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D. M. Ruthven[a]
[a] Department of Chemical Engineering, University of New Brunswick, Fredericton, N.B., Canada

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SORPTION AND DIFFUSION IN MOLECULAR SIEVE ZEOLITES

D.M. Ruthven
Department of Chemical Engineering
University of New Brunswick
Fredericton, N.B., Canada

ABSTRACT

Recent information concerning the kinetics and equilibria of sorption of various classes of molecule in four representative types of molecular sieve (4A/5A, 13X, natural erionite and H-chabazite) is reviewed. The general relationships between the crystal structure of the sieve, the molecular properties of the adsorbate (particularly the critical diameter and polar nature of the molecule) and the sorption/diffusion behaviour are emphasized.

INTRODUCTION

The industrial uses of zeolites, both as catalysts and as selective adsorbents, depend on the crystallographic structure of these materials. In contrast with other common microporous adsorbents such as activated carbon or silica gel, the pore structure of a zeolite is actually determined by the crystal framework and is therefore precisely regular with no distribution of pore size. The effective diameters of the micropores in the common zeolites range from about 3Å to 10Å depending on both the type of framework and the nature of the exchangeable cations. Molecules which are too large to enter the micropores are not adsorbed to any significant extent. This is the basis of the important molecular sieve separation processes such as normal/iso paraffin separation and shape selective catalytic cracking.

In addition to the simple molecular sieve effect, zeolitic adsorbents show a pronounced selectivity towards polar molecules and molecules with high quadrupole moments. This is due to the ionic nature of the crystal which gives rise to a highly non-uniform electric field within the micropores. Molecules which can interact energetically with this field (i.e. polar or quadrupolar molecules) are therefore adsorbed more strongly than non-polar species. The uses of molecular sieves as drying agents, as selective adsorbents for H_2S/CO_2 and for air separation depend on this effect.

Most of the industrial separation processes in which a molecular sieve adsorbent is employed make use of a fixed bed system operated in a cyclic manner. The dynamic capacity of the adsorbent bed and the time required for regeneration are determined by the kinetics and equilibrium of sorption. The proper design and optimization of such processes therefore requires detailed knowledge of the adsorption behaviour. Although a wide range of zeolites, both, natural and synthetic, are known, industrial applications are limited to a few of the more readily available types. Detailed structural information has been summarized by Breck(1). The present review is limited to four representative structures: the natural zeolites chabazite and erionite and the synthetic zeolites A and X.

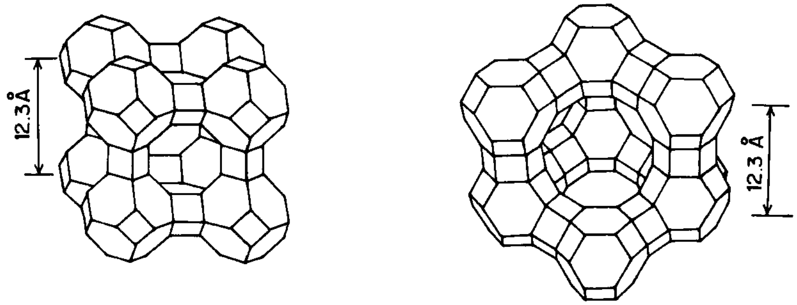
Type A zeolites are widely used as selective adsorbents and drying agents while the type X (and the structurally isomorphous type Y) zeolites are important as cracking catalysts. Erionite occurs in commercial quantities in the zeolite deposits of Oregon and Nevada and has been used as a shape selective cracking catalyst(2). Chabazite is not widely used industrially but it is of some historical interest since it was among the first of the zeolites to be investigated as a potential molecular sieve(3).

In addition to the comprehensive general treatise of Breck(1) the specific areas of sorption and diffusion in molecular sieves have been reviewed by Barrer (1964 and 1971)(4,5), Walker, Austin and Nandi (1966)(6), Riekert (1970)(7), Schirmer (1971)(8) and Kiselev (1971)(9). In the present review no attempt is made at a comprehensive treatment but rather selected aspects of the subject are discussed with emphasis on the different patterns of behaviour which are observed for different systems and the extent to which these observations can be explained in terms of simple theoretical models. The systems selected for detailed discussion are for the most part those which we have studied at the University of New Brunswick but these systems are, in a general way, representative of the systems of industrial interest.

