12. Robinson, R. A., and R. H. Stokes, Electrolyte Solutions, Butterworths, London (1965).
13. Bremer, M. F., and E. L. Cussler, *AIChE J.*, **16**, 832 (1970).
14. Seidell, A., Solubilities of Inorganic Compounds, 4th ed., W. F. Linke (ed.), Am. Chem. Soc., Washington (1965).
15. Medley, J. A., and M. W. Andrews, *Textile Res. J.*, **30**, 855 (1960).

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Counterdiffusion of Liquid Hydrocarbons in Type Y Zeolite: Effect of Molecular Size, Molecular Type, and Direction of Diffusion

This paper presents experimental results on the counterdiffusion of liquid hydrocarbons in the Y zeolite as determined by an unsteady state technique using the zeolite powder. The critical diameter of aromatic molecules counterdiffusing with respect to cyclohexane into NaY zeolite has a marked effect upon the counterdiffusion rate. For a given molecular type, the single parameter of critical molecular diameter correlates the size effect well. Molecular type, for example, toluene vs. phenol, also has a pronounced effect on the counterdiffusion rate. Those molecules showing stronger interactions with the zeolite have lower counterdiffusion rates. In both NaY and SK-500, the diffusion coefficients for adsorptive counterdiffusion are an order of magnitude greater than the diffusion coefficients for desorptive counterdiffusion indicating that factors other than simple intracrystalline diffusion as such are also important in zeolite counterdiffusion. Simple diffusion models do not account for the differences observed indicating that a more sophisticated approach is necessary.

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SCOPE

Zeolites play a very important role in the chemical and petroleum industry as both adsorbents and catalysts (Collins, 1968). Adsorbent applications utilize the strong selective adsorption which zeolites often show toward a compound or a class of compounds or the very fine, uniform pore structure which permits the adsorption of molecules smaller than a given critical diameter. Adsorbent applications involve the diffusion of at least one species and often the counterdiffusion of different species within the pore structure, and thus design of adsorption units requires information on diffusion and/or counterdiffusion rates (Roberts and York, 1967; Gehrhardt and Kyle, 1967; Fukunaga et al., 1968). Such information is not generally available, and thus the design of such units remains mainly an empirical art. In catalytic applications since the locus of catalytic activity for many reactions is within the pore structure, the simultaneous counterdiffusion of reactants and products must occur within the structure. The presence of diffusion limitations in zeolite catalysts would reduce the activity observed and for multiple-step reactions could also alter the selectivity. Thus a quantitative understanding of counterdiffusion in zeolites is important to the engineering design of zeolite catalysts and of processes utilizing them.

Very little information is available on counterdiffusion in zeolites. Furthermore, counterdiffusion rates are grossly different from single component unidirectional rates, cannot be estimated from single component rates, and thus must be determined independently (Satterfield and Katzer, 1971). Studies of the counterdiffusion of hydrocarbons in large pore zeolites under practical conditions are necessary to provide an understanding of the important variables affecting it. Such work will probably not immediately result in the development of theoretical models for zeolite

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diffusion because of the complexity of the situation but should provide practical models and correlations which will aid understanding the importance of diffusion in zeolite applications.

This paper reports a study of the counterdiffusion of aromatic hydrocarbons in the Y zeolite. Counterdiffusion rates were measured by a simple liquid-phase, unsteady state technique. The effect of molecular size over a broad range of alkylaromatics, of diffusate-zeolite interactions which were altered by changing the molecular type, and of direction of diffusion upon the counterdiffusion rate was studied. The objectives of the work were to examine the applicability of standard models to zeolite counterdiffusion, to develop practical models and correlations for zeolite counterdiffusion, and to develop a better understanding of the mechanism of the counterdiffusion process.

CONCLUSIONS AND SIGNIFICANCE

The rate of counterdiffusion of hydrocarbons in the Y zeolite pore structure was studied by measuring the rate of desorption of a preadsorbed aromatic hydrocarbon from zeolite single crystals suspended in a second, liquid hydrocarbon (desorptive counterdiffusion) and by measuring the rate of adsorption of a selectively adsorbed solute from solution into solvent saturated zeolite crystals (adsorptive counterdiffusion). An unsteady state technique was used, and NaY and SK-500, an ion exchanged Y, were studied.

The effective diffusion coefficient for the adsorptive counterdiffusion of alkylaromatic hydrocarbons from cyclohexane solution into NaY is an exponential function of the critical molecular diameter of the aromatic and decreases by over four orders of magnitude in going from toluene to 1,3,5-triethyl benzene. The single parameter of critical molecular diameter correlates the size effect well for the aromatic hydrocarbons. Even though the free pore diameter of the Y zeolite is 0.74 nm, molecules having a critical molecular diameter of 0.92 nm still freely counterdiffuse with cyclohexane in the pore structure. This occurs because the three-dimensional, supercage nature of the pore structure allows molecules to pass one another and because the molecules are sufficiently deformable to pass through a pore aperture smaller than its critical molecular diameter. An increase in the strength of the aromatic diffusate-zeolite interaction resulting from changing the species being adsorbed causes a decrease in the adsorptive counterdiffusion coefficient. The effective diffusion coefficient for toluene is over four orders of magnitude larger than that for phenol although their critical molecular diameters are the same. The work establishes correlations of the effect of molecular size and of molecule-zeolite interaction upon the counterdiffusion rate over a wide range of these parameters and under conditions of practical interest. Considerably more such information will be needed before the counterdiffusion coefficient can be predicted for a system chosen at random.

The effective diffusion coefficients for adsorptive counterdiffusion of the selectively adsorbed aromatic are more than an order of magnitude greater than those for desorptive counterdiffusion of this component. Those for the desorptive counterdiffusion of the nonselectively adsorbed component are even less. These differences in the diffusion coefficient with the mode of diffusion should not occur with simple intracrystalline diffusion as such and indicate that the diffusion process is strongly influenced by other factors, probably strong interaction between the zeolite and the diffusate. An adsorption phenomena associated with the more strongly adsorbed species and which produces added resistance to diffusion appears to be responsible for the differences between adsorptive and desorptive counterdiffusion.

Diffusion in zeolites is a type of surface or volume diffusion in which the diffusing molecule can never leave the influence of the pore surface while within the pore structure. Diffusion and counterdiffusion in zeolites is affected by a larger number of variables than is normal surface diffusion and is very markedly affected by several of these, for example, steric and interaction effects between diffusate and zeolite, and between counterdiffusing molecules. Satterfield and Katzer (1971) have shown that the rate of counterdiffusion of aromatic hydrocarbons in Y zeolite is strongly affected by the nature of the counterdiffusing species, whereas Whang (1961) has shown that ethylene and ethane, and ethylene and isobutane counterdiffuse independent of one another on the surface of Vycor glass. Habgood (1958) found for diffusion in NaA (effective pore diam. $\cong 0.4$ nm) that the diffusion coefficient for N_2 (kinetic diam. $= 0.37$ nm) is about 20 times that for methane (kinetic diam. $= 0.39$ nm).

