume of a pellet). H.E.T.P. was calculated by the following equation

$$\text{H.E.T.P.} = \frac{LM^2}{16\, l^2} \tag{9}$$

The quantities in (9) were obtained in the following manner. If one draws tangents to the points of inflection of the peak, then M is the distance on the baseline between the points where the two tangents intersect it. l is the distance on the recorder chart measured from the point corresponding to the start of the chromatogram to the peak maximum. The constants A, B, and C were calculated by the least squares method.

RESULTS AND DISCUSSION

Diffusion experiments were performed on 5A and 13X molecular sieves H-, Na- and natural mordenites with CO_2, SO_2, NO, and NO_2 as pulse gases. Although 5A and 13X molecular sieves do not possess the desired acid stability for the pulse gases used, it is interesting to compare their results with those obtained from acid-stable mordenites. They also have very different pore systems for diffusion: one-dimensional for mordenites as compared with three-dimensional for 5A and 13X sieves.

A typical plot of H.E.T.P. versus u is shown in Figure 3 for the diffusion of SO_2 on Na-mordenites at temperatures between 133° and 261°C. The C-values were calculated by fitting the experimental data with Equation (1) using the method of least squares. From Equation (1) one notices that D_{eff} increases as C decreases. This is illustrated in Figure 3 in that the limiting slope of the curve at higher carrier flow rates decreases as the temperature increases.

Zeolite type A is a three-dimensional network with sodalite units linked by four bridging oxygen ions. It has an effective pore diameter of 4Å (Linde 4A). When 40% or more of sodium cations within 4A molecular sieves are exchanged by Ca cations (Linde 5A), the effective pore diameter increases to about 5Å. In faujasite type zeolite

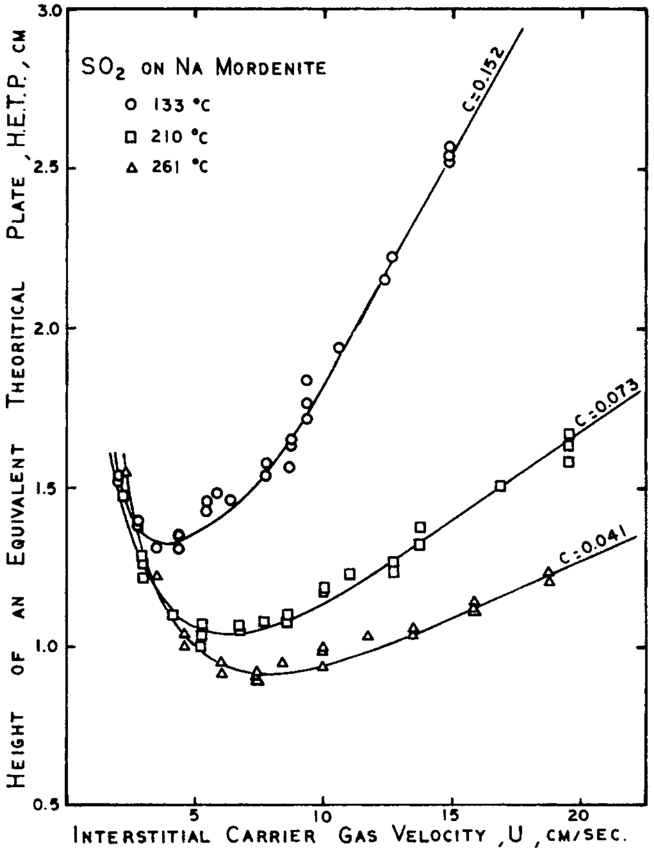

Fig. 3. H.E.T.P. as a function of intersticial gas velocity for SO_2 on Na-mordenite.

