U = velocity outside the boundary layer, in./min.
W = aluminum plate weight, lb.
x = coordinate parallel to the plate surface
Z = variable defined by Equation (14), dimensionless

Greek Letters

α = constant defined by Equation (6)
θ = time, min.
μ = viscosity
ρ = mass density, lb./cu.in.
ω = mass fraction, dimensionless

Subscripts

A, B, C = component, $A, B, C,$
e = evaluation outside the boundary layer
L = evaluation at $x = L$
s = evaluation at the plate surface

Superscripts

i = initial
f = final
— = average

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Sorption and Diffusion of Gaseous Hydrocarbons in Synthetic Mordenite

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Diffusion coefficients for the C_1 to C_4 paraffin hydrocarbon gases in single crystals of the synthetic zeolite (molecular sieve) sodium mordenite were determined from transient sorption rate and desorption rate measurements over the temperature range 25° to 140°C. and pressure range 0 to 20 cm. Hg, and found to be of the order of 10^{-9} to 10^{-10} sq. cm./sec. Diffusion coefficients for desorption were from three to sixty times smaller than those for sorption. Activation energies for methane and ethane were 1.7 and 1.9 kcal./mole, respectively.

Equilibrium sorption capacity and diffusion coefficients are markedly affected by the conditions of synthesis and by mechanical treatments such as grinding. For propane at 29°C. and at 2.0 cm. Hg pressure, the sorption capacity in 2.5 μ crystals was only 50% of that in 21 by 21 by 33 μ crystals and the diffusion coefficient was only 1/50 of that in the larger crystals. Light mechanical grinding of the larger crystals lowered the sorption capacity 30% and the diffusion coefficient by a factor of 35.

Mordenite is a zeolite (molecular sieve) having the ideal formula (hydrated) in the sodium form of $Na_2O(Al_2O_3)(SiO_2)_{10}{\cdot}6H_2O$. By varying the synthesis conditions, the atomic ratio of silicon to aluminum can be varied from about 4½ to 5½ without essentially altering the crystal structure, although the cation density will change. Mordenite is one of the few zeolites that will undergo complete hydrogen ion exchange in moderately acidic media without destruction of the crystal structure. The structures of zeolites in general are described, for example, in the book by Hirsch (*22*) and the review of Breck (*17*). They all consist of a three-dimensional framework of SiO_4 and AlO_4 tetrahedra, which can be arranged in a variety of ways. The crystal structure of mordenite was reported by Meier in 1961 (*23*) to be such that the principal sorption channels are formed by twelve-membered rings of silica-alumina tetrahedra, the passageways being elliptical in shape with major and minor diameters of 7.0 and 5.8 Å. However, the sorption characteristics of mordenite as reported during the period 1948-1954 by Barrer and co-workers (*4* to *6*, *12* to *14*) on material synthesized in his laboratory are consistent only with passageways with restrictions of the order of 4 Å. in diameter, so Meier suggested that stacking faults existed in Barrer's mordenite. But, stacking faults seem to imply considerable strain and a more plausible explanation is that the pores of this and other zeolites may be partly obstructed in various places by cations or by other substances. The

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location of all the cations in mordenite is not known, although some are thought to be in the main channels, since the effective cross section of the pores varies with the number and nature of the cations present. The fact that considerable quantities of alumina can be leached out of mordenite without altering the structure also suggests that some alumina may sometimes be present as small clumps partially blocking passageways rather than as part of the main structure.

In the ideal mordenite structure small side cavities with diameters of 3.9 Å. are located along the main channels so the structure is effectively a parallel array of noninterconnected elliptical tubes with many smaller side cavities branching off each tube. The size of the main channels is larger than that of the other synthetic and natural zeolites except for faujasite type zeolites such as the synthetic zeolites Linde X and Y. Synthetic mordenite is available in substantially larger single crystals than the Linde zeolites, and, like the faujasite types of zeolites, its pores are sufficiently large to admit molecules of many substances of interest in industrial separations and catalysis.

In 1960 Keough and Sand disclosed the synthesis of a mordenite which apparently permitted sorption of larger molecules than did Barrer's mordenite, and this was subsequently made available as a commercial material (Zeolon) by the Norton Company. More recently, Ames (*1* to *3*) determined cation exchange equilibria for a synthetic Linde mordenite (AW-300) and for the Norton Company synthetic mordenite (Zeolon). The ion-exchange properties of the Linde mordenite indicated that it had a smaller effective pore diameter than did the Norton Company mordenite. The only other equilibrium sorption studies on a relatively open form of Na-mordenite are those of Barrer and Peterson (*11*) and of Eberly (*19*). All these studies used specially purified samples of mordenite prepared by the Norton Company, Worcester, Massachusetts. The treatment of either natural or synthetic mordenite with aqueous hydrogen chloride replaces the cations with hydrogen, providing a more accessible structure, and Barrer and Peterson report some sorption studies on H-mordenite from the Norton Company. No diffusion studies on the open-structured mordenite as made by the Norton Company have been previously reported.

APPARATUS AND PROCEDURE

Mordenite

Most of the studies were made with one batch of Na-mordenite synthesized by the Norton Company under conditions to produce as large single crystals as possible (this material is identified as special batch No. 3821). The crystals were fractionated by us, by settling in water, into four portions of decreasing particle size. The third portion, which had a narrow particle size distribution, was studied and the others discarded. The portion first settling contained a significant fraction of large, apparently amorphous, particles. The average crystal in the third portion was shoe-box shaped with dimensions 21 by 21 by 33 μ. The standard deviation of the size distribution was ± 5 μ. Under an optical microscope the crystals appeared to be fairly well-formed with some small dark spots appearing in the interior. Late in our study, electron micrographs by the carbon envelope method, made by Dr. H. P. Studer of the Shell Development Company, became available which showed that while some of the crystals appeared to be fairly well-formed, others looked quite rough. Electron micrographs made at M.I.T. showed fairly rough edges, suggesting the possible existence within the individual particles of crystallites of the order of 0.1 to 1 μ size. It is unfortunately difficult to deduce much about interior crystalline order from micrographs of exterior crystal surfaces.

