Rates of Sorption and Diffusion of Hydrocarbons in Zeolites

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The kinetic patterns of sorption, desorption, and sorbate exchange have been studied for several C_2-C_5 hydrocarbons in synthetic zeolites of the mordenite, T and Y structures. The rate observations can best be represented by a model of sorption on interstitial sites in the solid, rather than by a model based on the analogy with macroporous sorbents. Two cases of interstitial diffusion have to be distinguished for this purpose. The number of vacant sites changes in time during the process of sorption, whereas it can remain constant if one sorbate is exchanged against another one. Rate measurements for both types of processes are reported and their interrelation is discussed.

Catalytic reactions in zeolite crystals involve sorption and mass transport of reactants and products in the solid. The rates of mass transport must be known in order to understand the kinetics of catalytic reactions in quantitative terms.

The results of several investigations on the rates of sorption and diffusion in various gas-zeolite systems have been published, and the field has been reviewed by Walker, Austin, and Nandi (*1*). Some of these investigations were limited to one particular solid or gas; the case of countercurrent mass transport, which takes place in a catalytic reaction where reactant and product are present, has rarely been considered. The assumption has been made quite generally that the rate of sorption into zeolites follows Fick's law. It is not a priori evident that such a behavior must necessarily be expected on the basis of any reasonable molecular model, consistent with the equilibrium properties of the system.

We have investigated equilibria and rates for the sorption of various gases in a number of zeolite catalysts; the results are reported here as far as they may be of general interest. The rate measurements were tested against appropriate solutions of the diffusion equation. Deviations from this trial solution as well as some general observations will be discussed in terms of molecular models.

The crystal structures of zeolites have been reviewed by Fischer and Meier (*2*). Zeolites of three different structural types have been used in the present study. Mordenite has a pore structure that can be visualized as consisting of parallel noninterconnected elliptical tubes with major and minor free diameters of 7.0 and 5.8 Å., respectively; small side cavities of 3.9 Å. free diameter are located along these main channels.

Zeolite Y has the structure of the mineral faujasite. It contains almost spherical cavities of 12-Å. diameter that are three-dimensionally interconnected through openings of approximately 8 Å. free diameter. Smaller cavities, 7 Å. in diameter, are connected to these large cages through openings of 2.6 Å. diameter.

The structure of the synthetic zeolite T corresponds closely to that of the related minerals offretite and erionite (*3*). It contains cavities of 6 Å. free diameter that are connected through elliptical openings with free diameters of 3.6 and 4.8 Å., respectively.

The above pore dimensions are based on lattice parameters and crystallographic ion radii. They are of the same order of magnitude as the dimensions of sorbed molecules. Molecular dimensions can only be defined in terms of effective cross sections, which depend on the type of experiment under consideration. The crystallographic pore dimensions of zeolites can therefore not be understood in the same sense as the dimensions of macroscopic objects, for example, capillaries whose diameters are large compared to molecular dimensions. Furthermore, the above pore diameters are based on the ideal framework structures, neglecting possible lattice faults and not considering the cations, whose exact lattice positions are in most cases unknown.

EXPERIMENTAL PROCEDURE

The change in the amount of sorbate in the solid was obtained by recording the change of pressure in a constant volume of gas (1.10 liter), which was opened at time zero to a much smaller volume (0.050 liter) containing the zeolite sample as a powder in a thin layer. The pressure difference against a known pressure in a separate volume was measured with 1% accuracy by a capacitance manometer (Granville-Phillips type O3), calibrated in nine ranges from 0.1 to 700 torr pressure difference at full scale. The system was evacuated by a mercury diffusion pump with liquid nitrogen trap; no carrier gases were used. A schematic diagram of the apparatus is shown in Figure 1. During the sorption measurements, the temperature of the sample vessel was controlled by immersion in a mixture of solid carbon dioxide and acetone (−80°C. ± 1°C.) or in a circulating water bath (regulating to ±0.2°C. at temperatures between 20° and 70°C.). The zeolites were loaded with the sorbate in a stepwise procedure; sorption rates and one equilibrium point were obtained in each step, as is schematically illustrated in Figure 2. Since the system consisting of the solid sorbent and the gas of constant volume is closed, the sum of the number of moles of sorbate in the solid (s) plus the number of moles in the gas $\left(p\cdot\frac{V_g}{R^\circ T_g}\right)$ is a constant during each sorption step:

$$s + p\cdot\frac{V_g}{R^\circ T_g} = \text{const.} \tag{1}$$

We have $s_0 = 0$ at the beginning of the first uptake into an empty sorbent; the representative point in the p-s plane will move along a straight line from A_1 until it reaches the isotherm i at B_1, where the system is in equilibrium (Figure 2). The representative point will move from A_2 to B_2 if the procedure is then repeated in the second sorption step with an increased initial pressure and without evacuating the solid. For the desorption process the movement is reversed; the initial states are then

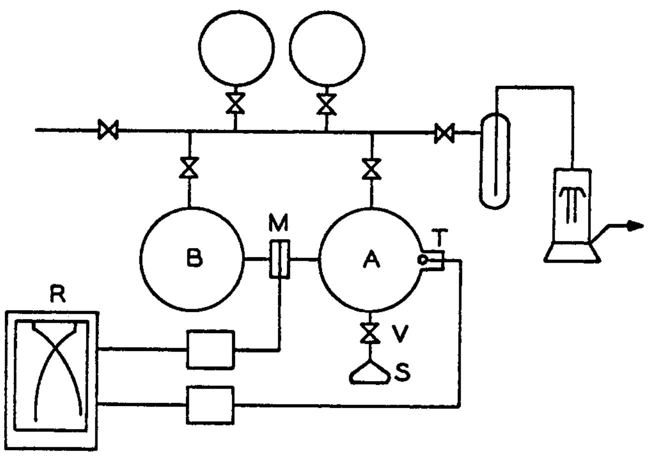

Fig. 1. Schematic diagram of apparatus: *A, B*, vessels of constant volume kept at 25°C.; *M*, membrane capacitance pressure transducer; *S*, sample vessel; *R*, recorder; *T*, thermal conductivity cell; *V*, valve. Auxiliary equipment (mercury manometers for calibration, gas purification system, etc.) is not shown.

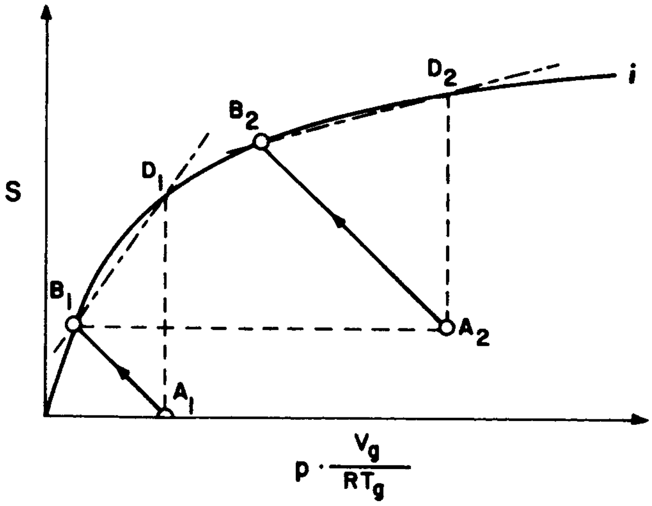

Fig. 2. Schematic representation of two sorption steps in the *p-s* plane.

represented by points above the isotherm. The endpoints B_1, B_2, ... determine the equilibrium isotherm and the recorded movements from A_i to B_i reflect the kinetics of sorption at different levels of saturation. By adjusting the reference pressure toward the end of a sorption experiment and simultaneously increasing the sensitivity of the measuring device, one can obtain an accurate record of the rate of sorption near equilibrium.