TABLE 2. RESULTS ON 5A

Gas	Temp, °C	β'	K	$D_{eff} \times 10^2$ cm²/s	Energy of activation, Kcal/mole	Heat of adsorption, Kcal/mole
SO_2	133	1.67	0.18	2.7	4.3	2.2
	210	1.27	0.23	5.9		
	261	1.13	0.26	9.8		
NO	165	8.99	0.04	0.045	19.0	8.9
	210	3.75	0.08	0.34		
	261	1.74	0.17	2.29		
NO_2	133	1.66	0.18	2.5	2.8	2.2
	210	1.26	0.23	4.3		
	261	1.15	0.25	5.9		
CO_2	210	11.93	0.03	0.35	6.9	7.3
	261	5.96	0.05	0.74		
	325	3.39	0.09	1.40		

TABLE 3. RESULTS ON 13X

Gas	Temp, °C	β'	K	$D_{eff} \times 10^2$ cm²/s	Energy of activation, Kcal/mole	Heat of adsorption, Kcal/mole
NO	133	2.03	0.25	2.1	4.2	2.2
	210	1.52	0.32	4.9		
	261	1.41	0.34	7.1		
NO_2	133	1.67	0.30	2.3	3.3	2.2
	210	1.27	0.37	4.0		
	261	1.15	0.41	6.2		
CO_2	210	16.31	0.03	0.20	8.5	8.2
	261	7.20	0.08	0.44		
	325	3.89	0.14	1.0		

(Linde 13X) the sodalite units are arranged in a tetrahedron and linked by six bridging oxygen ions. The lattice of the faujasite may be viewed as a tightly packed bed aggregate of oxygen atoms interlaced with large voids (super cages of 12Å diameter). The small pore system, consisting of the interiors of the sodalite cages and the hexagonal prisms branching from the large voids, is inaccessible to most molecules. The results of diffusion study on these materials are summarized in Tables 2 and 3.

The diffusion coefficient measured by this method is the overall effective diffusion coefficient which includes the contribution from both the micropores and macropores. From work done in the laboratories in this department (*17*) the contribution from the inert binder is small. It is not possible to differentiate the contribution of micropores from that of macropores with the simple data analysis presented here. However, a detailed mathematical analysis is underway.

The effective diffusion coefficient for NO is considerably larger in 13X sieves than in 5A sieves due to the large openings of the faujasite type cages. There are evidences that NO reacts with 5A sieves (*1*) and thus is chemisorbed on the sieves. Sulfur dioxide was so strongly adsorbed on 13X sieves that no peak was observed at these temperature ranges. Although the openings of sieves relative to the size of the diffusing molecules is normally regarded as an important factor which affects the diffusional resistance, it is well known that the interactions between the cations in the cages and the gas molecules play an important role in both diffusion and adsorption. The fact that the effective diffusion coefficient of NO_2 is approximately the same in 5A and 13X sieves while that of CO_2 is smaller in 13X sieves than in 5A sieves may be due to the interaction between the surface and the gases. Thus, it is not unreasonable to find that the diffusional resistance is larger in 13X than in 5A for some gases as different cations are present in these two sorbents.

Energy of activation and isosteric heat of adsorption are also included in Tables 2 and 3. The Arrhenius type plots of log D_{eff} versus $1/T$ for these systems are shown in Figures 4 and 5. They range from 2.8 to 19 kcal/mole for 5A sieves and 3.3 to 8.5 kcal/mole for 13X sieves. It is interesting to note that low diffusion coefficient is associated with high activation energy. This is consistent with the fact that low diffusion coefficient means high diffusional resistance and thus the molecules encounter higher energy barriers. The isosteric heat of adsorption ranges from 2.2 to 8.9 kcal/moles and varies similarly as the energy of activation.

In contrast to type A zeolite and faujasite which consist of sodalite units with three dimensional pore structure, mordenite has only a one-dimensional tubular pore system. The elliptical channels in mordenite are parallel and provide the main paths for diffusion. The channels are interconnected with small but generally inaccessible cross channels (*18*). The results of diffusion study on mordenites are summarized in Tables 4, 5, and 6. As the diffusion in mordenites is one-dimensional, one would expect that the effective diffusion coefficient should be smaller than that in a three dimensional diffusion. This is true if one compares the values of the effective diffusion coefficient in Tables 4, 5, and 6 to those in Tables 2 and 3. The results shown in Tables 4, 5, and 6 also indicate the effects of the type of cation upon the diffusion of the inorganic gases reported in this study. The Na cations in Na-mordenite are exchanged by hydrogen to produce H-mordenite while natural mordenite contains Ca as well as Na cations.