Barrer (1949) observed a linear relationship between the activation energy for diffusion and the diffusate radius for permanent gases diffusing in K-mordenite. The rate of diffusion and of counterdiffusion of liquid aromatic hydrocarbons in the Y zeolite has been shown by Satterfield and Cheng (1971; Cheng, 1970) and Satterfield and Katzer (1971, Katzer, 1969), respectively to be highly dependent upon the critical diameter of the molecules involved. Satterfield and Cheng (1971; Cheng, 1970), and Barrer and Brook (1953) have shown that the diffusion rate of a series of compounds of similar size and shape in type Y and natural chabazite respectively show a strong dependence on the strength of molecule-zeolite interactions as determined by the type of molecule involved. A systematic study of the effect of molecular size and type has not been carried out nor has a truly satisfactory model for zeolite diffusion been developed. Because of the commercial importance of zeolites as adsorbents and catalysts and because of the important role which diffusion may play in such applications, it is desirable to understand and to be able to quantitatively describe the diffusion process in zeolites.

This work was directed toward determining the effect of molecular size over a broad range of molecular diameters for molecules of the same type, of the strength of molecule-zeolite interactions, and of the direction of diffusion upon the counterdiffusion rate. The suitability of several simple diffusion models was also investigated.

CHARACTERIZATION OF MATERIALS USED

Zeolites

NaY and SK-500, a rare earth-ammonium exchanged Y zeolite, were used. The SK-500 (Lot No. 12979-17) was supplied in the uncalcined powder form by the Linde Division of Union Carbide and was used in the powder form after activation. A mixture of rare earth cations which was predominantly lanthanum and low in cerium was used by Linde in the exchange. The calculated unit cell formula for the SK-500 is

$$\overset{+3}{\mathrm{Re}}_{8.8}\,\overset{+}{(\mathrm{NH_4})}_{21.1}\,\overset{+}{\mathrm{Na}}_{8.3}\,[(\mathrm{AlO}_2^-)_{55.7}\,(\mathrm{SiO}_2)_{136.3}]\cdot\mathrm{ZH_2O}$$

The NaY used for the adsorptive-desorptive counterdiffusion studies (Lot Number 12, 119-69) had a calculated unit cell formula of

$$\mathrm{Na}_{57}\,[(\mathrm{AlO}_2^-\overset{+}{)}_{57}\,(\mathrm{SiO}_2)_{135}]\cdot\mathrm{ZH_2O}.$$

That used for the studies of the effect of molecular size and type (Lot Number 3607-67) was very similar in composition.

The zeolite was sieved through a 28-mesh screen to remove lumps and agglomerates which might not have broken up easily under vigorous stirring in the diffusion run. The NaY (Lot Number 12, 119-69) was highly crystalline before and after activation (Katzer, 1969). Hydrocarbon saturation values for all zeolites in this study are indicative of highly crystalline material and are in accord with previously reported values (Katzer, 1969; Satterfield and Cheng, 1971; Breck and Flanigen, 1968). All zeolites were given a standard air activation (described below), and all calculations are based on the dry weight of the zeolite. The particle size distribution of the zeolite was quite narrow, and the NaY and SK-500 had essentially the same particle size and particle size distribution. The mean diameter of the zeolite particles was 1.10 μm.

Hydrocarbons

The organic compounds used were all examined for impurities by gas chromatography prior to their use, and choice of source of the organic compound, discrimination between batches of the same organic, and even choice of the organic compound itself was based on purity to reduce as much as possible the effects of impurities on the counterdiffusion rate. Impurities have been shown to affect the counterdiffusion rate (Katzer, 1969; Cheng, 1970). All liquid organics were stored in the dark over freshly activated, 13X zeolite pellets until used. Table 1 gives the purity of all organics used as determined by chromatographic analysis.

EXPERIMENTAL PROCEDURE

The zeolite in the form of single crystals was first activated by heating at a rate of 0.5°K/min. from 323 to 773° under a stream of predried air. The zeolite powder was placed as a bed less than 10 mm deep in a pyrex activation tube which was inserted horizontally in a muffle furnace. The furnace was held at 773°K for an additional three hours. The activation tube containing the activated zeolite was then removed, cooled, sealed, and evacuated. Greaseless, high-vacuum, o-ring sealed ground joints and stopcocks were used to avoid contamination of the zeolite.

For desorptive counterdiffusion the zeolite was first saturated with one hydrocarbon and then placed in a second, liquid hydrocarbon to determine the counterdiffusion rate. For benzene and cumene the zeolite was saturated from the vapor phase by equilibrating with the degassed, liquid hydrocarbon which was held a few degrees below the temperature of the zeolite bed. This produced essentially complete saturation of the zeolite pore structure without inducing capillary condensation in the bed. The saturation time was 5 hours for benzene and 17 hours for cumene. For 1-methyl naphthalene (1-MN), which has a relatively low vapor pressure, an amount of 1-MN slightly greater than that required to insure saturation of the pore structure was added to a small tube connected at a right angle to the activation tube. The activation tube was evacuated and the 1-MN thoroughly degassed. The 1-MN was then poured into and mixed with the zeolite in the tube, and the evacuated tube was equilibrated at 319°K for 3 and 5 hours respectively for SK-500 and NaY. Saturation was by direct contact and vapor-phase transfer since the tube was evacuated, and complete saturation was indicated. For adsorptive counterdiffusion the zeolite was not presaturated with a hydrocarbon but was placed directly in the liquid hydrocarbon in the diffusion flask and allowed to become saturated.

Table 1. Purity and Critical Molecular Diameter of Organic Compounds Studied

Organic compound	Purity, mole %	Critical molecular diam., nm
Benzene	99.98	0.675
Toluene	99.89	0.675
Phenol	≅100.0 (No impurities detected)	0.675
1,4-Dimethyl benzene (*p*-xylene)	99.97	0.675
1,3-Dimethyl benzene (*m*-xylene)	99.996 (Matheson) 99.9994 (Chem. Samples Co.)	0.74
Isopropyl benzene (Cumene)	99.95	0.675
1,3-Diethyl benzene	99.80	0.74
1,3-Diisopropyl benzene	99.96	0.74
1,3,5-Trimethyl benzene (Mesitylene)	≅100.0 (No impurities detected)	0.84
1,3,5-Triethyl benzene	99.96	0.92
Naphthalene	≅100.0 (No impurities detected)	0.74
1-Methyl naphthalene	99.38	0.79
1-Ethyl naphthalene	99.94	0.79
2-Ethyl naphthalene	99.99	0.74
Cyclohexane	99.74 (Chromato-quality) 99.03 (Matheson)	0.69

The counterdiffusion runs were carried out in an apparatus consisting of a stirred, 500 ml Morton flask in a constant temperature bath (± 0.05°K). For desorptive counterdiffusion, at $t = 0$ the presaturated zeolite was placed in the vigorously stirred flask which already contained a known quantity of the second hydrocarbon. Samples of about 1 ml each were removed at predetermined time intervals using a hypodermic syringe and needle, and the zeolite in the sample was immediately separated from the mixture by forcing it through a Millipore filtering unit attached to the syringe. Precautions were taken to insure that each sample was representative (Katzer, 1969). The hydrocarbon phase was analyzed by gas chromatography giving a direct measure of the amount of preadsorbed hydrocarbon which had diffused out at the time of the sample.