The evaluation of this type of kinetic experiment on the basis of the diffusion equation has been worked out by Barrer (*4*). His treatment is equivalent to that of transient diffusion from a well-stirred solution, as described by Berthier (*5*) and Crank (*6*), because the pressure in the gas phase is constant in space but variable with time. The condition at the phase boundary of the solid is given by the material balance and by the equilibrium isotherm, if we assume that the phase boundary (the crystal surface) is in equilibrium with the gas. If I_b is the total flux of sorbate into the solid from the phase boundary (in moles per unit of time), $(c)_b$ the concentration of sorbate in the solid at the phase boundary, and p the pressure in the gas phase, we have

$$\frac{V_g}{R^\circ T_g} \cdot \frac{dp}{dt} + I_b = 0 \tag{2}$$

$$(c)_b = f(p) \tag{3}$$

and obtain as boundary condition

$$\frac{V_g}{R^\circ T_g} \cdot \left(\frac{df(p)}{dp}\right)^{-1} \cdot \frac{d(c)_b}{dt} + I_b = 0 \tag{4}$$

Berthier (*5*) and Crank (*6*) give solutions for the isotherm

$$(c)_b = K \cdot p \tag{5}$$

$$\frac{df(p)}{dp} = K \tag{6}$$

and Barrer (*4*) approximated the isotherm by this form for the present purpose. However, since only the derivative $df(p)/dp$ enters into Equation (4), this approximation can be made for any part of the isotherm, provided the appropriate slope (given by the dash-dotted lines B_i–D_i in Figure 2) is used in the evaluation of each sorption experiment. The kinetic measurements were evaluated on this basis, using Crank's compilation (*6*) and Berthier's tables (*5*). The technique has the advantage that very fast sorption processes can be recorded accurately—the response time of the system was smaller than 0.5 sec. The operating conditions can be so adjusted that the relative pressure change remains quite small.

In addition, the kinetics of desorption were observed at low degrees of saturation by recording the pressure drop between the diffusion pump and the sample as a function of time when this pressure drop was smaller than 10^{-2} torr and proportional to the flow rate of gas being desorbed from the solid.

The rates of exchange of one sorbate originally in the solid against another one from the gas were measured in the same apparatus. The composition of the gas phase was then monitored by its thermal conductivity with a thermistor bridge and continuously recorded together with the pressure. Because the exchange involves necessarily bulk diffusion of both sorbate components in the gas phase, the evaluation of exchange rates is more complicated. The solution for the corresponding problem of heat conduction, as given by Carlslaw and Jaeger (*7*), was adapted to describe the system. The bulk diffusion in the gas phase was studied separately by measuring the rate of condensation of carbon dioxide from binary mixtures with nitrogen or helium, while the bottom of the vessel, which normally contains the zeolite, was cooled with liquid nitrogen. A characteristic length (formally equivalent to a boundary-layer thickness) can be calculated from the rate of this process and from the diffusivity in the gas phase. This quantity must be known to calculate the binary diffusivity in the solid from the observed rate of exchange. The exchange experiments were restricted to pressures below 8 torr, where the diffusivity in the gas phase is relatively high; the values of diffusion coefficients in the gas phase were estimated. The resulting binary diffusivities in the solid can only indicate the correct order of magnitude, since the evaluation must be based on several subsidiary measurements and estimates. The following synthetic zeolite materials were used:

Designation	Composition (dry)	Structure	Approximate crystal diameter, μm.
HMo	$H_{0.94}Na_{0.06}AlO_2(SiO_2)_{6.4}$	Mordenite	2 to 5
NH_4Y	$(NH_4)_{0.94}Na_{0.06}AlO_2(SiO_2)_{2.86}$	Y	1
NH_4KT	$(NH_4)_{0.75}K_{0.25}AlO_2(SiO_2)_{3.67}$	T	needles, 5 × 0.7
NH_4T	$(NH_4)_{0.95}K_{0.05}AlO_2(SiO_2)_{3.49}$	T	needles, 5 × 0.7

Synthetic hydrogen mordenite was a commercial product from the Norton Company (H-Zeolon); the hydrogen content of this material as given above is based on the aluminum and sodium contents and was not determined by analysis. NH_4Y, NH_4KT, and NH_4T were synthesized in our laboratory and identified by x-ray diffraction. The hydrogen forms of zeolites Y and T (designated as HY, HKT, and HT, respectively) were prepared by calcination of the corresponding ammonium forms in air at 400°C. for 4 hr. Sample weights always refer to the dry materials. All zeolites were first degassed at 360°C. for at least 5 hr. until the static pressure in the system was smaller than 10^{-4} torr.

The gases used were obtained from the Mathieson Company. Carbon dioxide was instrument grade; the other gases were C.P. grade; pentane supplied from Chemicals Procurement Laboratories was 99% pure. All sorbates were stripped from permanent impurities by condensation at −195°C. and evacuation to 10^{-3} torr.

EXPERIMENTAL RESULTS

Validity of Fick's Law

Tentatively assuming that the rate of sorption is controlled by diffusion in the solid, one can evaluate a time constant

$$\tau = \frac{R^2}{D} \tag{7}$$

from the rate of sorption; the length R characterizes the size of the crystals. This time constant can be computed from the observed kinetics for different degrees of advancement of the uptake within each sorption step and for different regions of the degree of saturation (θ) as one proceeds from one sorption step to the next. The time constant τ should be constant, independent of the degree of advancement of the process within each step, independent of the degree of saturation (θ), and independent of the direction of the flow (that is equal in sorption and desorption), if the following assumptions are correct:

1. The diffusion equation (Fick's law)

$$\frac{\partial c}{\partial t} = D \operatorname{div} \operatorname{grad} c \tag{8}$$

describes the variation of the concentration of the sorbate in the solid (c), D being a constant.

2. The sorbate in the solid is always in equilibrium with the gas at the phase boundary.

3. The zeolite crystals are of the same size and shape.

Table 1 shows as an example the time constants τ that were obtained in two series of sorption and desorption experiments with ethane at -80°C. in HY and HMo. The time constants were evaluated for three degrees of advancement within each sorption step (70%, 90%, and from the relaxation time of final approach to equilibrium). Spherical geometry was assumed in the case of HY and linear geometry for HMo in consideration of the structure; however, the choice of the geometry is not critical for the resulting pattern of τ. In the first two columns, the initial and final degrees of saturation are given for each step. In a sorption experiment the final degree of saturation (θ_f) is larger than the initial degree of saturation (θ_0); the reverse is the case for desorption. The time constants listed in the last lines for either system were thus obtained in desorption.