Chemical analysis of the Na-mordenite (by the Norton Company) gave the unit cell formula $Na_{6.72}H_{0.65}Al_{7.37}Si_{40.63}O_{96}$ x H_2O. Thus about 8.8% of the sodium was replaced by hydrogen, presumably during the washing operations subsequent to synthesis. The theoretical water content for the above formula (completely hydrated) as determined by Meier's unit cell formula is 12.5 wt.% (twenty four molecules of water per unit cell). The water contents of the Na-mordenite as determined experimentally were 11 to 13 wt.%. An x-ray analysis of the Na-mordenite crystals (powder) by the Norton Company indicated that they contained about 5% of the zeolite analcite. Some of this material was presumably retained in the sized sample we studied. One run with benzene was made with H-mordenite obtained by acid exchange in our laboratories of this Na-mordenite. Chemical analysis indicated that the silicon-aluminum atom ratio was unchanged by this treatment. The sodium content was not determined but it is believed that the acid treatment was sufficiently drastic that the remaining sodium was negligible.

The sorption of propane (two runs) was also studied on one sample of Na-mordenite of about 2.5 μ size produced in the Norton Company pilot plant and presumed to be essentially equivalent to commercial material and studies (four runs) were made of the sorption of propane on two samples of Na-mordenite which had been crushed by grinding to reduce the particle size.

Apparatus

The experimental apparatus was essentially a McBain-Bakr spring balance contained inside a sorption case. The zeolite (10 to 15 mg.) was spread in a thin layer (about 0.1 mm.) on a cylindrical quartz weighing pan suspended from a sensitive and carefully calibrated quartz spring (sensitivity of about 540 cm./g.). Fresh zeolite samples were introduced by melting a soldered joint at the top of the Pyrex sorption case. The zeolite weight gain during sorption was determined with a cathetometer which could read the spring extension to ± 0.005 cm. (± 0.06 wt. % of the zeolite).

Pressure was measured with a quartz Bourdon type gauge consisting of a coiled hollow tube with a platinum mirror on the end, which deflected a light beam to an indicating scale 3 ft. away. The pressure could be read to about ± 0.6 mm. Hg and since the ratio of gas volume to zeolite weight was very high, the pressure remained essentially constant during a run. The zeolite had a bed density of about 1.0 g./cc. The crystal density of the Na-mordenite, calculated from the unit-cell formula, was 1.80 g./cc. The zeolite was desorbed at 350°C. under vacuum (pressure of 10 μ or less) for 4 hr. and then cooled from 3 to 5 hr. before a sorption measurement was made. Pressurization of the sorption case required from 5 to 10 sec., after which the zeolite weight gain was followed closely for about 1 hr. with the cathetometer. The system was then allowed to equilibrate overnight or longer. For the next run the zeolite was then desorbed by heating under vacuum at 350°C. for 4 hr.

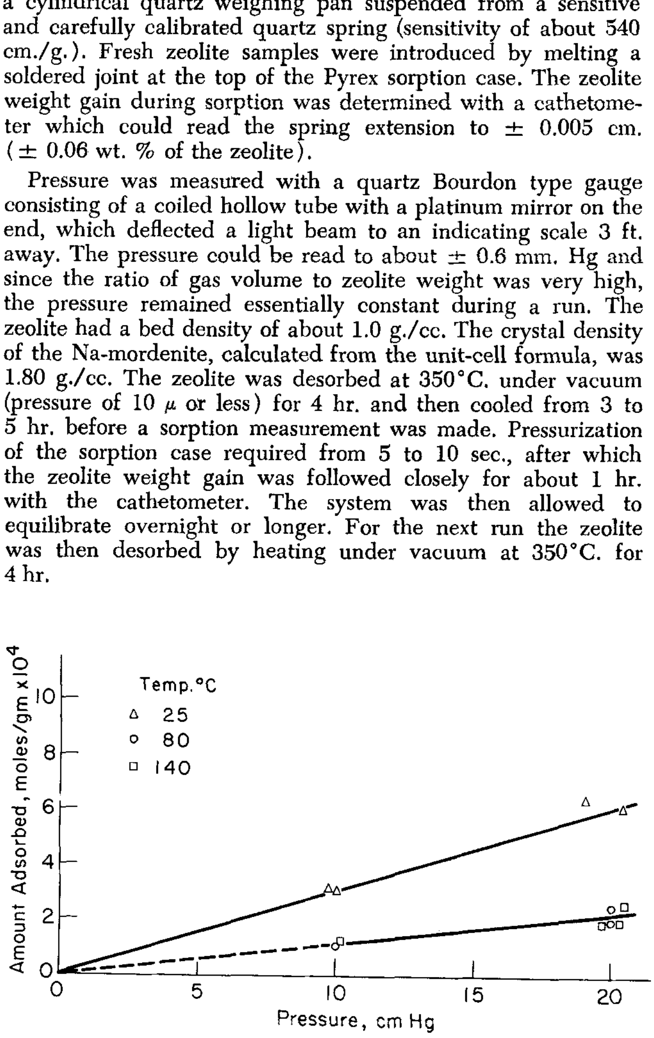

Fig. 1. Sorption isotherms of methane on Na-mordenite.

The introduction of zeolite and the sealing of the apparatus were time-consuming, so a number of sequential runs (up to as many as nineteen but more typically about five) of sorption and desorption were performed on each sample of zeolite. In some cases only one hydrocarbon gas was studied in the sequence, in other cases as many as four different gases were studied. Nineteen series of runs were made on the size-fractionated Na-mordenite prepared in the Norton Company pilot plant (33 by 21 by 21 μ), one on this mordenite after acid exchange, one on 2.5 μ size Na-mordenite, and two on crushed samples of the large crystals of Na-mordenite.

The absorbates were primarily methane, ethane, propane, and *n*-butane (Matheson C. P. Grade, 99.0% min. purity) which were previously dried by passage through a 4-ft. column of activated Linde 4A zeolite.

RESULTS AND DISCUSSION

Sorption Equilibria

The sorption isotherms for the four hydrocarbon gases on sodium-mordenite at 25°, 80°, and 140°C. are shown in Figures 1 through 4. The vapor pressures here are sufficiently low that extra zeolitic sorption into capillaries of 20 Å. diameter and larger, reported by Barrer and Peterson (*11*) for their mordenite, would not be observed here, even if such capillaries existed. Butane was the only sorbate whose isotherm, nearly horizontal at the higher sorption pressures, indicated complete saturation in the Na-mordenite. The butane saturation value is essentially the same as that quoted by Barrer and Peterson for butane on Norton Company mordenite, which was calculated by plotting the quantity of vapor sorbed against partial pressure, on log-log coordinates, extrapolating the linear portion of the curve, obtained at low pressures, to the saturation vapor pressure. The only other sorbates they studied on Na-mordenite were oxygen, nitrogen, and argon. The Na-mordenite used in the present work had 8.8% of the sodium replaced by, presumably, hydrogen, and it also had a higher silicon-aluminum atom ratio than Barrer's sample (5.51 vs. 4.75), but this seemed not to affect its capacity for butane.