For adsorptive counterdiffusion the activated, unsaturated zeolite was placed in the liquid hydrocarbon in the stirred flask and was allowed to completely equilibrate by stirring for one-half hour. Then at $t = 0$ a known quantity of the second hydrocarbon was added to the stirred flask. Samples were removed at predetermined intervals and treated as described previously. This gave directly the rate of adsorptive counterdiffusion of the second hydrocarbon into the zeolite. For runs which did not reach equilibrium in four days the zeolite-hydrocarbon mixture was placed in a one-neck flask with a ground joint and equilibrated at the run temperature until equilibrium was reached. Those organics which are solids at room temperature were first dissolved in cyclohexane (the hydrocarbon in the flask) and were added in solution form. For appreciable adsorptive counterdiffusion to occur in the hydrocarbon being adsorbed from solution into the saturated zeolite must be strongly preferentially adsorbed over the bulk-phase hydrocarbon.

The counterdiffusion process was modeled according to Fick's law in spherical geometry for the component whose diffusion rate was measured. Spherical geometry is most appropriate because diffusion occurs in three dimensions in the Y zeolite, and the individual particles are compact, many-sided polyhedra which are best approximated by a sphere (Katzer, 1969). The solution to the unsteady state diffusion equation with the proper initial and boundary conditions is given by Crank (1956), Carman and Haul (1954), and Rudolff (1965). The data were fit to the solution, and point values of the effective diffusion coefficient D_{eff} were determined for $M_t/M_\infty \rightarrow 0.0$ and $= 0.60$. Details are given by Moore (1971) or Katzer (1969). The word "effective" will be dropped in the remainder of this paper in discussing diffusion coefficients.

RESULTS AND DISCUSSION

Effect of Molecular Size

The effect of molecular size on the counterdiffusion rate was determined from studies of the adsorptive counterdiffusion of a series of aromatic hydrocarbons with varying molecular dimensions. NaY (Lot No. 3607-67), 298°K, and cyclohexane as the bulk-phase hydrocarbon were used in all runs. Cyclohexane was used because its size and shape are similar to those of the aromatic molecules studied and because aromatic compounds are strongly preferentially adsorbed by the zeolite relative to cyclohexane resulting in large fractional uptakes of the aromatic and thus increased accuracy. Fractional uptake is the fraction of aromatic added which is adsorbed by the zeolite. The average variation in the diffusion coefficient between repeat runs was about 15%. The two cyclohexanes investigated gave practically the same results.

Dimensions of the organic molecules studied were determined by drawing each molecule to scale using bond lengths, bond angles, and Van der Waals radii given in the literature (Pauling, 1960; Sutton, 1958; Weast, 1968). The critical molecular diameter, the diameter of the smallest circle through which the molecule can freely pass, was the principal molecular parameter determined. These values are listed in Table 1. Critical molecular diameters ranged from 0.675 for benzene to 0.92 nm for 1,3,5-triethyl benzene. Other methods of determination of molecular size or the use of slightly different constants would give slightly different values but the relative order would remain the same.

Even though the crystallographically defined free pore diameter of the Y zeolite is 0.74 nm, molecules having a critical molecular diameter of 0.92 nm freely counterdiffuse with cyclohexane in the pore structure. This occurs because the pore structure is three-dimensional in nature consisting of supercages interconnected by pore apertures and because the molecules involved are sufficiently deformable to pass through a pore aperture smaller than its critical molecular diameter. This free counterdiffusion behavior is to be contrasted with the behavior of a one-dimensional pore structure such as the mordenite pore structure in which molecules as large as these cannot counterdiffuse since in doing so they must pass one another in the tubular pore and are not able to do so (Katzer, 1969; Satterfield et al., 1971).

The counterdiffusion rate is a very strong function of the critical diameter of the molecule being adsorbed as shown in Figure 1. The diffusion coefficient and rate decrease by over four orders of magnitude as the critical molecular diameter increases from 0.675 to 0.92 nm. Figure 1 also shows that the diffusion coefficient correlates well as an exponential function of critical molecular diameter. The diffusion coefficient for $M_t/M_\infty \rightarrow 0$ and $= 0.60$ are included on the figure. The diffusion coefficient usually decreases somewhat with approach to equilibrium due to a particle size distribution in the zeolite crystals and due to nonideal diffusion behavior (Satterfield and Katzer, 1971; Katzer, 1969). For very rapid rates only the value at $M_t/M_\infty = 0.60$ could be accurately determined, and thus this value only is given. The shaded area in Figure 1 outlines the region in which most of the data fall. For a given molecular type the data are best correlated by the single parameter of critical molecular diameter. Other molecular size parameters as maximum molecular diameter or the average of the critical diameter and the maximum diameter do not give satisfactory correlations of the diffusion coefficient. Other factors are present and are responsible for the deviations from the correlation. The diffusants which have a critical molecular diameter of 0.74 nm have diffusion coefficients which span three orders of magnitude. Similarly the diffusion coefficient for phenol, which has the same critical molecular diameter as toluene is four orders of magnitude below that of toluene. This behavior results from differences in the strength of the diffusate-zeolite interactions and will be discussed below.

The effect of molecular size upon the diffusion rate as observed for counterdiffusion is very similar to the effect observed for single component unidirectional diffusion of permanent gases and hydrocarbons in zeolites (Habgood, 1958; Nelson and Walker, 1961; Barrer, 1949; Brandt and

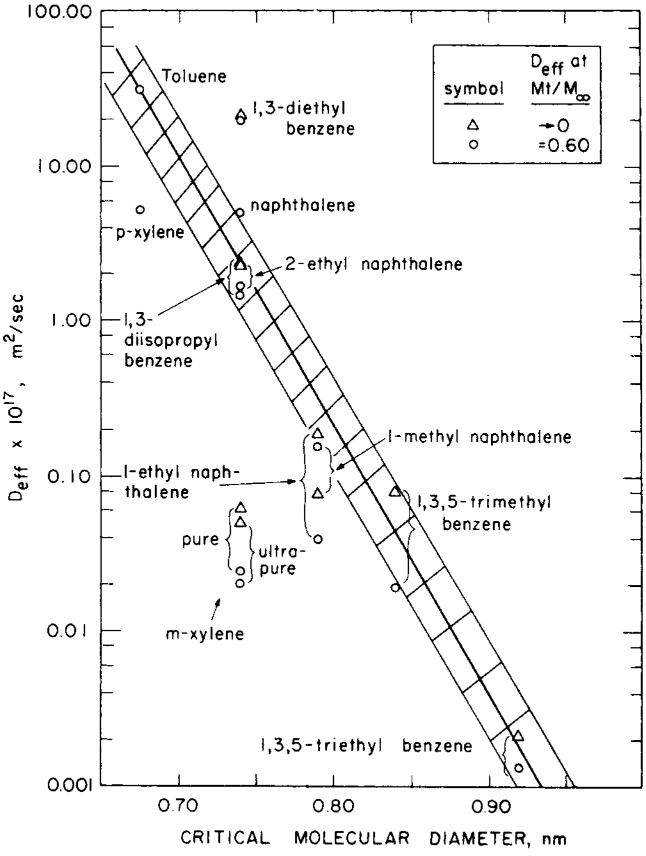

Fig. 1. Dependence of effective diffusion coefficient on critical diameter of diffusate, adsorptive counterdiffusion into cyclohexane saturated NaY at 298°K.