Two different patterns of the dependence of R^2/D on the degree of advancement of the uptake and on the degree of saturation are apparent in Table 1. In the case of sorption into HY, 15 values of τ were observed in this particular series of experiments. These values fluctuate around the mean of 450 sec. with a r.m.s. deviation of ±25%. The time constant is nearly independent of the degree of equilibration (the average for the columns are 370 sec. ±14%, 490 sec. ±32%, and 490 sec. ±14%), independent of the degree of saturation (the averages for the rows are 400, 500, 490, 500, 380 sec., respectively) and not substantially different in desorption (610 sec. ± 15%). The pattern of time constants observed in an analogous series of experiments with HMo is quite different. Here the coefficient R^2/D increases by an order of magnitude within each step as the system approaches equilibrium. In this case the kinetics of sorption can no longer be described by the diffusion equation, not even with a concentration-dependent diffusion coefficient, since R^2/D evidently does not depend on concentration (θ), but rather on the degree of advancement (or time) within each step. Furthermore, in this system the time constant depends on the direction of the flux. The value observed in desorption is about twice the value observed in sorption, whereas D must be a scalar quantity.

The results shown in Table 1, as well as those discussed below, were reproduced repeatedly with fresh zeolite samples. The r.m.s. deviation of the time constant τ for a given system, temperature, degree of saturation, and degree of advancement was found to be typically ±15% for values of τ that were greater than 30 sec.

Deviations from the diffusion equation were also observed in other systems, although they were not always as pronounced as in the case C_2H_6/HMo. For example, the sorption of n-pentane in HKT can still be described by the diffusion equation, although with certain limitations. Figure 3 shows the observed rate of sorption for this system; the degree of saturation went from $\theta_0 = 0$ to $\theta_f = 1$, and the initial pressure was sufficient to keep the boundary condition constant ($\theta_b = 1$) in this experiment. The uptake follows the diffusion equation for cylindrical geometry rather closely up to $\theta \approx 0.8$; later on, the rate is significantly slower. This result may be compared with the rate data for the stepwise sorption shown in Table 2. The first three columns of R^2/D in Table 2 (for $\Delta s/\Delta s_f = 0.5$, 0.7, and 0.9, respectively) indicate that the time constant increases monotonically with θ, equivalent to a monotonous decrease of D with concentration. The values of R^2/D in the last column were calculated from the relaxation time for the final approach to equilibrium, involving 1 to 3% of the uptake. They do not fall into the pattern of time constants characterizing the rate for at least 90% of the sorption.

Table 1. Time Constants R^2/D for Sorption and Desorption of C_2H_6 in HY and Hydrogen-Mordenite at -80°C.

C_2H_6 in	θ_0	θ_f	$\Delta s/\Delta s_f =$	0.7	0.9	→ 1
HY	0	0.29	$\frac{R^2}{D} =$ (sec.)	300	365	530
(-80°C.)	0.29	0.54		400	490	600
	0.54	0.71		415	570	480
	0.71	0.80		430	700	370
	0.80	0.84		310	340	490
	0.84	0.71				650
	0.71	0.56				680
		0				510
HMo	0.22	0.54		≤12	43	150
(-80°C.)	0.54	0.75		≤12	38	150
	0.75	0.84		16	52	135
	0.87	0.77			118	230

Table 2. Sorption of n-Pentane into HKT at 25°C.

θ_0	θ_f	$\Delta s/\Delta s_f =$	0.5	= 0.7	0.9	1
0.00	0.28	$R^2/D =$ (sec.)	175	280	330	8×10^3
0.28	0.55		465	610	650	6×10^3
0.55	0.77		850	910	1,500	4×10^3
0.77	0.85		1,150	1,980	2,400	4×10^3

The value of $R^2/D = 465$ sec., obtained from the rate for the initial 80% of the integral sorption (shown in Figure 3), represents evidently an average over the values of R^2/D at different levels of concentration. It is well known and has been emphasized by several authors (for example, *6*, *8*, *9*) that the form of the integrated diffusion equation, especially the initial part, which is always linear in the square root of time, is insensitive to a variation of D with concentration. The rate behavior in the stepwise sorption procedure is thus consistent with the kinetics of the integral process.

The equilibrium isotherms for the systems considered here are shown in Figure 4. The S-shaped isotherm for C_2H_6 in HY indicates attractive interactions between sorbed molecules.

The same type of rate behavior as described for C_5H_{12} in HKT was also observed for several other systems (C_2 to C_5 hydrocarbons in T and Y zeolites). Deviations from the diffusion equation were generally more pronounced for hydrocarbons in mordenites, in a way similar to the pattern described for C_2H_6 in HMo. The spread in the values of R^2/D was dependent on the sorbate (wider for C_3 and C_4 than for C_2H_6) and seemed to be too large to be explained by a spread in crystal size of the zeolites alone.