CRYSTAL STRUCTURE

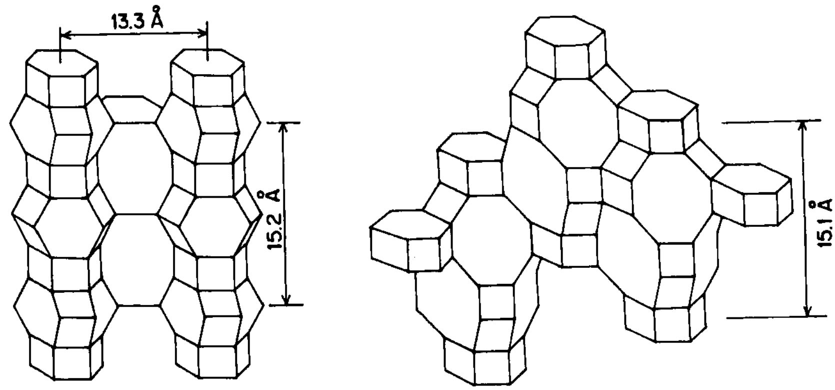
The framework of a molecular sieve crystal is built up from tetrahedral SiO_4 and AlO_4 units. Electrical neutrality is preserved by the presence of one univalent exchangeable cation (or equivalent) for each Al atom in the crystal. The crystal structures are complex and are best visualized in terms of secondary building units which are themselves small assemblages of SiO_4 and AlO_4 tetrahedra. The structures of the type A sieve, the type X or Y sieve erionite and chabazite are shown diagramatically in figure 1.

The structural unit of the type A framework (pseudo cell) consists of eight cubo-octahedral units (sodalite cages) placed at the corners of a 12.3Å cube and connected through 4-membered oxygen bridges to form a relatively large spherical cavity (free diameter $\sim$ 11.4Å, volume 776$Å^3$). The lattice of the crystal is built up from a cubic array of these cells. Each cavity is connected to the six neighbouring cavities through the 8-membered oxygen rings (windows). The six membered oxygen rings which give access to the sodalite cages are too small to admit all except the smallest of molecules (e.g. H_2O, NH_3) so most adsorbed species are in effect confined to the central cavity and the sodalite cage acts simply as a building block for the crystal structure. The effec-



(a) Linde A

(b) Linde X or Y



(c) Erionite

(d) Chabazite

FIGURE 1

Diagrammatic representation of the crystal structures of (a) Type A Zeolite, (b) Type X or Y Zeolite, (c) Erionite, (d) Chabazite. There is an oxygen ion at the centre of each line and the Si/Al ions, which are much smaller, are located at the vertices. The positions of the exchangeable cations are not shown.

tive diameter of the octagonal windows depends on the exchangeable cation. In the Ca^{++} form of the sieve (5A) the $6Ca^{++}$ cations are located in sites remote from the windows and the free diameter of the windows is then about 4.3Å. Because of the effects of molecular vibration this sieve can admit molecules with critical diameters up to about 5.5Å. This includes normal, but not branched or cyclic hydrocarbons. Exchanging the $6Ca^{++}$ ions for $12Na^+$ ions gives the 4A sieve in which the windows are partially obstructed. The 4A sieve can admit only molecules with critical diameters less than about 4.4Å. This sieve will not adsorb hydrocarbons larger than ethane at any significant rate. In the K^+ form (3A sieve) the window aperture is even smaller (∿3Å) because of the larger cation, and only very small molecules such as H_2O, NH_3 etc. are admitted. The 3A sieve is therefore a useful selective drying agent which will not adsorb larger molecular species.