For the case of sulfur dioxide, the effective diffusion co-

TABLE 4. RESULTS ON NATURAL MORDENITE

Gas	Temp, °C	β'	K	$D_{eff} \times 10^2$ cm²/s	Energy of activation, Kcal/mole	Heat of adsorption, Kcal/mole
NO	133	3.80	0.14	0.064	8.2	4.8
	210	1.53	0.33	0.36		
	261	1.22	0.39	0.72		
NO_2	133	1.61	0.31	0.14	6.3	2.4
	210	1.12	0.42	0.71		
	261	1.07	0.44	0.80		

TABLE 5. RESULTS ON Na-MORDENITE

Gas	Temp, °C	β'	K	$D_{eff} \times 10^2$ cm²/s	Energy of activation, Kcal/mole	Heat of adsorption, Kcal/mole
SO_2	133	2.15	0.24	0.76	5.3	2.7
	210	1.44	0.33	2.0		
	261	1.28	0.37	3.8		
NO_2	133	2.41	0.21	0.37	6.3	2.9
	210	1.55	0.31	1.4		
	261	1.36	0.35	2.3		

efficient decreases as the hydrogen ions are replaced by sodium cations. When some of the sodium cations are replaced by Ca cations as in natural mordenite, no sulfur dioxide peak could be observed, indicating strong interaction between the surface and the gas molecules. The increase in activation energy is again consistent with the decrease in effective diffusion coefficient. It is interesting to note that β' is larger in Na-mordenite than in H-mordenite. As β' may be regarded as the initial slope of the adsorption isotherm, this may indicate that at least at very low partial pressure Na-mordenite may have relatively higher capacity than H-mordenite. (Strictly speaking, such an observation could only be made for a single column or two exactly identical columns as β' is dependent on the porosity of the column.)

The same behavior has been observed for the case of nitrogen oxide. The effective diffusion coefficient decreases in the following order: H-mordenite > Na-mordenite > natural mordenite, while the energy of activation increases in the same order. The values of β' are lower in natural mordenite than in sodium mordenite. This may be due to the relatively large size of Ca cations which block certain paths of diffusion. This is also consistent with the fact that synthetic mordenites (H- and Na-mordenite) are of large port variety while the natural mordenite has small ports. The semi-log plot of log D_{eff} versus $1/T$ is also shown in Figures 4 and 5. Reasonably straight lines are obtained. Thus, it is felt that the activation energies are essentially constant in the temperature range studied.

TABLE 6. RESULTS ON H-MORDENITE

Gas	Temp, °C	β'	K	$D_{\text{eff}} \times 10^2$ cm²/s	Energy of activation, Kcal/mole	Heat of adsorption, Kcal/mole
	133	1.97	0.24	0.80		
SO_2	210	1.14	0.38	1.9	4.4	2.9
	261	1.13	0.39	2.9		
	133	1.60	0.29	1.0		
NO_2	210	1.13	0.39	2.5	4.4	2.4
	261	1.04	0.41	3.9		
	210	28.5	0.02	0.053		
CO_2	261	8.74	0.06	0.25	13.1	12.0
	325	3.15	0.16	0.73		