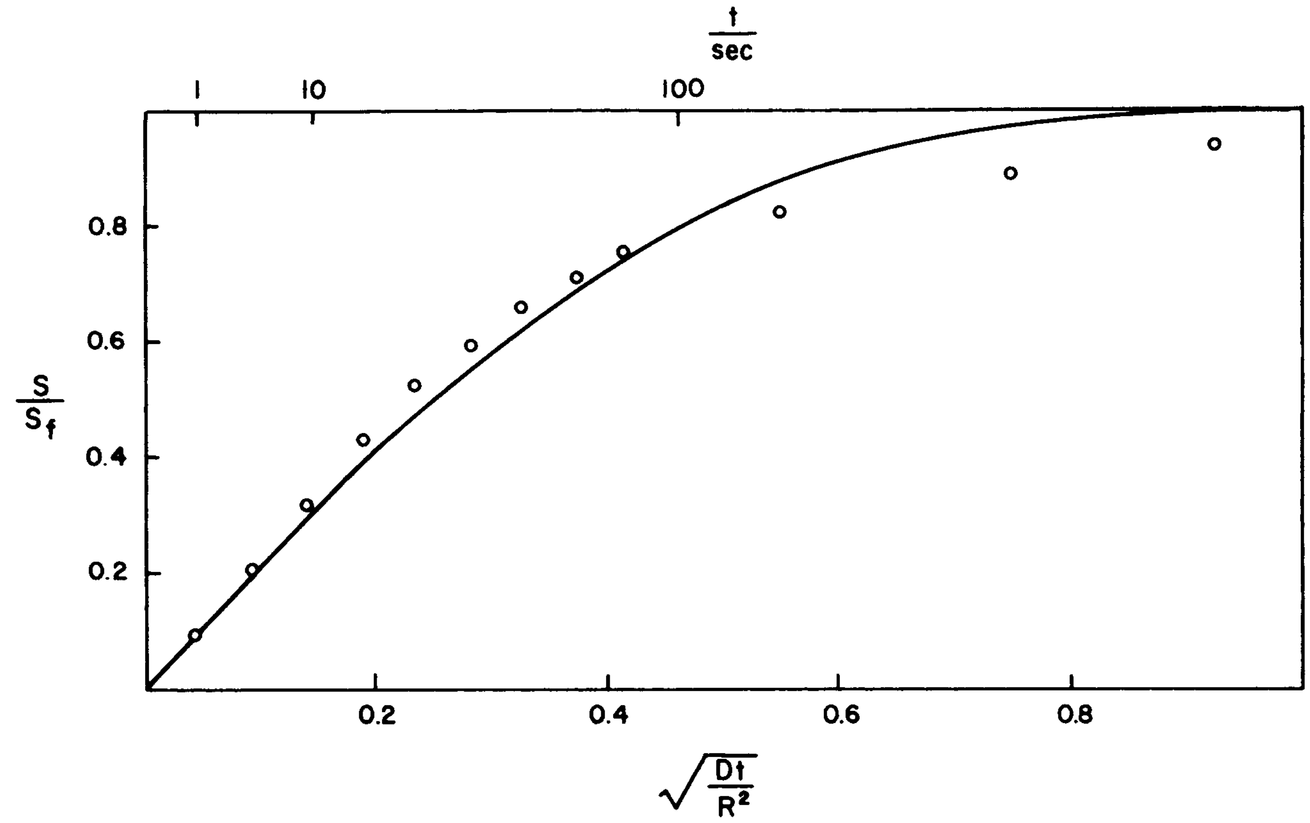

Fig. 3. Curve: Transient diffusion into a cylinder of infinite length and radius R for constant boundary condition and constant D. Points: Sorption of n-C_5H_{12} into HKT at 25°C.; $\theta_0 = 0$; $\theta_f \approx 1$; plotted against dimensionless time with $R^2/D = 465$ sec. The time scale in seconds for this experiment is indicated on the top of the figure.

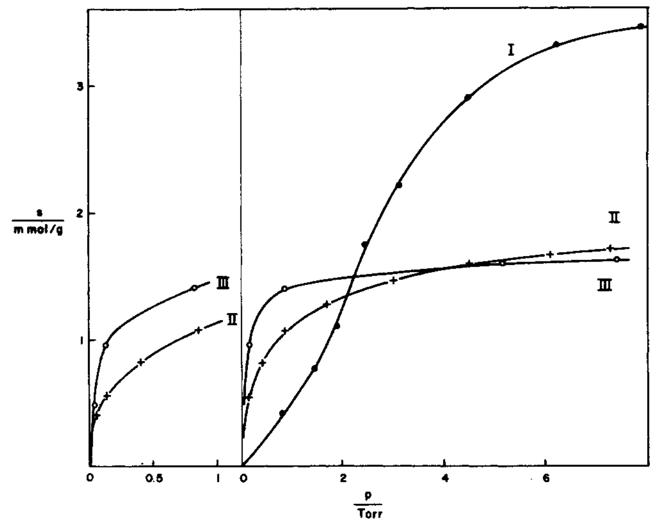

Fig. 4. Equilibrium isotherms: *I*: C_2H_6 in HY at −80°C.; *II*: C_2H_6 in HMo at −80°C.; *III*: n-C_5H_{12} in HKT at 25°C.

Discrepancies between observed sorption rates in zeolites and the behavior expected on the basis of Fick's law have been reported or are apparent throughout the pertinent literature. Different diffusion coefficients were observed in sorption and desorption for C_2H_6 in Na mordenite by Satterfield and Frabetti (*10*).

Temperature Dependence of Sorption Rates

The temperature dependence of the coefficient R^2/D, evaluated from the rates of integral sorption experiments, is shown in Figure 5 for the system n-pentane/HKT. The

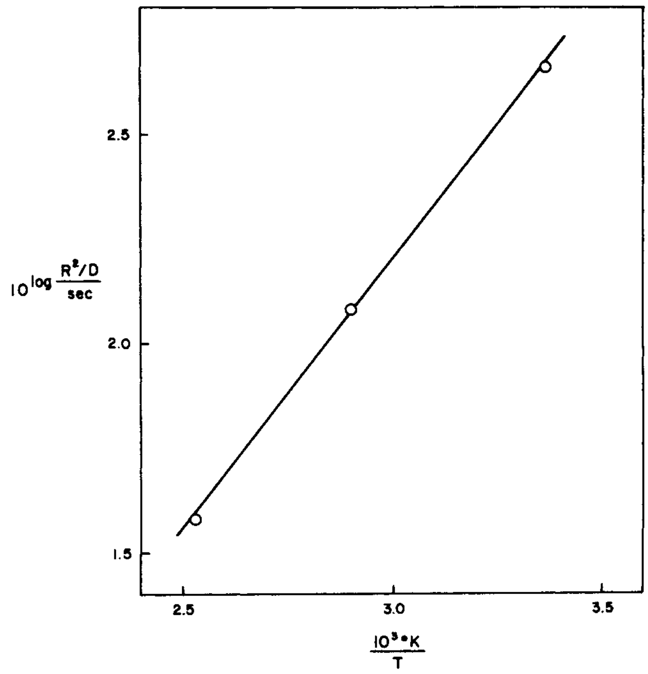

Fig. 5. Temperature dependence of the coefficient R^2/D, characterizing the rate of sorption of n-C_5H_{12} in HKT.

diffusion coefficient follows Arrhenius' law with an activation energy of $q_D = 5.9$ kcal./mole. The heat of sorption of n-pentane in HKT was obtained from the temperature dependence of the equilibrium isotherm and was found to be $(\Delta H_S)_{0.1} = -12.6$ kcal./mole at $\theta = 0.1$ and $(\Delta H_S)_{0.8} = -8.8$