Rudloff, 1964; Satterfield and Cheng, 1971). Figure 2 shows that previously reported data is also correlated well as ln (D_{eff}) vs. ($d_{\mathrm{pore}} - d_{\mathrm{mol}}$). Although most of the studies contain insufficient data to justify a linear relationship, in all cases the slope of the lines drawn through the points is quite high and remarkably similar considering the differences in the systems represented. The value for cumene, $> 700 \times 10^{-17}$ m²/s, from the results of Satterfield and Cheng (1971) for adsorption of cyclic hydrocarbons into empty Y zeolite lies above the figure and below the extrapolated line through the other points. This could be because the value is inaccurate due to the rapid rate or because the slope of the line through the data is decreasing with smaller diameter molecules. Careful examination of Figure 2 indicates that a curved line may be warranted for some of the data. A decrease in the slope should occur as the critical diameter of the diffusate becomes small relative to the pore aperature. Figure 2 also shows that the molecular size effect for desorptive counterdiffusion (Satterfield and Katzer, 1971) is the same as that for adsorptive counterdiffusion.

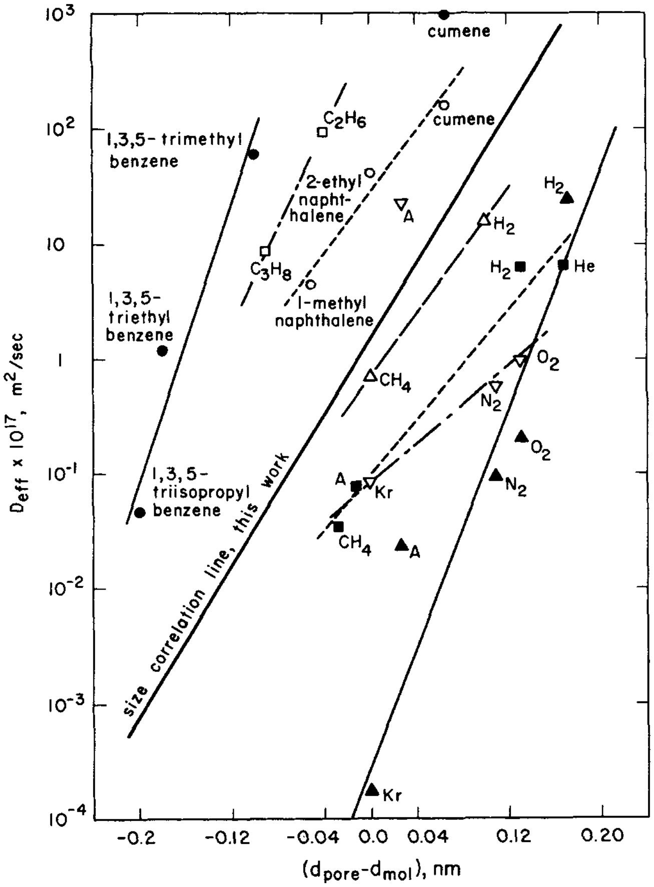

Fig. 2. Dependence of effective diffusion coefficient on critical molecular diameter-correlation of previous data.

○ SK-500, desorptive counterdiffusion into cumene, 281°K (Katzer, 1969).

● NaY, single component adsorption, 303°K (Cheng, 1970).

□ NaA, single component desorption, 523°K (Nelson and Walker, 1961).

△ NaA, single component adsorption, 273°K (Habgood, 1958).

■ Chabazite, single component adsorption, 323°K, D_{eff} multiplied by 10^{-9}, then plotted (Rudloff, 1965).

▲ K-mordenite, single component adsorption, 195°K, $d_{pore} = 0.41$ nm assumed, D_{eff} multiplied by 10^{+1}, then plotted (Barrer and Brook, 1953).

▽ K-mordenite, single component adsorption, 291°K, $d_{pore} = 0.41$ nm assumed (Barrer and Brook, 1953).

The diffusate molecule as it moves from one cage to another in diffusing through the pore structure passes through pore apertures which have approximately the same diameter as the diffusate. This situation is best modeled as diffusion across periodic high energy barriers which are considered to be the pore aperture (Katzer, 1969). When the critical diameter of the diffusate approaches or is larger than the pore aperture, there is overlap of the electron clouds and/or deformation of the molecule in passing through the pore aperture. The energy barrier which a molecule must cross in passing through the pore aperture should be expressible in terms of a potential function in which the repulsive term is dominant, for example, for the Lennard-Jones potential function $E_p = \sum_{i=1}^{12} b r_i^{-12}$ where only the interaction with the 12-member oxygen ring is considered. Substitution of this for E in the Arrhenius form of the diffusion coefficient yields $D_{\mathrm{eff}} = D_0 \exp - [E_p/RT]$. If D_0 is constant, this yields an exponential dependence on molecular diameter as was observed experimentally. Comparison with experiment would indicate that E_p is linearly dependent on critical molecular diameter as observed by Barrer (1949) for diffusion in mordenite. A more detailed analysis of E_p was not within the scope of this work.

In summary the effective diffusion coefficient is a strong exponential function of the critical molecular diameter, ($d_{\mathrm{pore}} - d_{\mathrm{mol}}$), of the diffusate when the critical molecular diameter is similar to that of the pore aperture, and for molecules of similar type and shape the relationship is essentially linear over a wide range of diffusion coefficients.

Effect of Diffusate-Zeolite Interactions

The strength of interaction between the diffusate and the zeolite markedly affects the rate of counterdiffusion. The strength of the aromatic diffusate-zeolite interaction is indicated by the degree of preferential adsorption of the aromatic over cyclohexane by the zeolite and is expressed in this work as fractional uptake, defined as the fraction of aromatic hydrocarbon added which is adsorbed by the zeolite. Fractional uptake is a direct measure of the strength of the aromatic diffusate-zeolite interaction if the ratio of zeolite to organics added is held constant in all runs as was done here. Larger fractional uptakes indicates stronger interactions.