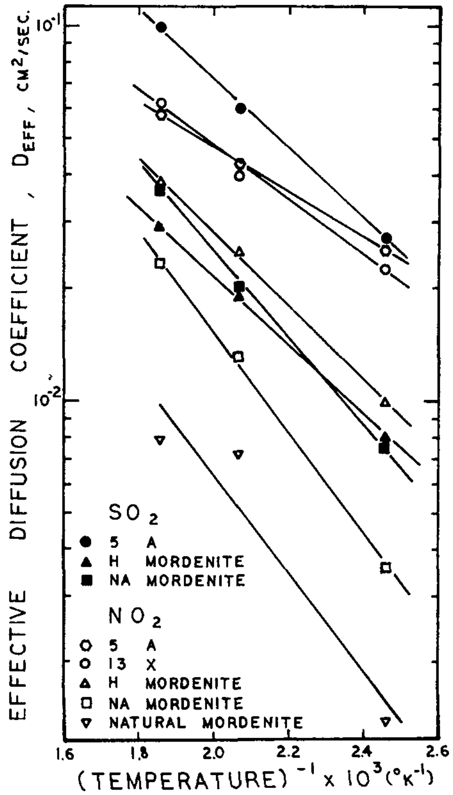

Fig. 4. Effective diffusion coefficient as a function of temperature for SO_2 and NO_2.

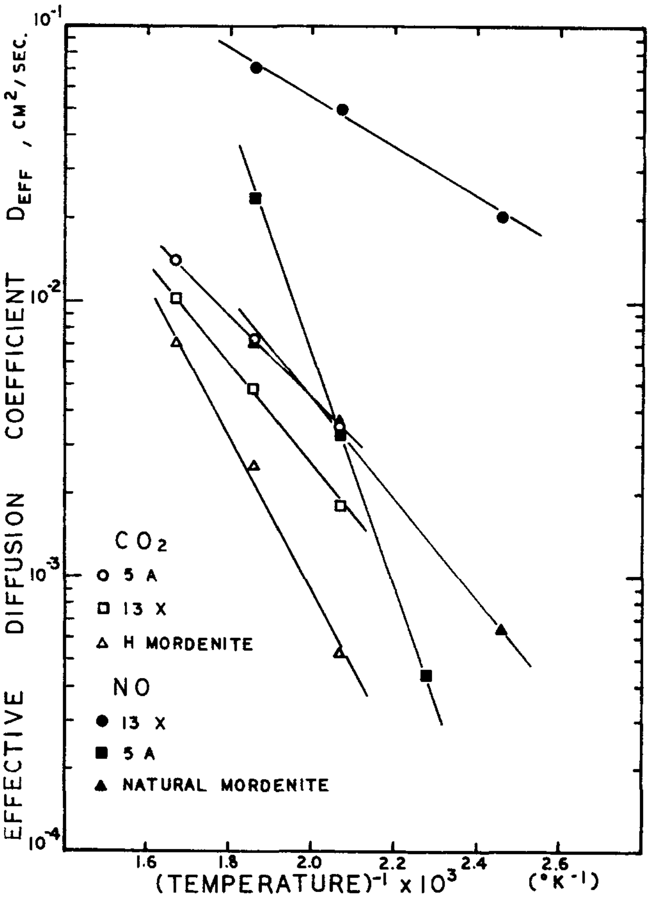

Fig. 5. Effective diffusion coefficient as a function of temperature for CO_2 and NO.

Essentially no experimental data are available for comparison. Sargent and Whitford (*15*) reported a study on the diffusion of CO_2 on 5A sieves at temperatures between −25°C and 25°C. Estimation of the energy of activation from their data gives a value of 7 kcal/mole which is in close agreement with the value reported here. Extrapolation of the data from this study to the temperature range reported by Sargent and Whitford (*15*) also yields close agreement in effective diffusion coefficient.