The volume of the sorbed butane, calculated at a density equal to that of liquid butane at the temperature of sorption, is about 45% of the total Na-mordenite main tube volume, the latter calculated from the crystal structure of Meier (*23*). This is equivalent to each butane molecule occupying 10.3 Å. of the main tube length. (The length of a butane molecule is about 7.8 Å.) The total volume of the main tube plus side cavities of the mordenite used here is calculated to be 0.189 and 0.199 cc./g. for the sodium and hydrogen forms, respectively, based on the dehydrated weight. That of the main tube alone is calculated to be 0.107 and 0.113 for the two forms, respectively.

The size of the benzene molecule is close to that of the mordenite channels, so its sorption is a critical test of the extent of blocking of the passageways. Two studies with benzene at 2.0 cm. Hg and 100°C. showed that the Na-mordenite adsorbed 2.50 wt.% benzene and the H-mordenite 6.02 wt.%, based on the weight of the zeolite before sorption. These are equivalent in Na-mordenite to occupation of 38% of the main tube volume, and in H-mordenite to 67% of this volume. However, the mordenite samples may not have reached equilibrium under these conditions. At 25°C. the zeolite slowly gained weight over a week, so no well-defined value could be obtained.

Eberly (*19*) studied sorption of benzene, cyclohexane, and *n*-hexane on Norton Company Na- and H-mordenite. Benzene was studied at 223° to 260°C. and vapor pressures up to 6 mm. Hg on Na-mordenite. None of his conditions corresponded to complete saturation of Na-mordenite and the maximum amount sorbed (at 223°C. and 0.45 mm. Hg) was about 3.0 wt.% benzene. A Langmuir plot of the data at the lowest temperature gave a saturation value equivalent to about 70% of the main tube volume. His and our studies are not exactly comparable but it would appear that the passageways in the two samples of Na-mordenite were open to about the same extent. His Na-mordenite had a high silicon-aluminum atom ratio (5.29), but apparently none of the sodium was exchanged by hydrogen.

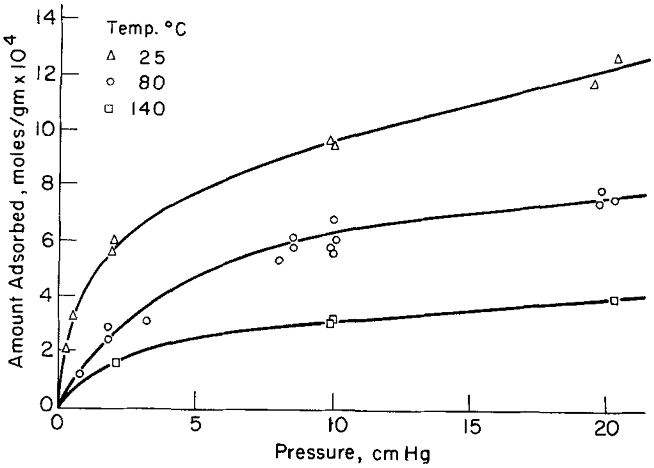

Fig. 2. Sorption isotherms of ethane on Na-mordenite.

One study here with ethylene at 2 cm. Hg and 30°C. showed 3.5 times more sorbed on Na-mordenite at equilibrium than was observed with ethane.

In the present study, the sorption values of methane at 80° and 140°C. were close to the minimum values detectable with the experimental apparatus used, for example, 2.2 × 10^{-4} moles methane/g. zeolite were sorbed at 20 cm. Hg (0.35 wt.%). At these temperatures, about 1.0 × 10^{-4} moles methane/g. were instantaneously and irreversibly sorbed, even at pressures of the order of 0.10 cm. Hg, that is, this portion of the methane could not be desorbed by evacuation at the sorption temperature. However, this sorption must have occurred within the crystals, since the amount sorbed was about 200 times that equivalent to a monolayer on the external areas of the crystal.

Isoteric heats of sorption on Na-mordenite at low coverages were calculated from the equilibrium sorption isotherms by the relationship:

$$q_{\text{iso}} = -R\left[\frac{\partial(\ln p)}{\partial\left(\frac{1}{T}\right)}\right]_x$$

where p is the pressure of the sorbate gas in contact with the zeolite and x indicates that the calculation is made for constant amount sorbed. The heats of sorption for methane, ethane, and propane were about 3.7, 6.0, and 9.0 kcal./mole, respectively. As would be expected they are somewhat greater than the heats of vaporization. Butane saturated the zeolite so readily that the isotherms for the several sorption temperatures essentially overlapped one another, making it impossible to apply the above expression. Barrer and Peterson reported values of 2 to 7 kcal./mole for hydrogen, argon, oxygen, and nitrogen in Na-mordenite. Eberly reported values for benzene, cyclohexane, and *n*-hexane of 18 to 25 kcal./mole.

It was disquieting to discover that the conditions of synthesis can have a substantial effect on the equilibrium sorption capacity of Na-mordenite. Taking the amount of propane sorbed at 2 cm. Hg and 25°C. as a basis, a sample of Norton Company pilot plant mordenite, which had an average crystal diameter of about 2.5 μ, sorbed only

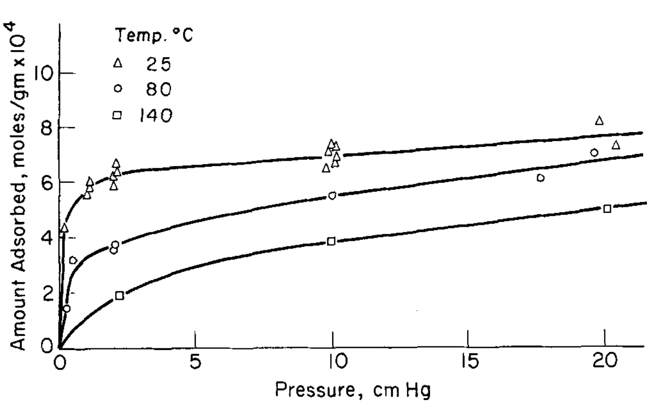

Fig. 3. Sorption isotherms of propane on Na-mordenite.

about 50% of the amount of propane as did the 21 by 21 by 33 μ crystals principally used in the present work. Light mechanical grinding also had a marked effect. Light grinding of the 21 by 21 by 33 μ crystals with a mortar and pestle for a few minutes under first dry and then wet conditions reduced the sorption value to 80% of that of the unground material. Grinding for a longer time and fractionating by settling produced a sample of average particle diameter of 7.5 μ which had a sorption capacity at the above conditions of only 70% of the original. In both cases the crushing process may have partially closed or blocked some of the sorption channels. It would be interesting to determine if the saturation sorption capacities are also affected markedly by conditions of synthesis and mechanical grinding. The effects on the diffusion coefficients are very pronounced and are described below.