The diffusion coefficient for *m*-xylene is almost two orders of magnitude below that indicated by the correlation in Figure 1. Meta-xylene is more strongly adsorbed, 90% fractional uptake, than the other compact hydrocarbons whose diffusion coefficients fall near the correlation line and which have fractional uptakes of 65 to 80%. The diffusion coefficients for repeat runs with the standard *m*-xylene and with ultra-pure *m*-xylene were the same within experimental error (Figure 1 and Table 1) indicating that this difference was not due to impurities. Phenol, a different type of molecule, has the same critical diameter as toluene or *p*-xylene but exhibits a diffusion coefficient which is four orders of magnitude below that for toluene. The fractional uptake for phenol is 94% compared with 78% for toluene. Phenol is much more strongly preferentially adsorbed, interacts more strongly with the zeolite, and diffuses much more slowly, having a rate similar to that of 1,3,5-triethyl benzene. The strong interaction of phenol is independently predictable because it has not only the π-electrons of the aromatic ring which interact with the cations of the zeolite but the polar —OH group which also shows strong specific interactions with the cations (Kiselev and Lopatkin, 1968; Satterfield and Cheng, 1971; Katzer, 1969).

The correlation between strength of interaction and diffusion coefficient is shown in Figure 3. The solid points on

Figure 3 are for those molecules with a 0.74 nm critical diameter, and the solid line is drawn to give a best fit for these compounds. The wide spread which occurred for these compounds in Figure 1 is well correlated in terms of fractional uptake which is a measure of the strength of the aromatic-zeolite interaction. The reason for the apparent positive deviation of naphthalene is not clear but may result from the fact that the molecular diameter of naphthalene is fixed, whereas for the substituted benzenes rotation of the ethyl or isopropyl groups result in a larger molecular diameter. The resulting distribution of diameters larger than the critical one could result in a lower diffusion rate for these compounds compared with naphthalene. The open points (Figure 3) are for those molecules with a critical diameter of 0.675 nm, and the dashed line indicates the trend which exists for them. The inclusion of phenol on this figure clearly indicates the large effect that diffusate-zeolite interactions have on the diffusion rate. The location of the lines again illustrates the molecular size effect.

Clearly strong interactions between the diffusate and the zeolite slow the counterdiffusion process. Barrer and Brook (1953) have illustrated the presence of this effect for the diffusion of a series of similar sized organics in natural chabazite. Satterfield and Cheng (1971; Cheng, 1970) have observed similar behavior for the single-component adsorptive diffusion of pure hydrocarbons into NaY and two forms of HY having different degrees of ion exchange. Table 2 summarizes their findings. The 1,3,5-triisopropyl cyclohexane molecule is slightly larger than the 1,3,5-triisopropyl benzene molecule but diffuses more rapidly. Its rate does not vary significantly between the sodium and hydrogen forms, whereas that for 1,3,5-triisopropyl benzene changes markedly. The 1,3,5-triisopropyl cyclohexane has no π-electrons and does not interact specifically with the cations in the structure. Similarly the —OH group on phenol adds to the interaction with the cation and causes a slower rate. In the sodium form the cations in type II sites, of which there are 32 per unit cell are positioned such that they can interact specifically with adsorbed molecules (Breck, 1964). Such interaction is evidenced by the substantially higher heat of adsorption of benzene and cumene on NaY than HY (Tuang et al., 1967; Khudiev et al., 1968) and the significantly higher heat of adsorption of benzene over cyclohexane on NaY and CaY (Klaychko et al., 1967).

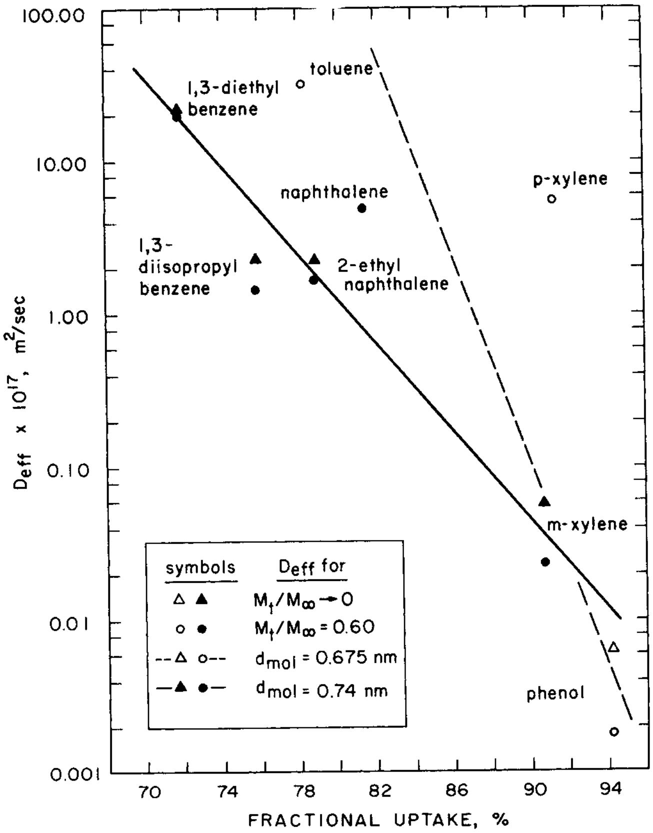

Fig. 3. Dependence of effective diffusion coefficient on strength of diffusate-zeolite interaction as indicated by fractional uptake.

TABLE 2. UNIDIRECTIONAL DIFFUSION OF HYDROCARBONS INTO THE Y ZEOLITE (Cheng, 1970)

Compound diffusing into zeolite	Temp., °C	$D_{eff} \times 10^{17}$, m²/s, at $M_t/M_\infty \rightarrow 0$ NaY	HY(I)*	HY(II)†
1,3,5-Trimethyl benzene	0	13	>100	—
1,3,5-Triisopropyl benzene	30	0.047	3.2	9.3
1,3,5-Triisopropyl cyclohexane	30	4.9	3.2	8.7

* HY(I): 75% ion exchanged to hydrogen, remainder sodium.
† HY(II): 97.7% ion exchanged to hydrogen, remainder sodium.

Effect of Direction of Diffusion

Adsorptive counterdiffusion and desorptive counterdiffusion were studied to define more clearly the modeling and mechanism of counterdiffusion. These studies involved the benzene-cumene-NaY and cumene-1-MN-SK-500 systems. For the desorptive counterdiffusion of 1-MN from SK-500 into cumene at 281°K the diffusion coefficients are 4.07 and 2.60 × 10^{-17} m²/s at $M_t/M_\infty \rightarrow 0$ and $= 0.60$ respectively for this work, and 4.30 and 3.07 × 10^{-17} m²/s at $M_t/M_\infty \rightarrow 0$ and $= 0.60$ respectively for work reported previously (Katzer, 1969; Satterfield and Katzer, 1970). The variation between the studies is within the run-to-run variation in this work which is about 15%. The SK-500 used here is a different batch from that used previously but was very similar in chemical composition. The hydrocarbons were of comparable purity. The diffusion coefficients for cumene desorptive counterdiffusion from NaY into benzene determined in this work were slightly higher on the average than those reported earlier (Satterfield and Katzer, 1971). This was probably because the activation procedure was changed between the two studies.