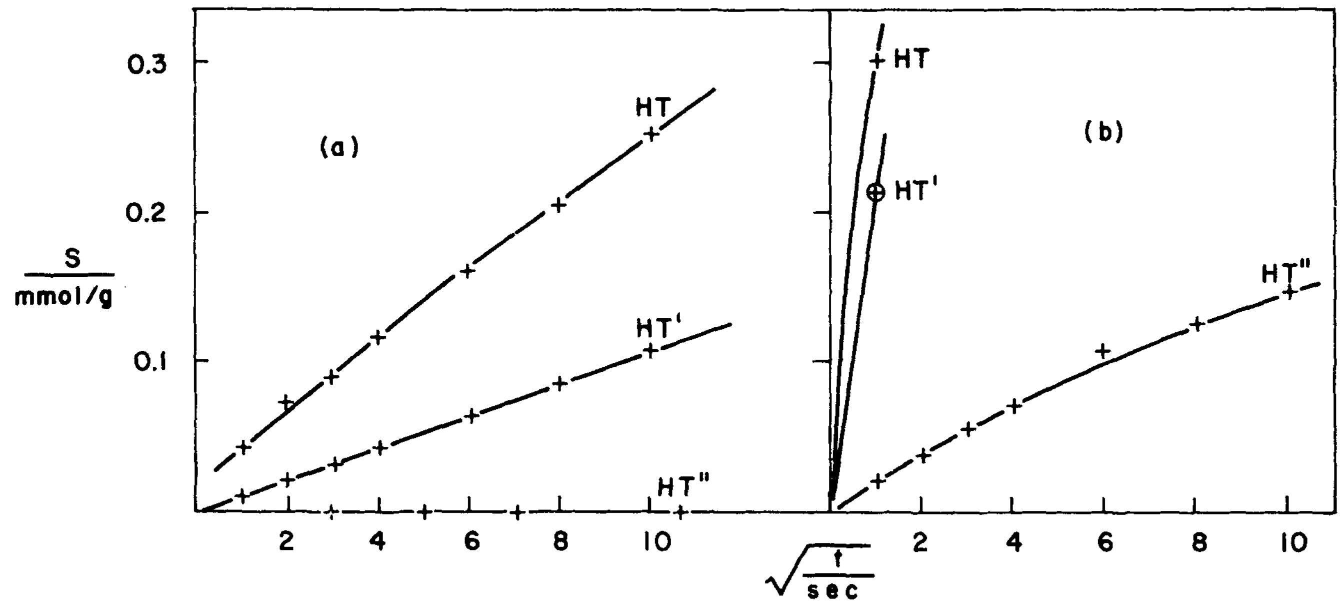

Fig. 6. Kinetics of sorption of (a) *n*-butane and (b) trans(2)butene into different preparations of HT at 25°C.; $\theta_0 = 0$.

kcal./mole at $\theta = 0.8$. The activation energy of diffusion (q_D) is substantially smaller than the value of the heat of sorption A similar result was obtained for C_2H_4 in NaY ($q_D = 5.8$ kcal./mole; $(\Delta H_S)_{0.1} = -8.5$ kcal./mole). Several other authors (*10* to *12*) have also observed that for sorption in zeolites the values of the heats of sorption are significantly different from the activation energies of diffusion.

Dependence of the Sorption Rate on the Nature of the Sorbate and the Pretreatment of the Solid

The initial rates of sorption of *n*-butane and trans(2)-butene at 25°C. and equal pressure ($p_0 = 7.5$ torr) into different preparations of HT are shown in Figure 6. Zeolite HT was obtained through calcination of NH_4T at 400°C; HT′ was then derived from HT by calcining this material 15 hr. at 565°C., and HT″ by calcining HT at 800°C. for the same length of time. The calcinations were carried out in air and the solids were brought to the calcination temperature at a rate of approximately 5°C./min. The sorption capacities of HT and HT″ were 2.2 and 1.0 mmole trans-butene per gram, respectively, at 25°C. The rates of sorption depend critically on the calcination temperature and is generally much smaller for *n*-butane than for transbutene. Diffusion coefficients characterizing the initial sorption rate were calculated from these and similar experiments with C_3H_8 and C_2H_6. They are listed in Table 3; a uniform crystal radius of $R = 3.5 \cdot 10^{-5}$ cm. was assumed. No simple correlation between the sorption rates, on the one hand, and the molecular size or molecular weight, on the other, is apparent from the coefficients in Table 3.

TABLE 3. DIFFUSION COEFFICIENTS CHARACTERIZING THE INITIAL RATE OF SORPTION IN DIFFERENT PREPARATIONS OF HT

Sorbent		Sorbate (°C.) C_2H_6 (−80)	C_3H_8 (25)	*n*-C_4H_{10} (25)	trans-C_4H_8 (25)
HT	D, sq. cm./sec. =	2×10^{-10}		6×10^{-13}	$\geq 5 \times 10^{-10}$
HT′				10^{-13}	2×10^{-10}
HT″		3×10^{-10}	5×10^{-15}	$\leq 5 \times 10^{-16}$	10^{-11}

Rates of Exchange of One Sorbate Against Another One

The rates of exchange of C_2H_6 in the zeolite against carbon dioxide from the gas phase and vice versa—involving a countercurrent migration of different substances in the solid—were measured in HT and HMo. The results of such an experiment with HT (calcined at 700°C.) are shown in Figure 7. On the left of this figure, the observed composition of the gas phase, characterized by the partial pressures of C_2H_6 and CO_2, is plotted against time. The zeolite was initially loaded with 2.19 mmoles of carbon dioxide per gram and with no C_2H_6; at the end of the experiment the solid contained 1.74 mmoles of carbon dioxide per gram and 0.38 mmoles C_2H_6 per gram. The sum of the number of sorbate molecules in the solid was thus approximately constant, as was the total pressure in the closed system. On the right of Figure 7, the advancement of the C_2H_6 uptake is plotted on a logarithmic time scale for this experiment (curve I) and for the sorption of pure C_2H_6 under the same conditions of temperature and pressure, but with no carbon dioxide in the system (curve II). The sorption of pure C_2H_6 into the partially empty sorbent is roughly 20 to 30 times faster than the exchange process. However, the rate of exchange is influenced by the binary diffusion in the gas phase. A quantitative evaluation of this and a similar experiment, taking into account the resistance due to diffusion in the gas phase as outlined in the description of experimental procedure, yielded the time constants R^2/D_{AB} for the binary diffusion in the solid that are listed in the last column of Table 4. The time constants R^2/D, characterizing the rates of sorption of the pure sorbates into the same solid at approximately the same degree of saturation ($\theta = 0.7$ to 0.9), were found to be at −80°C.:

$$R^2/D_{CO_2} = 500 \text{ sec. } \pm 20\%$$
$$R^2/D_{C_2H_6} = 800 \text{ sec. } \pm 30\%$$

TABLE 4. EXCHANGE OF CARBON DIOXIDE AND C_2H_6 IN HT AT −80°C.

Initial condition sorbate(1)	$(\theta_1)_0$	Gas(2)	Final loading $(\theta_1)_f$	$(\theta_2)_f$	$(\theta_1 + \theta_2)_f$	R^2/D_{AB}, sec.
C_2H_6	0.87	CO_2	0.72	0.15	0.87	6×10^3
CO_2	0.85	C_2H_6	0.67	0.22	0.89	8×10^3