The structure of the faujasite zeolites (types X and Y) is closely related to the A type structure. The same cubo-octahedral units are connected in a tetrahedral arrangement through 6-membered bridges. This gives a very open three dimensional pore structure in which the larger cavities are interconnected through 12-membered oxygen rings with free aperture about 7.4Å. These sieves can admit quite large molecules including branched chain hydrocarbons and aromatics. The difference between the X and Y sieves lies in the Si/Al ratio which is about 1-1.5 for type X and 1.5-3.0 for type Y. Although these sieves have the same framework they have different numbers of exchangeable cations and this leads to differences in both adsorptive and catalytic properties.

The structures of erionite and chabazite are more difficult to describe in detail. The secondary building unit for the erionite framework is the cancrinite cage which has five hexagonal and six square faces. These units are interconnected through 6-membered oxygen bridges and stacked in columns to yield a structure with hexagonal symmetry containing ellipsoidal cavities (6.3 x 13Å, volume 406Å^3) interconnected through distorted octagonal windows (free aperture 3.6 x 5.2Å). The chabazite structure is similar in that it contains ellipsoidal cavities of about the same size (6.7 x 10Å) interconnected through similar 8-membered oxygen windows.

These structures are similar to the type A structure in that they contain discrete cavities interconnected through octagonal windows but they differ from the A type structure in that the cavities are smaller, ellipsoidal rather than spherical, and the windows are distorted from the regular octagonal form. These differences are reflected in the adsorption behaviour.

SORPTION EQUILIBRIUM

Sorption of most species in molecular sieves is probably best regarded as physical adsorption since no electron transfer is involved although the energetics of the process are such that the heats of sorption may be quite high (∿20 kcal/mole or more). **Equilibrium** data are commonly presented as isotherms showing the adsorbed phase concentration plotted against partial pressure (or, for liquid phase systems, concentration). **The structural regularity** of molecular sieves makes it possible to apply a more detailed theoretical analysis than is feasible with other systems and, for very simple adsorbates such as the rare gases a fair prediction of the isotherm may be obtained from basic molecular physics.

Henry's Law Constants

For any adsorption system in which there is no dissociation, the equilibrium isotherm must approach linearity in the low concentration region. The Henry's Law constant K (defined by $c = Kp$) is simply the ratio of the partition functions for adsorbed and gaseous molecules duly corrected for the difference in potential energy:

$$K = \frac{f_z}{f'_g kT} \cdot \exp[(u_g - u_z)/kT] \qquad (1)$$

For a monatomic species, or for a polyatomic species in which the rotational and internal freedom are not significantly modified by sorption:

$$\frac{f_z}{f'_g} \exp[(u_g - u_z)/kT] = Z_1 = \int_V \exp(-u(\underline{r})/kT) \cdot d\underline{r} \qquad (2)$$

where Z_1 is the configuration integral for an occluded molecule. The temperature dependence of the Henry constant follows the usual vant Hoff equation

$$K = K_0 \, e^{q_0/RT} \qquad (3)$$

with the limiting heat of sorption given by

$$\frac{q_0}{RT} = 1 - \int_V \frac{u(\underline{r})}{kT} \cdot \frac{\exp[-u(\underline{r})/kT]}{Z_1} \cdot dr \qquad (4)$$

Since the positions of all ions in the zeolite framework are known from x-ray crystallographic studies it is in principle possible to calculate $u(\underline{r})$, and hence Z, K and q_0, by summing the contributions arising from the dispersion, repulsion and polarization energies of interaction for a probe molecule with each atom or ion of the lattice. For molecules with significant dipole or quadrupole moments the electrostatic energies must also be included. Such calculations have been performed for the inert gases (for which the electrostatic energies are zero) in both A and X sieves$^{(10-13)}$. The values of K and q_0 so obtained are in fair agreement with experimental results. There is however considerable uncertainty in the force constants since significantly different values are obtained by each of the three well known methods (Kirkwood-Müller$^{(14-15)}$, Slater-Kirkwood$^{(16)}$ and London$^{(17)}$). There is further uncertainty concerning the extent to which the oxygen atoms in the structure are ionized and in the distribution of the cations between available sites. A small asymmetry in the distribution of cations has a large effect on the estimated polarization energy. The extent of the agreement between theory and experiment is illustrated in figure 2. While the calculations show that the magnitude of the Henry constants and heats of adsorption can be adequately accounted for by the forces of physical and