Sorption Rate

Past investigators of diffusion in zeolites have treated the crystals as homogeneous media characterized by an overall diffusion coefficient D_E (sq.cm./sec.) for each sorbate, the sorbate flux within the crystal being assumed to follow Fick's law. Usually the concentration at the outside surface of the zeolite crystal is taken as the equilibrium concentration in contact with the gas phase. The pertinent mathematical expressions and solutions are given by Crank (*18*) and in a recent review by Walker et al. (*24*).

For a crystal of arbitrary shape, the solution for short times becomes

$$\frac{M_t}{M_\infty} = \frac{2\,A}{V}\sqrt{\frac{D_E t}{\pi}} \tag{1}$$

For crystals 33 by 21 by 21 μ this becomes

$$\frac{M_t}{M_\infty} = 1.32 \times 10^3 \sqrt{D_E t} \tag{2}$$

Calculated values of D_E would be somewhat different if it were assumed that all the pores in the mordenite crystals were in parallel, so that access was available only from two opposing faces of the crystal, as shown by Equation (3). Sorption rates are usually measured gravimetrically in either a constant-pressure or constant-volume apparatus. The largest diffusion coefficients which can be determined are set by the nature of the transients within the apparatus, including instrument response time, and the particle size under study. Taking as a rough measure of the first a maximum rate of sorption corresponding to attaining a value of M_t/M_∞ of 0.3 in about 10 sec., the highest diffusion coefficient readily measurable by this type of unsteady state technique becomes about 10^{-11} sq.cm./sec. for 1 μ particles and 10^{-7} for 100 μ particles. (The fastest rates which could be accurately measured in our apparatus corresponded to diffusion coefficients of about one-tenth of the above, that is, about 10^{-12} and 10^{-8} sq.cm./sec., respectively.)

The commercial Linde synthetic zeolites X and Y presently available have crystal sizes in the range of 0.1 to 1 μ and that of Norton commercial synthetic mordenite is about 2.5 μ. The ability to obtain single crystals of mordenite of about 25 μ size was an important factor in choosing this material for the present study. Naturally occurring zeolites can be obtained in substantial size. Thus Barrer and Fender (*7*) were able to report diffusion coefficients of 1.6 by 10^{-6} to 4.8 by 10^{-6} sq.cm./sec. for water vapor at 45°C. in partially dehydrated natural chabazite, gmelinite, and heulandite by measurements with individual crystals weighing from 0.01 to 0.5 g. With beds of powder or pressed pellets of the magnitude of 1 cm., effective coefficients for diffusion in the interstices of powder beds or pellet pores as high as about 10^{-3} cm./sec. become measurable. Diffusion coefficients for water vapor in zeolites are orders of magnitude greater than those for nonpolar gases. Diffusion coefficients of nonpolar gases of the order of 10^{-3} to 10^{-6} sq.cm./sec. which have been reported from measurements on beds of zeolite powders or on pressed pellets of synthetic zeolites are so large that they would seem to represent diffusion in the interstices between the individual zeolite crystals instead of diffusion within the individual crystals themselves.

Previous studies on intracrystalline diffusion seem to have been restricted to mordenite and smaller pore zeolites, particularly naturally occurring materials. These include studies of gases such as propane, *n*-butane, and dichloromethane in natural chabazite and krypton in natural levynite (*6*) *n*-butane in erionite (*10*), and in chabazite (*9*) and nitrogen and methane in synthetic Linde 4A (*21*), in addition to the study by Barrer and Fender noted above. For diffusing substances other than water, the diffusion coefficients reported in these studies vary in the range of 10^{-12} to 10^{-14} sq.cm./sec. at temperatures of 20° to 200°C. Values for the apparent activation energy E_D for molecules such as water, argon, krypton, and nitrogen and saturated hydrocarbons are reported ranging from 3 to 11 kcal.

Typical plots of the experimental data for sorption and desorption (M_t/M_∞ vs. $t^{1/2}$) are shown in Figures 5 and 6 for the C_1 to C_4 paraffin hydrocarbons at 25°C. and 10 cm. Hg pressure. The diffusion coefficients D_E were calculated from the slope of the linear portion of these plots, generally for $M_t/M_\infty < 0.3$ and $t < 10$ min., with Equation (2). In a few runs, particularly those showing rapid sorption, a linear portion of the sorption plot was not observed. For these runs a line from the first data point to the origin was used to define the slope. Thus the highest diffusion coefficients reported here may represent slightly lower values than would have been obtained with a more rapidly responding apparatus. The diffusion coefficient

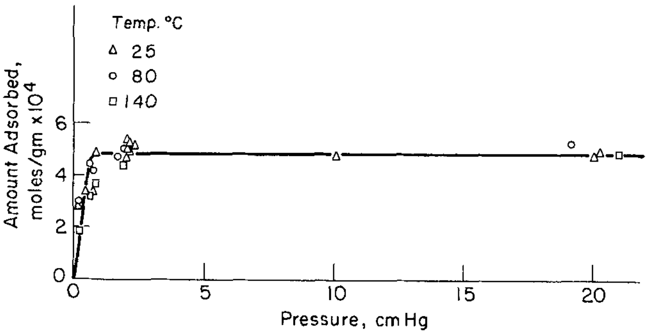

Fig. 4. Sorption isotherms of butane on Na-mordenite.

D_E represents an averaged value over the concentration range from zero to the equilibrium concentration.