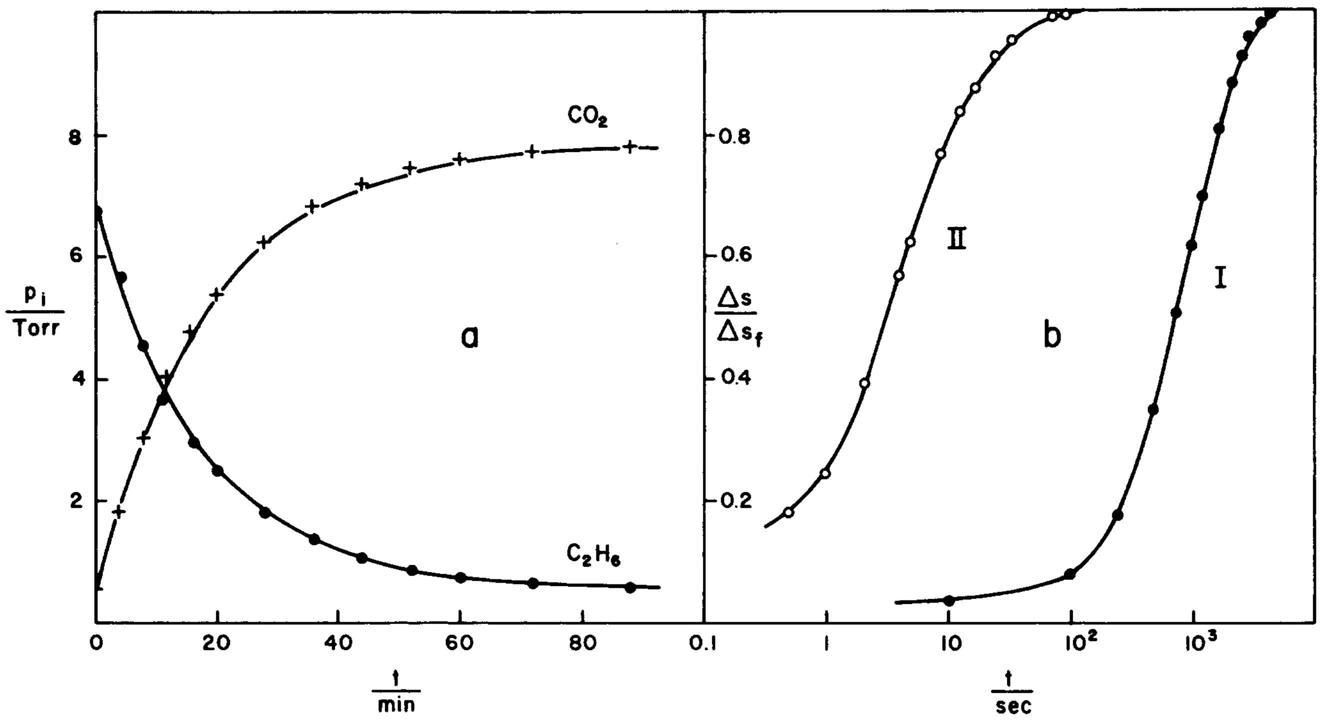

Fig. 7. Kinetics of exchange of C_2H_6 from the gas phase against carbon dioxide sorbed in HT at −80°C.: (*a*) time dependence of partial pressures; (*b*) kinetics of C_2H_6 uptake in exchange against carbon dioxide (*curve I*) and C_2H_6 uptake into partially empty zeolite (*curve II*) on a logarithmic time scale.

The binary diffusion coefficient (D_{AB}), characterizing the rate of exchange in the solid, is thus roughly one order of magnitude smaller than the diffusion coefficients (D_i), characterizing the rates of sorption into the partially empty sorbent. These results and similar observations with HMo demonstrate that a countercurrent migration of different sorbed substances is possible in both zeolites.

The rate of sorbate exchange in zeolites has also been investigated by Barrer and Fender (*13*), who studied the replacement of D_2O against H_2O in large crystals of chabazite, gmelinite, and heulandite. They found that the binary diffusion coefficient D_{AB} in the solid is related to the diffusion coefficient D, characterizing the rate of sorption of H_2O or D_2O by the expression

$$D_{AB} = D\left(\frac{d\ln\theta}{d\ln p}\right)_{eq} \qquad (9)^*$$

This expression is tantamount to

$$D_{AB} = D(1-\theta) \qquad (10)$$

because the factor $\left(\frac{d\ln\theta}{d\ln p}\right)_{eq}$ is derived from the equilibrium isotherm, and Barrer and Fender (*12*) also observed that the Langmuir isotherm is approximately valid for these systems.

DISCUSSION

In order to rationalize the observed rate phenomena, we will consider two models, representing the migration of sorbed molecules into or out of a zeolite crystal.

In the first model, one visualizes the sorbent as consisting of a large number of capillary pores and cavities, which are wide enough so that gas molecules in the pores coexist with adsorbed molecules on the pore walls. By definition, the gas molecules are not under the influence of significant forces due to the particles of the solid lattice; their potential energy is independent of position, as long as they are not adsorbed on the pore walls. The sorption or desorption process can then be described as bulk or Knudsen diffusion, coupled with adsorption and desorption at the walls. This model of a porous sorbent has been treated by Weisz (*9*) in a very general way. He has shown that in such a system the sorption rate is always characterized by an apparent diffusivity, which is the product of the diffusivity of the gas, the ratio of the number of mobile (gaslike) particles to the total number of sorbed molecules in the sorbent at equilibrium, and geometric factors. The model implies therefore that the apparent diffusivity is nearly temperature independent if the sorption proceeds to saturation, and that it shows an activation energy equal to the value of the heat of sorption at small degrees of saturation. The observed temperature dependence of sorption rates and sorption equilibria in zeolites does not agree with this expectation. It also seems difficult to imagine a gaslike movement of sorbed molecules through the crystal at constant potential energy, because the sizes of the periodically spaced restrictions in the zeolite structures are of the same order of magnitude as the gas collision cross sections of the sorbed particles. The sorbed molecules are therefore necessarily under the influence of significant attractive forces due to the particles of the zeolite lattice, at least when they pass through openings between larger cavities. The potential energy of a molecule migrating through a zeolite crystal cannot then be constant, but it will vary in space with the periodicity of the lattice structure.

The model of the macroporous solid has been mentioned here because it should be considered as a limiting case, and because it seems to fit the terminology of "adsorption on an internal surface," which is frequently used in this field. It must be remembered that in this terminology the

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*Equation (9) is formally similar to a relation between the diffusivity in a binary substitution alloy and the average of the tracer diffusivities of its components, which was derived by Darken (*14*). The assumptions underlying Darken's derivation do not apply to the present case.

terms surface and adsorption do not have the usual physical significance, which is related to the existence of a phase boundary. In the present paper, the term surface is used exclusively to denote a macroscopic phase boundary between solid and gas. An internal phase boundary cannot be defined, and it has been pointed out by Gibbs (*15*) that the macroscopic concepts of surface, capillary, etc., are not meaningful in pores of molecular dimensions.

We have a different situation, leading to the alternate model, if we drop the assumption that the sorbate can exist in a gaslike state in the zeolite. In the simplest case, we will then have an array of equivalent sorption sites in the lattice, each site accommodating one sorbate molecule. The equilibrium positions (interstitial sites) of the sorbed molecules are separated by potential energy barriers, as illustrated schematically in Figure 8. A sorbate particle can jump to a vacant adjacent site by surmounting the energy barrier; a random movement of sorbed molecules in the lattice is thus possible. This type of interstitial migration must be distinguished from the migration of a component of the lattice due to its thermal disorder, which is commonly described as interstitial diffusion, for example, the diffusion of Ag^+ in Ag-halides. Whereas the concentration of interstitial ions in an ionic crystal depends primarily on temperature and is always very small, the concentration of guest molecules on interstitial positions in a zeolite can be rather large, does not depend on lattice disorder, and varies in space and time as sorption or desorption proceed.

We can derive rate equations describing the migration of sorbate particles on interstitial sites for two distinct types of processes. On the one hand we have sorption or desorption, where the degree of occupancy of sites changes in time and space (case α); on the other hand we have the exchange of one sorbate against another one, where the degree of occupancy can be constant (case β). A sorbate particle will jump to a nearest neighbor sorption site with an average frequency $z\nu$, if all z neighboring sites are empty and with an average frequency ν to any particular nearest neighbor site where z is the coordination number of the sites. The frequency ν will depend int. al. on the energy barrier q and on the temperature. The average jumping frequency will be reduced to $z\nu\theta$ if the fraction θ of nearest neighbor sites is occupied.