Table 3 summarizes the adsorptive and desorptive counterdiffusion results for the cumene-1-MN-SK-500 and cumene-1-MN-NaY systems. The diffusion coefficients at $M_t/M_\infty \rightarrow 0$ and $= 0.60$, and the time required to reach $M_t/M_\infty = 0.60$ are given. The amount of zeolite and bulk-phase organic used was the same for all runs, and the amount of 1-MN added to the zeolite for 1-MN adsorptive counterdiffusion was equal for all runs. For desorptive counterdiffusion approximately 74% of the 1-MN desorbed and for adsorptive counterdiffusion approximately 24% of the 1-MN added was adsorbed. The rate of 1-MN adsorptive counterdiffusion into SK-500 at and above 298°K is too rapid for accurate measurement.

In all cases the diffusion coefficients for adsorptive counterdiffusion are at least an order of magnitude greater than those for desorptive counterdiffusion (Table 3). The total amount of 1-MN diffusing into the zeolite for adsorptive counterdiffusion is about one-third of the amount diffusing out of the zeolite for desorptive counterdiffusion; and because the total concentration change in the zeolite is less

Table 3. Effective Diffusion Coefficient for Adsorptive and Desorptive Counterdiffusion of 1-Methyl Naphthalene in SK-500 and NaY*

Zeolite	Direction of 1-Methyl naphthalene diffusion	Temp., °C	$D_{eff} \times 10^{17}$, m²/s $M_t/M_\infty \rightarrow 0$	$M_t/M_\infty = 0.6$	Time to $M_t/M_\infty = 0.6$, min.
SK-500	ADS	−15	5.7	2.1	6.6
SK-500	DES	−17	0.43	0.14	91.0
SK-500	ADS	0	46.0	16.0	0.55
SK-500	DES	0	0.98	0.84	17.0
SK-500	ADS	8	—	32.0	0.38
SK-500	DES	8	4.2	2.4	6.0
SK-500	DES	25	28.0	25.0	0.67
NaY	ADS	25	8.3	—	1.9
NaY	DES	25	2.0	1.4	8.1

* Cumene was counterdiffusing species in all cases.

for adsorptive than for desorptive counterdiffusion, the concentration gradients at any fractional approach to equilibrium should be less for adsorptive than for desorptive counterdiffusion. However the absolute rate of diffusion (grams of organic per gram zeolite per unit time) is greater for the adsorptive than for the desorptive process even though the concentration driving force is less. For example at 273°K the absolute rate of desorptive counterdiffusion for the initial portion of the run in grams of 1-MN per gram zeolite per minute is 0.065 for adsorptive counterdiffusion and 0.034 for desorptive counterdiffusion. The diffusion coefficients differ by much more than do the absolute rates of diffusion because they reflect the differences in both the diffusion rate and the concentration gradient or driving force. For adsorptive counterdiffusion the diffusion rate is higher, and the concentration gradient or driving force is lower than for desorptive counterdiffusion resulting in a much higher value for the diffusion coefficient.

Similar behavior was observed but not studied by Katzer (1969). He attributed the difference in diffusion coefficients to added resistance in the desorptive counterdiffusion mode due to strongly adsorbed species in the 1-MN saturated SK-500. The presence of strongly adsorbed species was indicated by the red-violet color of the saturated zeolite and the presence of radical ions (Katzer, 1969; Neikam, 1971). For adsorptive counterdiffusion such species were not present, formed slowly, and thus could not hinder diffusion. Katzer (1969) also found that the rate and diffusion coefficients for cumene desorption from SK-500 into 1-MN were smaller than the respective values for 1-MN adsorptive or desorptive counterdiffusion. The diffusion coefficient for cumene desorptive counterdiffusion at 281°K is 1.74×10^{-17} m²/s at $M_t/M_\infty \rightarrow 0$. Very similar behavior was observed for the benzene-cumene-NaY system which will be discussed next.

Table 4 summarizes the results for the benzene-cumene-NaY system. For temperatures of 298°K and higher the benzene adsorptive counterdiffusion rate is so rapid that only the value at $M_t/M_\infty = 0.60$ could be accurately determined. Since cumene is not selectively adsorbed over benzene, cumene adsorptive counterdiffusion could not be studied.

The diffusion coefficients for benzene adsorptive counterdiffusion are an order of magnitude larger than those for benzene desorptive counterdiffusion. Furthermore for the desorptive counterdiffusion of cumene from NaY into benzene the diffusion coefficient is even lower than that for benzene desorptive counterdiffusion and less than one-thirtieth that for benzene adsorptive counterdiffusion (Table 4). In benzene adsorptive and cumene desorptive counterdiffusion, benzene and cumene counterdiffuse in the same direction relative to each other and relative to the zeolite. The only apparent difference is the relative concentration of the two species present. The absolute rates of diffusion for the benzene-cumene-NaY system fall in the same relative order as the effective diffusion coefficients but do not differ by as large a factor. The explanation is the same as for the 1-MN system. At 281°K the absolute rate of diffusion in grams aromatic per gram zeolite per minute for the initial part of the run is 0.0262 for benzene adsorptive counterdiffusion, 0.0226 for benzene desorptive counterdiffusion, and 0.0171 for cumene desorptive counterdiffusion. The application of a number of standard diffusion models, for example, diffusion coupled with reaction or adsorption, did not result in a consistent explanation of the data.

Cheng (1970) reports that for the cumene-cyclohexane-NaY system the diffusion coefficient for cumene adsorptive counterdiffusion is less than that for cyclohexane desorptive counterdiffusion. A similar relationship is reported between mesitylene adsorptive counterdiffusion and cyclohexane desorptive counterdiffusion for the mesitylene-cyclohexane-NaY system. These results show an opposite trend to the results obtained in this study. The difference between the two studies probably results from the use of different types of hydrocarbons (two aromatics versus one aromatic and one paraffin) but clarification seems desirable.