Effect of Gas Pressure

Over the pressure range up to 10 cm. Hg the sorption diffusion coefficient increased with bulk gas pressure, the effect being particularly marked with propane and butane (Figure 7). One can likewise say that the diffusion coefficient increases with sorbate concentration, since this also increases strongly with increasing pressure. The effect of sorbate concentration on D_E was more precisely determined by successive step increases in pressure for a given zeolite sample, allowing equilibration to occur after each step. The diffusion coefficients are then average values over the concentration range corresponding to the given pressure step. By this method, the diffusion coefficient for ethane in Na-mordenite at 80°C. was found to be essentially independent of concentration over the pressure range of 0.8 to about 2.0 cm. Hg (Figure 8). For butane at 145°C., however, Figure 8 shows that the diffusion coefficient approximately doubled between 0.28 and 2.0 cm. Hg. Habgood (*21*) also noted an increase in D_E with increasing concentration for methane in Linde 4A zeolite, although most investigators of small pore zeolites ($d < 4$ Å.) have observed diffusion coefficients to decrease with increased concentration. This has been attributed to molecule-molecule interference effects within the narrow pore structure, which may not be as critical in the somewhat larger pores of mordenite at low sorbate concentration.

For ethane, propane, and *n*-butane the desorption coefficient decreased moderately with increased equilibrium pressure before desorption, that is, with increased sorbate concentration in the Na-mordenite. It was also observed for all hydrocarbons that the rate of diffusion into the zeolites at high values of M_t/M_∞ was much less than would be predicted from the theoretical expression with the early rate of diffusion used to predict a value of the diffusion coefficient, as shown in Figure 9. For example, for butane at 27°C. and 2.0 cm. Hg, a diffusion coefficient can be calculated from the time required for M_t/M_∞ to reach 0.5. Using this calculated diffusion coefficient, we find that the predicted time required for achieving 90% saturation is about one-quarter of that actually found. The function of M_t/M_∞ vs. $(\text{time})^{1/2}$ actually found also varied significantly with temperature, as illustrated by Figure 10 for ethane sorption at three different temperature levels. At the high temperature the fractional approach to equilibrium is initially more rapid than at lower temperatures, but then slows down excessively at higher fractions sorbed.

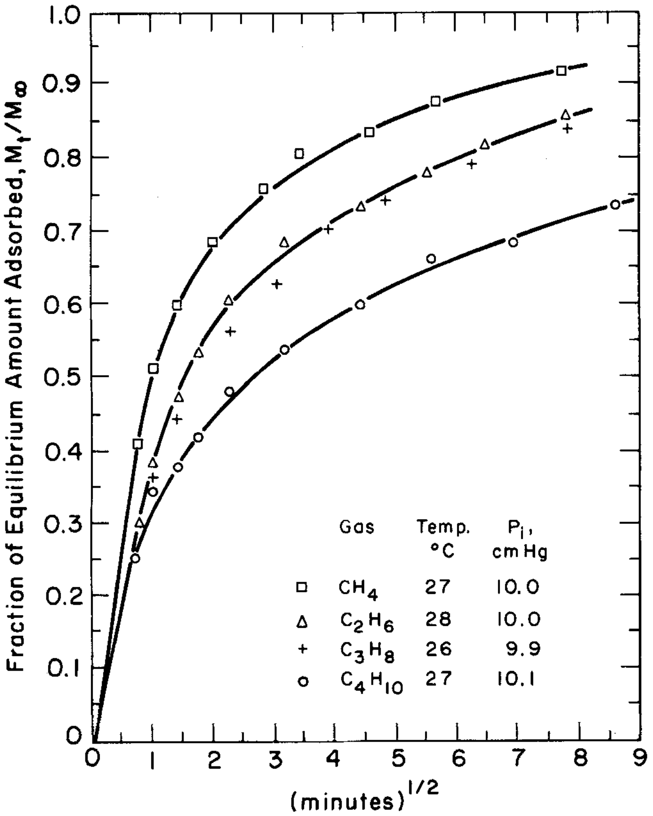

Fig. 5. Adsorption rate of C_1-C_4 hydrocarbons on Na-mordenite.

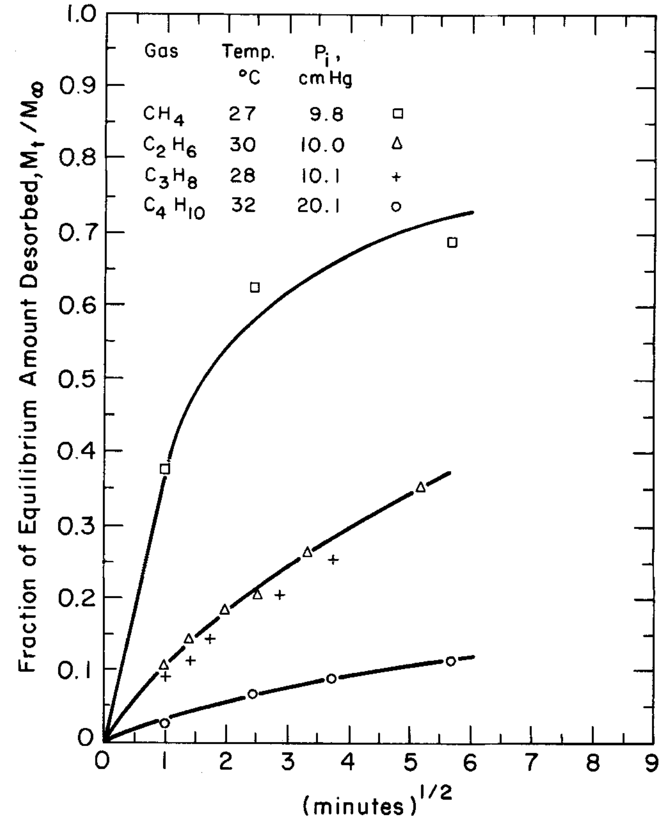

Fig. 6. Desorption rate of C_1-C_4 hydrocarbons on Na-mordenite.

Summary of Diffusion Coefficients

The average values for the diffusion coefficients at 25°C. and 10 cm. Hg sorbate pressure (calculated from both sorption and desorption rate measurements) for Na-mordenite are shown in Table 1. An error analysis (*20*) for the data for ethane indicates that the standard deviation for D_E (ads) was ± 25% and D_E (des) ± 40%. The diffusion coefficients are seen to decrease with increasing molecular weight or molecular diameter. This effect was especially marked for the desorption diffusion coefficients. The desorption coefficients are also seen to be much lower than the sorption diffusion coefficients; the difference is particularly great with the higher molecular weight hydrocarbons.