In case α, the sorbate consists of a single component (Figure 9*a*). If n_1 is the number of particles in plane 1 (which is perpendicular to the x direction), n_2 the number of particles in the parallel plane 2, and m the number of sites in either plane, then the net flow $\dot{n}$ from plane 1 into plane 2 per unit of time will be

$$\dot{n} = n_1\left(1 - \frac{n_2}{m}\right)\nu - n_2\left(1 - \frac{n_1}{m}\right)\nu = \nu(n_1 - n_2) \qquad (11)$$

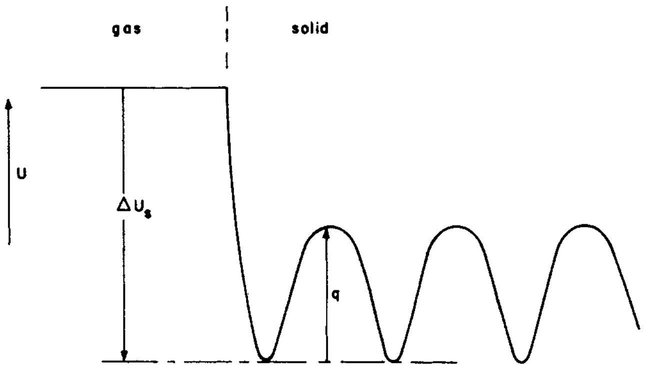

Fig. 8. Potential energy diagram for sorbed molecules on interstitial sites (schematic).

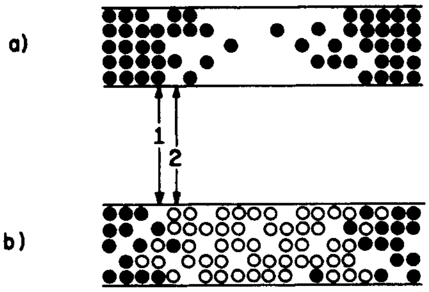

Fig. 9. Schematic representation of interstitial diffusion: (*a*) sorption of one component into an empty sorbent; (*b*) exchange of sorbate *A*(○) against sorbate *B*(●).

In this expression it has been assumed for simplicity that there are two nearest neighbor sites in the x axis. If A is the area of the planes considered, and δ is the distance between sites, then the concentration would be $c = n/\delta A$, and we obtain

$$n_1 - n_2 = -A\delta\,\frac{\partial c}{\partial x}\cdot\delta \qquad (12)$$

$$\frac{\dot{n}}{A} = I = -\nu\delta^2\,\frac{\partial c}{\partial x} = -D\cdot\frac{\partial c}{\partial x} \qquad (13)$$

Although the average jumping frequency $\overline{\nu}$ of the particles is now

$$\overline{\nu} = z\nu(1 - n/m) = z\nu(1 - \theta) \qquad (14)$$

and decreases with increasing saturation, this effect cancels out in the expression for the net flux. The result is Fick's law, Equation (8), with a diffusion coefficient

$$D = \nu\delta^2 \qquad (15)$$

independent of concentration. Essentially the same conclusion was reached by Barrer and Jost (*16*), who considered this type of interstitial diffusion from a thermodynamic viewpoint. The derivation given here demonstrates that the flux of a single component on interstitial sorption sites should not depend on the coordination number of the sites. The resulting Equations (13) and (15) would be unaffected if the sorbate could migrate only along very varrow channels—the coordination number of the sites being then $z = 2$—except that the diffusion would be anisotropic. The kinetics should also be the same if the sorption sites can accommodate more than one sorbate molecule.

The situation would be different, however, in case β, where two distinguishable species A and B, characterized by equal ν and occupying the same sites, are present. No gradient in the sum of the concentrations exists, but we have opposite and numerically equal gradients in concentration for either species. There will be no net flow of particles, since $(c_A + c_B)$ is constant in space and time, but there can be opposite equal fluxes of both species. Under these conditions of equal mobility for both components, the rate of binary diffusion must be equal to the rate of self-diffusion for either pure component at the same total concentration. The average jumping frequency $\overline{\nu}$ of any particle would be

$$\overline{\nu} = z\nu(1 - \theta) \qquad (16)$$

If the spatial distribution of sites permits a random movement in two or three dimensions (the coordination number of the sites being greater than 2), then an elementary counting procedure (Figure 9*b*) yields for the flux of either component in the x direction

$$I_j = \frac{\dot{n}_j}{A} = -\frac{\bar{\nu}\delta^2}{z} \cdot \frac{\partial c_j}{\partial x} = -D_{AB} \cdot \frac{\partial c_j}{\partial x} \tag{17}$$

Here the coefficient D_{AB} of binary diffusion for distinguishable but otherwise equivalent particles will depend on the total concentration; that is, on the degree of saturation

$$D_{AB} = \nu(1-\theta)\delta^2 = D(1-\theta) \tag{18}$$

The exchange can only proceed by a mechanism of single-file diffusion (*17*) if the coordination number of sorption sites is 2. The coefficient of binary diffusion would in this case be smaller than D_{AB} in Equation (18), as has been shown by Rickert (*18*).

A linear relation between the mean-square displacement $\overline{(\Delta x)^2}$ of a particle and the time t

$$\overline{(\Delta x)^2} = 2D_E t \tag{19}$$

is obtained, if one considers a random movement of particles (*19*). But this relation holds only if the probabilities of displacement are the same for all particles and are constant in time and space. For the system discussed here, Equation (19) will only be valid for binary interstitial diffusion (case β) with $D_E = D_{AB}$, if all particles perform the same random movement everywhere. Equation (19) would not be valid in case α, because the degree of occupancy, and therefore also the mobility of the sorbed particles, depends on time and position, contrary to the assumptions leading to Equation (19). Fick's law, Equations (8) and (13), however, must be valid in both cases (α and β) under the present assumptions. In case α, the diffusion coefficient D in Fick's law will be independent of concentration, because mobility and driving force depend both on concentration and their influences cancel in the resulting expression for D. In case β, the diffusion coefficient D_{AB} will be proportional to $(1-\theta)$.

The model of sorption on interstitial sites represents a number of experimental rate observations correctly:

1. The diffusion in the solid is activated, as must be expected, since the frequency ν will be temperature dependent

$$\nu = \nu_0 e^{-q/RT} \tag{20}$$

The activation energy q and the heat of sorption ΔH_s are not related, nor can any simple relation between ν and the molecular weight or size be expected.

2. The particles enter or leave the force field of the solid at the phase boundary. The activation energy for the transfer through the phase boundary must be higher in desorption than in sorption (Figure 8). If the transfer through the phase boundary limits the rate of desorption, the crystal surface being not in equilibrium with the gas, then the time constants characterizing the rates of sorption and desorption will be different.

3. The diffusion coefficient characterizing the rate of exchange (D_{AB}) is smaller than the diffusion coefficient characterizing the rate of sorption [Equation (18)].