Table 5 gives the activation energy and pre-exponential factor obtained from Arrhenius plots of the diffusion coefficients. The maximum error in the activation energy is about ±4.2 kJ per gram mole. For the cumene-1-MN-SK-

Table 4. Effective Diffusion Coefficients for Adsorptive and Desorptive Counterdiffusion in the Benzene-Cumene-NaY System

Direction of diffusion	Temp., °C	$D_{eff} \times 10^{17}$, m²/s $M_t/M_\infty \rightarrow 0$	$M_t/M_\infty = 0.60$	Time to $M_t/M_\infty = 0.60$, min.
Benz. ADS	8	13.1	3.4	2.9
Benz. DES	8	0.39	0.16	74.0
Cum. DES	8	0.19	0.067	299.0
Benz. ADS	15	23.0	5.8	1.5
Benz. DES	15	1.8	0.68	22.0
Benz. ADS	25	32.0	22.0	0.81
Benz. DES	25	4.1	1.9	6.9
Cum. DES	25	0.92	0.52	37.0
Benz. ADS	35	—	~100.0	~0.2
Benz. DES	35	10.1	6.7	2.2
Benz. ADS	45	—	113.0	~0.2
Benz. DES	45	14.3	13.0	1.4

500 system the activation energy for 1-MN adsorptive counterdiffusion is slightly lower than that for desorptive counterdiffusion and appears to be independent of the fractional approach to equilibrium. The small difference in activation energy between adsorptive and desorptive counterdiffusion at the same value of M_t/M_∞ is not sufficient to account for the differences observed in the diffusion coefficient between these diffusion modes and thus the pre-exponential factor varies in the same direction as does the diffusion coefficient (Table 5).

For the benzene-cumene-NaY system the difference in the activation energy between benzene adsorptive and desorptive counterdiffusion is considerable, whereas the difference between benzene and cumene desorptive counterdiffusion is smaller (Table 5). The activation energy for cumene desorptive counterdiffusion, 70.3 and 82.5 kJ per gram mole at $M_t/M_\infty \rightarrow 0$ and $= 0.60$ respectively, agrees well with the values reported previously by Satterfield and Katzer (1971), 72.8 and 82.9 kJ per gram mole at $M_t/M_\infty \rightarrow 0$ and $= 0.60$ respectively. The increase in activation energy as the run approaches equilibrium and in going from benzene adsorptive to benzene desorptive to cumene desorptive counterdiffusion is much larger than that required to account for the decrease in the diffusion coefficient between these conditions, and the pre-exponential factor compensates for the effect of the activation energy change (Table 5). The pre-exponential factor increases by at least two orders of magnitude between $M_t/M_\infty \rightarrow 0$ and $= 0.60$ and also increases significantly between benzene adsorptive, benzene desorptive, and cumene desorptive counterdiffusion. In contrast for the cumene-1-MN-SK-500 system there is a small anticompensation effect.

Because of the absolute regularity and periodicity of the zeolite pore structure and because the probable controlling resistance to diffusion is the motion of the diffusate molecule through the pore aperture from one supercage to another, it would appear that the diffusion coefficients could be rationalized on the basis of absolute rate theory. Accordingly the diffusion coefficient is given by

$$D = e\,\lambda^2 \frac{\underline{k}\,T}{\underline{h}} \exp\,[\Delta S^{\pm}/R]\exp[-E/RT]$$

where λ is the jump distance for the molecule (Glasstone et al., 1941). This is to be compared with $D_{\text{eff}} = D_0\, e^{-E/RT}$. For a given system the jump distance should be some constant distance within the pore structure, and the terms comprising the jump frequency exclusive of the exponential temperature coefficient, $e\,\underline{k}T/\underline{h}\,\exp\,[\Delta S^{\pm}/R]$, should also be fairly constant. Thus the pre-exponential factor D_0 should remain fairly constant, and the rate of diffusion should be influenced mainly by the height of the energy barrier that the diffusing molecule must cross, that is, the activation energy. As shown, however, D_0 varies over several orders of magnitude within the same run indicating that if λ is fairly constant, $\Delta S^{\pm}$ must increase significantly as the run approaches equilibrium. The reason for this change and the variation in E is yet to be defined but appears to be associated with adsorption-desorption phenomena within the structure. The clarification of such points will require considerable additional accurate data directed toward elucidating the mechanism of the diffusion process.

The reason for the difference between adsorptive and desorptive counterdiffusion is not totally clear. It might be due to strongly adsorbed impurities which produce an added resistance to diffusion. This was postulated for the cumene-1-MN-SK-500 system (Katzer, 1969). However, impurities are almost absent in the benzene-cumene-NaY system and no color formation is observed in it. In both systems the rate of diffusion and effective diffusion coefficient are highest when the concentration of the more strongly adsorbed (selectively adsorbed) aromatic hydrocarbon in the zeolite is kept low. This occurs in the adsorptive counterdiffusion of the selectively adsorbed hydrocarbon. When this species is present in high concentration in the zeolite phase as when it is desorbing from the zeolite or when it is the bulk hydrocarbon exterior to the zeolite, the diffusion coefficient is much lower. The higher concentration of the more strongly adsorbed aromatic in the zeolite phase results in an increased resistance to diffusion and consequently a lower rate of diffusion. It thus appears that an adsorption phenomena associated with the more strongly adsorbed species is responsible for the differences observed between adsorptive and desorptive counterdiffusion.

CONCLUSIONS AND SUMMARY

The rate of counterdiffusion of substituted aromatic hydrocarbons with cyclohexane in the Y zeolite is an exponential function of the critical diameter of the diffusate when the molecular type is not varied greatly. Previously reported data for counterdiffusion in Y for single-component adsorption of hydrocarbons into Y and for single component adsorption and desorption of gases and vapors with small pore zeolites follow a similar exponential relationship. Changes in the diffusate which affect the strength of the molecule-zeolite interactions affect the counterdiffusion rate, stronger interactions result in lower diffusion rates.

The effective diffusion coefficients for adsorptive counterdiffusion are an order of magnitude greater than those for desorptive counterdiffusion of the same component, the selectively adsorbed component. Those for the desorptive counterdiffusion of the nonselectively adsorbed component are even less. An adsorption phenomena associated with the more strongly adsorbed species which produces an added resistance to diffusion appears to be responsible for the difference between adsorptive and desorptive counterdiffusion.

The size effects are in accord with a model which considers the motion of the diffusate molecule through the

TABLE 5. ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR COUNTERDIFFUSION IN Y ZEOLITE

Zeolite	Key compound diffusing	Diffusion direction	E, kJ/mole ($M_t/M_\infty \rightarrow 0$)	$D_0 \times 10^4$, m²/s	E, kJ/mole ($M_t/M_\infty = 0.60$)	$D_0 \times 10^4$, m²/s
SK-500	1-Methyl Naphthalene	ADS	70.3	99	71.1	88
SK-500	1-Methyl Naphthalene	DES	75.3	43	73.2	11
NaY	Benzene	ADS	54.4	0.016	71.1	5.5
NaY	Benzene	DES	63.6	0.046	79.9	18
NaY	Cumene	DES	70.3	0.21	82.4	14

pore aperture to be the rate limiting step in the diffusion process. Large variations in $\Delta S^{\pm}$ as calculated from absolute rate theory for a given system or more importantly within a given run indicate the importance of phenomena other than simple diffusion as such to the mechanism of diffusion in zeolites.