Effect of Temperature

The apparent activation energies and standard deviations for sorption (E_D in $D_E = D_0 e^{-E_D/RT}$) were 1.7 ± 0.2 kcal./mole for methane and 1.9 ± 0.13 kcal./mole for ethane and that for ethane desorption was 3.8 ± 0.3 kcal./mole. These values for ethane are somewhat less than the average heat of sorption of ethane on Na-mordenite of 4 to 6 kcal./mole. For a diffusion process whose

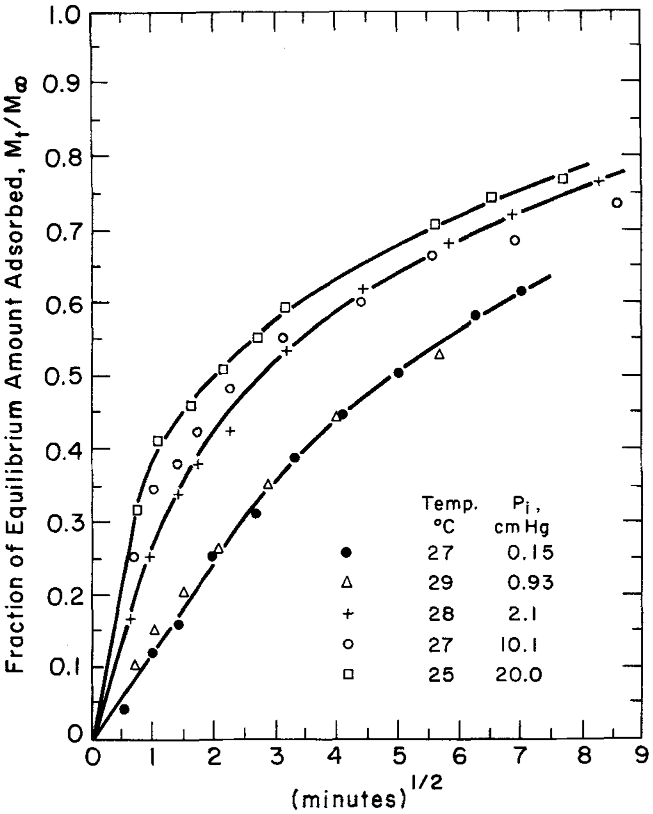

Fig. 7. Initial pressure effect for butane on Na-mordenite.

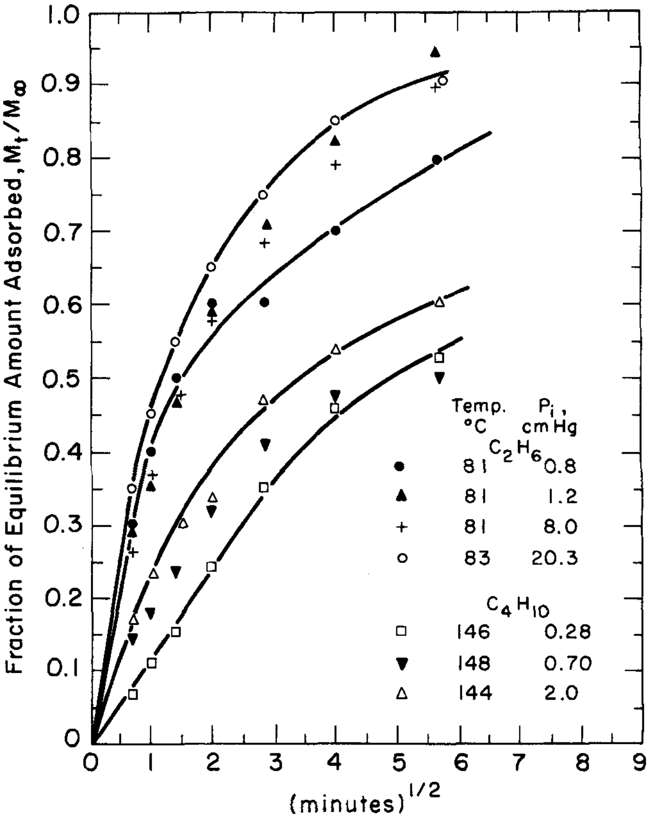

Fig. 8. Adsorption rate for successive pressurization steps on Na-mordenite.

rate is limited by rate of desorption, one would expect the true activation energy to be at least as large as the heat of desorption (or sorption). The propane and butane diffusion coefficients for sorption and desorption did not vary significantly with temperature over the temperature range studied (25° to 140°C.).

In theory, increasing temperature might have two opposite effects on diffusivity. The mobility of molecules would be expected to increase with increasing temperature because of the added thermal energy available but on the other hand, the rate of chemical interaction between the sorbate and the zeolite would also increase with increasing temperature. Thus, at a higher temperature, a greater fraction of the molecules might be strongly sorbed in the zeolite, thus decreasing their mobility by increasing the effective energy of activation for diffusion and, possibly, by molecule-molecule blockage effects within the zeolite passageways.

Two runs were made with benzene at 100°C. and 2 cm. Hg on Na- and H-mordenite. As noted above, the M_∞ values were not well defined and the linear portions of the M_t/M_∞ vs. $t^{1/2}$ sorption plots were difficult to establish. The benzene diffusion coefficient decreased rapidly with increasing concentration, possibly because of molecule-molecule blockage effects. Recognizing these uncertainties, we found that the diffusion coefficient for benzene in the Na-mordenite was approximately 5×10^{-10} sq.cm./sec. The sorption rate of benzene into the H-mordenite was about the same as that of the Na-mordenite, but because the equilibrium capacity was higher in the H-mordenite, the resulting diffusion coefficient was 50% lower. The diffusion coefficient for propane in H-mordenite was also found to be about 50% of that for Na-mordenite, although in this case the equilibrium sorption values were about the same.

Effects with Two Components

In one study the rate of sorption in the Na-mordenite was measured at 25°C. for a 50-50 mole % mixture of propane and nitrogen, each gas being present at a partial pressure of 2 cm. Hg. From measurements with the pure components the equilibrium wt.% sorption value for ethane is 45 times that of nitrogen. The diffusion coefficient for propane from the mixture was found to be about one-half the value expected for pure propane at 2 cm. Hg. Calculations (*20*) showed this could not be attributed to accumulation of nitrogen at the exterior crystal faces. Small amounts of sorbed species (modifiers) which are strongly held by the zeolite can cause a drastic reduction in the experimental diffusion coefficient but the effect here is more probably an accumulation in the pores of relatively unadsorbed nitrogen molecules which slow down the rate of diffusion of the hydrocarbon molecules.