In another respect, this model appears to be less satisfactory. It requires that the diffusion coefficient characterizing the rate of sorption is constant and independent of the degree of saturation, whereas in reality it seems to be the exception rather than the rule that this condition is fulfilled. However, the model of interstitial diffusion as discussed above was based on the assumption that only one type of energetically equivalent sorption sites exists in the solid. This assumption may be an oversimplification for many systems. The crystal structures of the zeolites are rather complicated; frequently the sorption isotherms appear to be a superposition of several Langmuir isotherms, as has to be expected for a sorbent containing different types of sites (*20*). This is also the case for the isotherms of C_2H_6 in HMo and C_5H_{12} in HKT shown in Figure 4. In the general case there will be several different frequencies ν_{ij} (or jumping probabilities) for the migration from a site of type i to a neighboring site of type j. If the degrees of occupancy θ_i of sites of different types i vary in space and time, then the assumption of random motion will no longer be true and deviations from Fick's law must be expected, as is best illustrated by an example.

Let us assume that we have two types of sites (Index 1 and 2) in the solid and therefore four frequencies (ν_{11}, ν_{12}, ν_{21}, ν_{22}) characterizing the probabilities of migration. Let us further assume that the sorbate can only migrate along channels that contain sites of type 1 ($\nu_{11} \neq 0$) and have pockets containing sites of type 2, so that sorbate particles cannot move from one pocket to another ($\nu_{22} = 0$). The sorbate is transported through the lattice by migration via type 1 sites and locally distributed between type 1 and type 2 sites. Two extreme cases can be visualized:

a. The migration along the channels is rate determining, that is

$$\nu_{11} \ll \nu_{12}; \quad \nu_{11} \ll \nu_{21}$$

Equilibrium between types 1 and 2 sites is then always established locally; the local concentration c_1 of particles on sites of type 1 is a function of the total concentration c and temperature only.

$$c_1 = f(c)$$

The flux (I) of sorbate molecules per unit cross section is proportional to the gradient of c_1; an apparent diffusivity results, which will be a function of concentration:

$$I = -D_1 \text{ grad } c_1 = -D_{\text{app}} \text{ grad } c \tag{21}$$

$$D_{\text{app}} = D_1 \cdot \frac{dc_1}{dc} \tag{22}$$

This situation is formally equivalent to the case of local equilibrium in a macroporous solid, as treated by Weisz (*9*). It would become identical with this case if particles on sites of type 1 could be considered as free gas molecules in a long pore. There is thus a continuous transition from the model of interstitial sites to the model of a macroporous solid. In contrast to the situation in macroporous solids, either type of site can be characterized by a lower free energy and thus be saturated first. The apparent diffusivity can, therefore, increase or decrease with total concentration, as has been observed by Tiselius (*11*).

b. The alternate extreme case will be encountered if

$$\nu_{11} \gg \nu_{12}$$

which is a priori as likely as the reverse condition. In this case, there can be no local equilibrium unless the whole system is in equilibrium. Again we have, for the flux of sorbate molecules

$$I = -D_1 \text{ grad } c_1 \tag{23}$$

But now c_1 is not a unique function of total concentration, dependent also on time, since c_1 and c_2 are not in equilibrium. Mathematical models corresponding to this situation have been developed by Wilson (*21*) and Danckwerts (*22*). The sorption process will then consist of two stages: diffusion of sorbate particles occupying sites of type 1 will be followed by a subsequent establishment of equilibrium between sites of types 1 and 2. Both processes will be uncoupled, and the rapid initial uptake will be followed by a slow first-order process, if the frequencies are sufficiently different. During the second stage the local transfer of sorbate from sites of type 1 to sites of type 2—not the diffusion—will be rate controlling. In this case, the kinetics of sorption cannot be described by Fick's law in a meaningful way (for example, C_2H_6 in HMo).

The different patterns of sorption kinetics that have been observed with zeolites thus can be understood, at least in principle. Deviations from the ideal laws of random diffusion—documented by a variation of the observable time constant τ—have to be expected if there are different sorption sites in the solid, which are not equivalent. It is of course recognized that additional complications can arise from an inhomogeneity of the sorbent, for example, if there is a significant spread in particle sizes or if deviations from the ideal lattice structure exist in a fraction of the crystallites. The model of migration in a lattice of different sorption sites can be worked out in more detail. However, the usefulness of further refinements is perhaps limited, as long as one can only determine the quantity R^2/D as an average for many crystals with a certain spread in size and shape.

CONCLUSIONS

Sorption rates of hydrocarbons in zeolites follow different kinetic patterns. Whereas in some systems the observed sorption rates can be rationalized as being controlled by activated diffusion in the solid, the diffusion equation is inadequate to describe the kinetics in other cases.

The observed rates and their temperature dependence are consistent with a model of sorption on interstitial sites in the lattice, the transfer through the phase boundary being followed by a migration onto vacant sorption sites in the solid. This model appears to be more adequate than the analogy with macroporous sorbents.

The concentration of vacant sites changes in space and time when an initially empty sorbent is being loaded; but it can remain constant if one sorbate is exchanged against another one. These two processes have to be distinguished; they are characterized by different but related diffusion coefficients.

A more complicated situation arises if the sorbent contains sites of different types, a condition that prevails in many zeolites. Such a system must not necessarily be in local equilibrium. The rate of the sequential process of migration and local distribution on sorption sites of different types then can no longer be described by only one coefficient.

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NOTATION

A = area of a cross section in the solid, sq. cm.
c = concentration of sorbate in the solid, mole/cc.
D = diffusion coefficient of a pure substance in the solid (sq. cm./sec.), defined by Fick's law, Equation (8)
D_{AB} = diffusion coefficient for countercurrent (binary) diffusion of substances A and B in the solid, defined by Fick's law, Equation (17)
D_E = diffusion coefficient characterizing mean square displacement of particles in the solid, defined by Einstein's Equation (19)
ΔH_s = enthalpy of sorption per mole of sorbate
$(\Delta H_s)_\theta$ = differential enthalpy of sorption at degree of saturation θ
I = flux of sorbate through unit cross-sectional area in the solid, mole/(sq. cm.)(sec.)
I_b = total flux of sorbate from the gas into the solid through the phase boundary solid/gas, mole/sec.
K = slope of equilibrium isotherm as defined by Equations (3) and (6)
n = number of sorbate particles
m = number of sorption sites
p = pressure
q = potential energy barrier
q_D = activation energy of diffusion
R = radius or characteristic length of zeolite crystals
R° = gas constant
s = amount of sorbate in the solid
Δs = change of amount of sorbate in the solid compared to s at the beginning of measurement ($t = 0$)
T = temperature of the solid, °K.
T_g = volume average of temperature of the gas phase, °K.
t = time
V_g = volume of gas phase
x = length coordinate
z = coordination number of sorption sites

Greek Letters

θ = degree of saturation of the sorbent
δ = distance between sorption sites in the solid
ν = frequency of migration of a sorbed particle to one of the adjacent empty sorption sites
ν_0 = value of ν at $T = \infty$
ν_{ij} = frequency of migration of a particle sorbed on a site of type i to an adjacent empty site of type j
τ = time constant of diffusion as defined by Equation (7)

Subscripts

0 = value at the beginning of experiment ($t = 0$)
f = final value at equilibrium
b = value at the phase boundary solid/gas

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