More systematic studies of zeolite diffusion in simple systems, for example, noble and permanent gases in small pore zeolites, are necessary for the development of theoretical models of zeolite diffusion. However diffusion and counterdiffusion studies with hydrocarbon molecules and large pore zeolites are also needed to provide information on transport processes in zeolites. This information will probably not immediately result in the development of theoretical models for zeolite diffusion because of the complexity of such systems but it should provide practical models and correlations which are of immediate use in exploring the role of diffusion in zeolite systems.

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NOTATION

b = empirical constant
D = diffusion coefficient, m^2/s
D_{eff} = effective diffusion coefficient, m^2/s
D_0 = pre-exponential factor, m^2/s
d_{pore} = diameter of pore aperture, nm
d_{mol} = critical molecular diameter, nm
E = activation energy for diffusion, kJ per gram mole
E_p = potential energy, J
$\underline{h}$ = Planck's constant, J/s
$\underline{k}$ = Boltzman's constant, J/°K
M_t = amount of material having diffused (out or in) to time t, g
M_∞ = amount of material having diffused (out or in) at equilibrium, g
R = gas constant, 8.314 J/mole, K
r = center-to-center distance between molecules or atoms, m
$\Delta S^{\pm}$ = entropy change J/(g mole °K)
T = temperature, °K
λ = jump distance, nm

LITERATURE CITED

Barrer, R. M., "Transient Flow of Gases in Sorbents Providing Uniform Capillary Networks of Molecular Dimensions," *Trans. Faraday Soc.*, **45**, 358 (1949).

———., and D. W. Brook, "Molecular Diffusion in Chabazite Mordenite, and Levynite," *ibid.*, **49**, 1049 (1953).

Brandt, W. W., and W. K. Rudloff, "Gaseous Diffusion in a Natural Zeolite in Relation to Crystalline Disorder," *Zeit. fur Phys. Chem. N.F.*, **42**, 201 (1964).

Breck, D. W., "Crystalline Molecular Sieves," *J. Chem. Educ.*, **41**, 678 (1964).

Breck, D. W., and E. M. Flanigen, "Synthesis and Properties of Union Carbide Zeolites L, X and Y," in Molecular Sieves, p. 47, Society of Chemical Industry, London (1968).

Carman, P. C., and R. A. Haul, "Measurement of Diffusion Coefficients," *Proc. Roy. Soc., Ser. A*, **222**, 109 (1954).

Cheng, C. S., "Diffusion Characteristics of Organic Liquids in Type Y Zeolites," Sc.D. thesis, Mass. Inst. Technol., Cambridge (1970).

Collins, J. J., "Where to Use Molecular Sieves," *Chem. Eng. Progr.*, **68**, 66 (1968).

Crank, J., The Mathematics of Diffusion, pp. 84-98, Oxford University Press, London (1956).

Fukunaga, P., K. C. Hwang, S. H. Davis, and J. Winnick, "Mixed-Gas Adsorption and Vacuum Desorption of Carbon Dioxide on Molecular Sieve," *Ind. Eng. Chem. Process Design Develop*, **7**, 269 (1968).

Gehrhardt, H. M., and B. G. Kyle, "Fixed-Bed, Liquid-Phase Drying with Molecular Sieve Adsorbent," *ibid.*, **6**, 265 (1967).

Glasstone, S., K. J. Laidler, and H. Eyring, The Theory of Rate Processes, pp. 195-201 and 516-641, McGraw-Hill, New York (1941).

Habgood, H. W., "The Kinetics of Molecular Sieve Action. Sorption of Nitrogen-Methane Mixtures by Linde Molecular Sieve 4A," *Can. J. Chem.*, **36**, 1384 (1958).

Katzer, J. R., "Counterdiffusion of Liquid Hydrocarbons in Zeolites," Ph.D. thesis, Mass. Inst. Technol., Cambridge (1969).

Khudiev, A. T., A. L. Klyachko-Gurvich, T. R. Brueva, Ya. I. Isakov, and A. M. Rubinshtein, "Heat of Adsorption of Benzene on Synthetic Faujasites," *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **4**, 694 (1968).

Kiselev, A. V., and A. A. Lopatkin, "Energy of Adsorption by Zeolites of Molecules of Different Structure," in Molecular Sieves, p. 252, Society of Chemical Industry, London, 1968.

Klaychko-Gurvich, A. L., A. T. Khudiev, Ya. I. Isakov, and A. M. Rubinshtein, "Influence of the Degree of Exchange of the Cation in Type Y Zeolites on the Heat of Adsorption of Benzene and Cyclohexane," *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **6**, 1305 (1967).

Moore, R. M., "Counterdiffusion of Liquid Hydrocarbons in Type Y Zeolite: Effect of Molecular Shape, Type and Direction of Diffusion," M.Ch.E. thesis, Univ. Delaware, Newark (1971).

Neikam, W. C., Sun Oil Company, Marcus Hook, Pa., private communication (1971).

Nelson, E. T., and P. L. Walker, "Some Techniques for Investigating the Unsteady-State Molecular Flow of Gas Through a Microporous Medium," *J. Appl. Chem.*, **11**, 358 (1961).

Pauling, L., The Nature of the Chemical Bond, 3rd ed., pp. 221-264, Cornell University Press, Ithaca, New York (1960).

Roberts, P. V., and R. York, "Adsorption of Normal Paraffins from Binary Liquid Solutions by 5A Molecular Sieve Adsorbent," *Ind. Eng. Chem. Process Design Develop.*, **6**, 516 (1967).

Rudloff, W. K., "Gas Diffusion and Sorption in Crystalline Model Compounds," Ph.D. thesis, Illinois Inst. Tech., Chicago (1965).

Satterfield, C. N., and C. S. Cheng, "Single-Component Diffusion of Selected Organic Liquids in Type Y Zeolites," *AIChE Symp. Ser. No. 117*, **67**, 43 (1971).

Satterfield, C. N., and J. R. Katzer, "The Counterdiffusion of Liquid Hydrocarbons in Type Y Zeolites," in Advances in Chemistry Series, **102**, p. 193, Am. Chem. Soc., Wash., D. C. (1971).

———., and W. R. Vieth, "Desorption and Counterdiffusion Behavior of Benzene and Cumene in H-Mordenite," *Ind. Eng. Chem. Fundamentals*, **10**, 478 (1971).

Schumacher, W. J., and R. York, "Separation of Hydrocarbons in Fixed Beds of Molecular Sieves," *Ind. Eng. Chem. Process Design Develop*, **6**, 321 (1967).

Sutton, L. E., ed., "Table of Interatomic Distances and Configurations in Molecules and Ions," Chemical Society, London (1958).

Tuang, H. C., B. V. Romanouski, K. V. Topchieva, and L. I. Piguzova, *Kinet. Katal.*, **8**, 594 (1967).

Weast, R. C., ed., Handbook of Chemistry and Physics, 48th ed., p. F-145, F-148, The Chemical Rubber Co., Cleveland, Ohio (1967-1968).

Whang, H. Y., "Counterdiffusion of Gases Through Microporous Solids," Sc.D. thesis, Mass. Inst. Technol., Cambridge (1961).

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