In a somewhat similar study a sample of Na-mordenite at 144°C. and 20 cm. Hg was allowed to equilibrate with methane and then was evacuated at 144°C., which removed 50% of the methane. The system was then pressurized with ethane at 10 cm. Hg and 144°C. The resulting diffusion coefficient of ethane was only about 1/15 of that to be expected in a sample previously desorbed for 4 hr. at 350°C. after contact with a hydrocarbon sorbate gas. It is evident that the presence of a second component in these very narrow passageways has a highly restricting effect on the rate of diffusion, unlike classical Knudsen diffusion in somewhat larger pores in which the rate of diffusion of one component is independent of the presence or absence of the second.

With butane and propane there was some indication that the first run on a given sample resulted in a slightly lower (about 25%) diffusion coefficient than those found after the second or third 4-hr. exposure of the zeolite to the 350°C. evacuation conditions; perhaps a slight degree of further dehydration occurred at 350°C. after the first 4-hr. exposure. Beyond this there was a tendency for the diffusion coefficients to decrease as more runs were made

TABLE 1. AVERAGE DIFFUSION COEFFICIENTS IN SODIUM-MORDENITE AT 25°C.

	Sorption		Desorption	
Gas	D_E, sq. cm./sec.	E_D, kcal./mole	D_E, sq. cm./sec.	$\frac{D_E(\text{ads})}{D_E(\text{des})}$
CH_4	33×10^{-10}	1.7†	12×10^{-10}	2.7
C_2H_6	22×10^{-10}	1.9	1.0×10^{-10}	22
C_3H_8	22×10^{-10}	~0	0.7×10^{-10}	31
C_4H_{10}	12×10^{-10}	~0	0.18×10^{-10}	67
C_6H_6*	5.5×10^{-10}	—	0.24×10^{-10}	—

* Temp. = 100°C., P_i = 2 cm. Hg, see text for discussion.
† For temperature range 25° to 80°C.

on the same zeolite sample; the sample was discarded if the irreversibility from the preceding sorption measurement was greater than 0.1 to 0.2 wt.%.

Comparison with Earlier Work

The only other sorption rate measurements reported on a Na-mordenite were those of Barrer and co-workers on the material synthesized in his laboratory (*6*, *12*, *13*). They did not investigate the hydrocarbon gases used in the present work, presumably because the rates for these gases would have been extremely low on his Na-mordenite. For krypton at 25°C. (critical molecular diameter = 3.9 A.), they reported a diffusion coefficient of 5.0×10^{-14} sq.cm./sec. The diffusion coefficients in Na-mordenite, even for larger molecules, are much higher in the present study, for example $D_E = 1.2 \times 10^{-9}$ sq.cm./sec. for butane at 25°C. (critical diameter = 4.9 A.).

Effects of Synthesis Conditions and Mechanical Grinding

Late in this study it was found that the sorption and diffusion characteristics of a second sample of Na-mordenite, consisting of smaller crystals and probably more representative of commercial material, had substantially different sorption and diffusion characteristics than the larger crystals studied. A sample of the Norton Company pilot plant Na-mordenite (AD7S) with an average crystal diameter of about 2.5 μ showed a rate of sorption per gram of zeolite (propane, 27°C., 2.0 cm. Hg) about 30% lower than that obtained with the 21 by 21 by 33 μ crystals. The calculated effective diffusion coefficient, based on the smaller crystal diameter and on the 50% lower equilibrium sorption capacity, was about 1/50 of that found for the 21 by 21 by 33 μ crystals. Electron micrographs made at M.I.T. of the 2.5 μ commercial samples showed them to be less well formed than the 21 by 21 by 33 μ crystals used in the present work. They also tended to form agglomerates of 10 to 20 crystals, although agglomeration was not observed with any of the other mordenite samples, crushed or uncrushed.

Mechanical distortion of zeolite crystals can also have a marked effect. A Na-mordenite sample consisting of the fourth (finest) cut from settling in water was ground in a mortar and pestle, first dry and then wet, and then fractionated by settling to obtain a sample with average particle diameter of 7.5 μ. The sorption rate for these crystals, per gram (propane at 29°C., 2.9 cm. Hg), was about 0.4 of that for the uncrushed 21 by 21 by 33 μ crystals and the calculated diffusion coefficient, based on the smaller crystal diameter and on the 30% lower equilibrium sorption capacity, was lower by a factor of about 35. It is known that dry grinding may cause a substantial local temperature rise and profound stressing of the surface, so the crushing process may have partially blocked or closed some of the mordenite sorption channels. This suggests that deleterious effects may result from the pelletizing or extrusion processes commonly used in compacting molecular sieves and other powders into pellets. Dry grinding causes more pronounced effects than

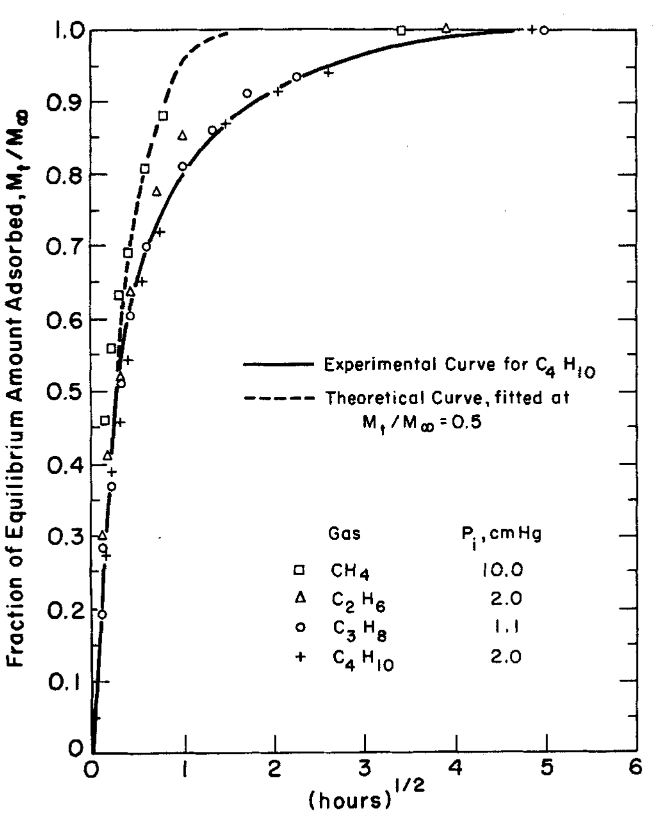

Fig. 9. Sorption rate at longer times for C_1-C_4 hydrocarbons on Na-mordenite; temperature 27°C.