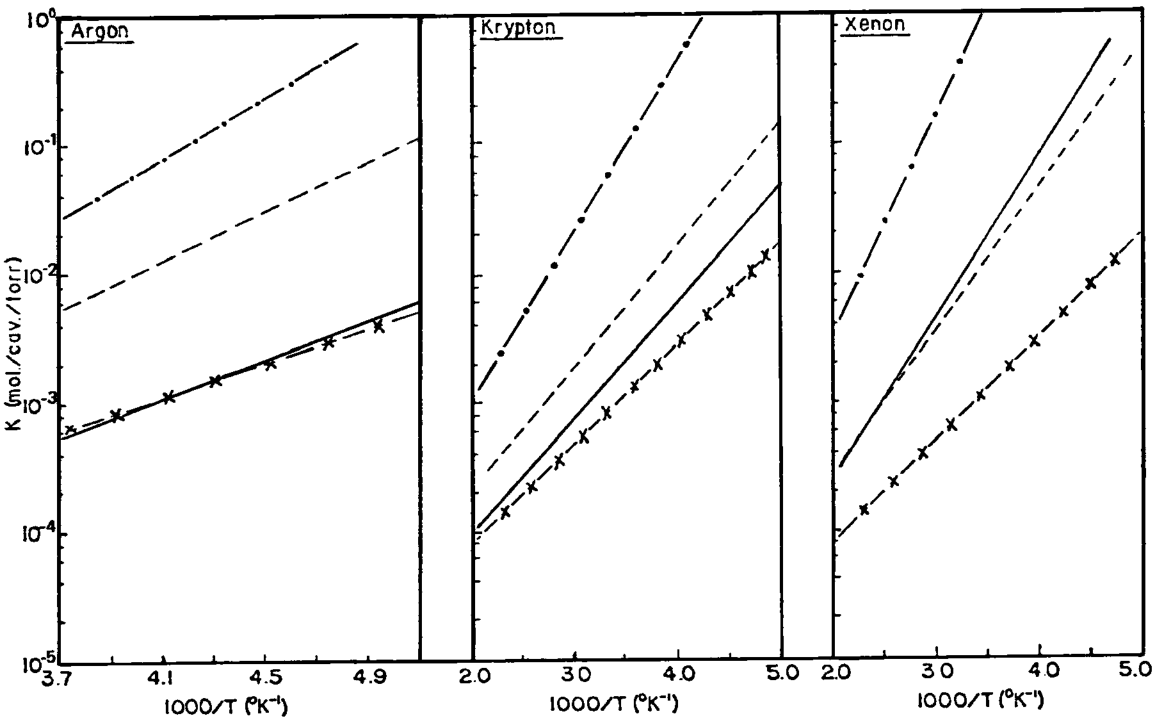


FIGURE 2. Comparison of experimental and theoretical Henry's Law constants for inert gases in 5A zeolite. (—, experimental; ---- calculated from Slater-Kirkwood expression(16); -·-, calculated from Kirkwood-Muller expression(14,15); -x-x-x, calculated from London expression(17); from Derrah and Ruthven(13) with permission of the Canadian Journal of Chemistry.)

adsorption, the accuracy of the calculations is not high even for these simple systems.

Extension of the theory to more complex molecules presents severe difficulties. It is necessary to allow for the electrostatic dipole and quadrupole interaction energies and to take account of molecular rotation. Except for simple spherical top molecules such as CH_4, it is incorrect to treat a polyatomic molecule as a single point centre of force. For the light paraffins in the 5A sieve, Spangenberg, Fiedler and Schirmer(18,19) have obtained fairly good agreement between the theoretical and experimental heats of sorption by treating the molecules as assemblages of $>CH_2$ groups. Each $>CH_2$ group was considered as a centre of force and the angle and distance between neighbouring carbon atoms in the chain were fixed at the equilibrium values. Sargent and Whitford(20) attempted to calculate the Henry constant and heat of sorption for CO_2 in 5A sieve, taking account of the quadrupole interaction energy (in addition to dispersion, repulsion and polarization) but the agreement between theory and experiment was poor.