The retention time t_m which is defined as

$$t_m = \beta' \frac{L}{u} \tag{10}$$

deserves some further consideration, as it is independent of the diffusion process and corresponds to equilibrium conditions. The ratio of the retention times characterizes the resolving power of solid adsorbents of gas chromatography and its temperature dependence. Normally t_m or β' will vary with pressure. However, in gas-solid chromatography a linear adsorption isotherm generally can be assumed due to the extremely low partial pressure of pulse

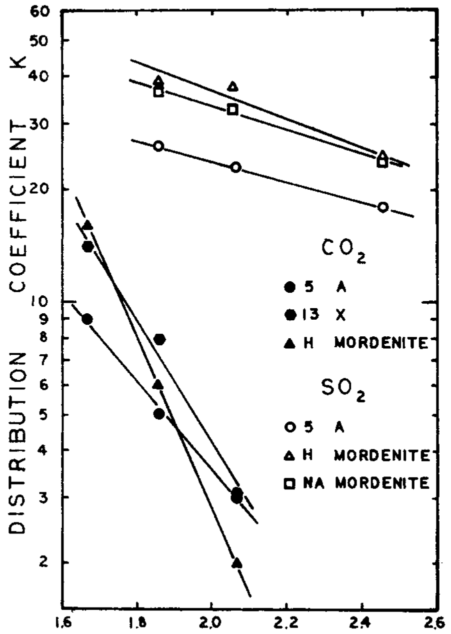

Fig. 6. Distribution coefficient as a function of temperature.

gas in the gas phase. Thus, t_m or β' may be assumed to be independent of pressure. It was found in this study that β' is essentially independent of the carrier gas flow rate. t_m is thus inversely proportional to u.

The resolving power of the solid sorbents may be determined by taking the ratio of the retention time of two gases at a given temperature and carrier gas flow rate in the same column. Higher values of the ratio means high resolution power. For example, the ratio of retention time of CO_2 to that of NO_2 in H-mordenite (25 at 210°C) is higher than that in 13X sieves (13 at 210°C). This certainly is not necessarily true at higher partial pressures of the pulse gases.

The effects of temperature upon the value of β' is also worth noting. A plot of log K versus $1/T$ is shown in Figure 6. It has been shown that the ratio of the retention time for two pulse gases increases exponentially with temperature (*13*). According to this consideration the adsorbents investigated here have unusual properties for the separation of CO_2 and other gases (NO, NO_2 and SO_2) with large values of retention time ratio. The resolution power for the other gases (for example, NO versus NO_2) is small as the ratios of β' for these gases are essentially unity and insensitive to temperature.

CONCLUSION

The GC technique was used to determine the effective diffusion coefficient and heat of adsorption of CO_2, NO_2, NO, and SO_2 on molecular sieve zeolites. This technique is especially suitable for measurements at high temperature and low sorbate concentration. It is very difficult to obtain measurements at these conditions by conventional vacuum techniques.

For the inorganic gases employed here, it was found that the diffusional resistance is decreased in the following order: natural mordenite > Na-mordenite > H-mordenite > (13X sieves, 5A sieves). This can be interpreted as the increased ease of flow in a three dimensional network (5A and 13X sieves) as opposed to the unidimensional network of mordenites. The interaction between the cations and the gas molecules also affects the diffusion as well as adsorption, possibly explaining the lower diffusional resistance of the 5A sieve as compared to the larger 13X for CO_2. Natural mordenite is of the small port variety while H- and Na-mordenites are of the large port ones. Natural mordenite thus offers higher diffusional resistance.

Isosteric heat of adsorption and energy of activation were obtained. They decrease in the following order: natural mordenite > Na-mordenite > H-mordenite > (13X, 5A) in agreement with the diffusion data. High resolution power was observed between CO_2 and other gases.

As the size of the pores in molecular sieve zeolites is in the same order as that of diffusing molecules, there is always interaction between the "surface" and the diffusing molecules. It is thus extremely difficult to predict the effects of molecular weight and types of molecules upon the effective diffusion coefficient. Although GC technique does not give information concerning the microscopic behavior of the system, it does provide macroscopic information which is required in adsorption and catalysis operations.

Zeolitic materials have been extensively used in petroleum industries and other industrial operations. Their potential for air pollution abatement is currently under investigation in the chemical engineering laboratories at Worcester Polytechnic Institute. Although 13X and 5A may have more favorable rates, mordenites may still be the desirable adsorbents because they are extremely stable in an acid environment.

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