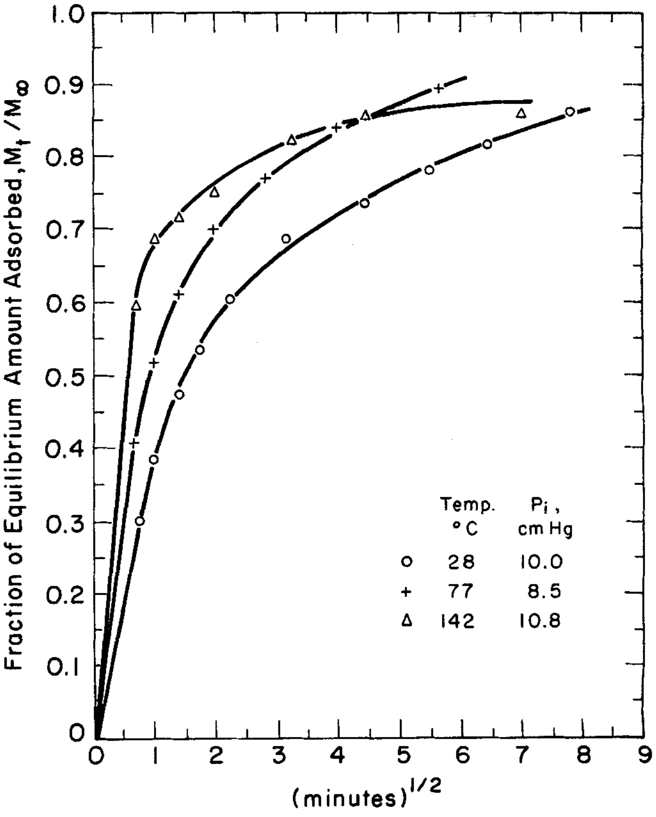

Fig. 10. Effect of temperature on rate of adsorption of ethane in Na-mordenite.

wet grinding and one may speculate that compacting of dry powders into pellets, as is frequently done in laboratory studies, may cause more severe effects than compacting of mixtures containing lubricants or of doughlike mixes. One might also expect that these effects would be more severe when the pore size of powders is only moderately larger than that of the diffusing molecules, as in molecular sieves, in contrast to the larger micropores ordinarily encountered. Habgood (*21*) also reported that diffusivity coefficients for nitrogen and methane in Linde 4A zeolite were substantially higher for the material in crystal form than in the form of extruded pellets (the latter presumably being commercial material). The diffusivities were sufficiently small so that intercrystalline diffusion was not a limiting step in the pellets, but in his case he interpreted the data as being consistent with the presence in his pellets of a nonadsorbing binder which sealed off a part of the crystal surface through which diffusion otherwise occurred. Brandt and Rudloff (*15*, *16*) observed that D_E decreased with decreasing particle diameter in crystals of the naturally occurring zeolite chabazite when they obtained the size reduction by soaking the crystals in water and cooling to −70°C. They postulated that fracture would occur along defects such as cracks and that therefore the smaller (fractured) particles had fewer high diffusivity paths, for example, large pores and cracks, than the larger particles.

Other Models for Diffusion in Mordenite

Much of the variation of the effective diffusion coefficient with experimental conditions comes from fitting data to the simple one-parameter Fick's law relationship, taking the concentration at the outside surface of the crystal to be that in equilibrium with the vapor phase, although it is evident that the process is much more complicated than this simple model implies. Several other sorption rate models were developed (*20*) and the transient sorption rates (and diffusion coefficients) predicted by them were compared with the experimentally observed sorption rates.

Diffusion in zeolites has obvious similarities to surface diffusion, with the difference that in zeolites usually the adsorbed molecule is within the range of significant van der Waals forces on all sides. If the sorption rate is assumed to be only that by surface diffusion within the mordenite tubes (no room is available for gas phase molecules) the surface diffusion coefficient D_s equals D_E. If it were assumed that all mordenite sorption tubes are parallel to the long (33μ) axis, with l_c being the half length of the crystal along this axis, D_s or D_E is given by

$$\frac{M_t}{M_\infty} = \sqrt{\frac{D_s t}{\pi l_c^2}} \quad (t \rightarrow 0) \qquad (3)$$

The surface diffusion coefficient calculated from the present sorption rate data and Equation (3) for ethane at 25°C. is 1.3×10^{-8} sq.cm./sec., a value about 10^4 times lower than that determined by Barrer and Gabor (*8*) for the surface diffusion of ethane on an amorphous alumino-silicate catalyst plug of average pore diameter of 25 Å. We calculate from Barrer and Gabor's data for methane, ethane, and propane that the activation energies for surface diffusion in their study were 2.7, 4.0, and 3.1 kcal./mole, respectively, which are fairly comparable to the values obtained here.

This work began with the thought that single crystals of mordenite, made from highly purified starting materials, might constitute a material having such regularity of pore structure that diffusion studies could be interpreted in a fundamental fashion. The slight alteration of synthesis conditions to change particle size seems, however, to have a marked effect on sorption and diffusion characteristics. The ramifications of this are yet to be explored. On the basis of saturation sorption capacity for butane, the large crystals of Na-mordenite studied by us would seem to be very similar to material studied by Barrer and Peterson, but this is not a very sensitive test and the amounts of material sorbed under conditions corresponding to less than saturation and diffusion characteristics are much more sensitive to variations in crystal structure. Samples of mordenite and other synthetic zeolites probably depart from ideality much more than was thought to be the case a few years ago. This fact and the marked effects of mechanical treatments on their properties have obvious important consequences in technological applications.

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NOTATION

A = surface area of crystal, sq.cm.
D_E = effective diffusion coefficient, sq.cm./sec.
D_s = surface diffusion coefficient, sq.cm./sec.
E_D = apparent activation energy, from $D_E = D_0 e^{-E_D/RT}$, kcal./mole
M_t, M_∞ = amount of adsorbate present in zeolite at time t, and at equilibrium, moles/g.
p = pressure, cm. Hg, p_i for initial pressure
R = gas constant, kcal./(mole) (°C.)
t = time, sec.
T = temperature, °K.
V = volume of crystal, cc.

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