The simple theory, represented by equations 1-4 is applicable only at sufficiently low sorbate concentrations such that the interaction between sorbate molecules can be neglected. In order to extend the theory to higher sorbate concentrations it is necessary to take account of sorbate-sorbate interaction and this makes a full calculation impractically difficult. This problem can be avoided if a suitable model can be found which provides an adequate representation of the isotherms.

Model Isotherms

If the intracrystalline void space can be regarded as containing a fixed number (c_s) of distinct identical adsorption sites and if there is no interaction between adsorbed molecules even when occupying neighbouring sites, the isotherm should follow the simple Langmuir equation:

$$\Theta = \frac{c}{c_p} = \frac{bp}{1 + bp} \qquad (5)$$

where the equilibrium constant b is simply related to the Henry's Law constant ($b = K/c_s$). The temperature dependence of b therefore follows equation 3 ($b = b_o \exp(q_o/RT)$. The Langmuir equation is qualitatively useful but it is quantitatively inadequate except for a few systems (Kr - 5A(13), SF_6, C_2F_6 and C_3F_8 - 13X(21)) and then only over a limited range of concentration ($\Theta < \sim 0.5$). Deviations arise both from interaction between adsorbed molecules and from heterogeneity of the adsorption sites. Several modified expressions have been developed to take account of these effects(22) but with only limited success(21,23-25).

The assumption of a fixed number of adsorption sites is also questionable for most zeolitic adsorbents. The capacity of the sieve does not reach a precise saturation limit but rather the saturation sorbate concentration increases slowly with applied pressure and decreases with increased temperature. The intracrystalline fluid thus exhibits some of the properties of a bulk liquid (compressibility, thermal expansion)(26,27). It is therefore perhaps more realistic to regard zeolitic sorption simply as the filling of the intracrystalline micropore volume by the condensed adsorbate. It has been shown that the saturation capacity of the sieve can be estimated with fair accuracy simply as the quotient of the micropore volume and the molecular volume of the saturated liquid sorbate(28). This principle holds well for temperatures below the normal boiling point of the liquid sorbate but, at higher temperatures, the molecular volume of the intracrystalline fluid is generally somewhat smaller than that of the saturated liquid. A linear interpolation between the molecular volume of the saturated liquid at the normal boiling point and the van der Waals 'b' at the critical temperature has been suggested as a simple approximate method of estimating the effective molecular volume of the intracrystalline fluid at temperatures above the boiling point(29,30).

This idea of volume filling of the micropores has been used as a basis for the development of a simple statistical thermodynamic model isotherm, applicable to those zeolites, such as type A, erionite and chabazite, in which the intracrystalline space is divided into discrete cavities interconnected through relatively small windows. As a simple idealization the potential energy is considered to be uniform throughout a cavity but with a significant barrier between cavities. An adsorbed molecule is therefore confined within a particular cavity but can move freely within that cavity. When a cavity contains more than one molecule the interaction is accounted for by a reduction in the free volume. Intermolecular attraction is neglected. Subject to these approximations the configuration integral for a cavity containing s molecules becomes:

$$Z_s = \frac{Z_1^s}{s!}(1 - s\beta/v)^s \qquad (6)$$

where $Z_1 = KkT$ is the configuration integral for a cavity containing only one molecule. This leads to the following expression for the equilibrium isotherm$^{(31,32)}$:

$$c = \frac{Kp + [Kp(1-2\beta/v]^2 + \ldots + \frac{[Kp(1-m\beta/v]^m}{(m-1)!}}{1 + Kp + \frac{1}{2!}[Kp(1-2\beta/v)]^2 + \ldots + \frac{[Kp(1-m\beta/v)]^m}{m!}} \qquad (7)$$

where the saturation limit, in molecules per cavity is given by m(integer) $\leq v/\beta$. The molecular volume (β) may be estimated from the density of the saturated liquid sorbate and the cavity volume (v) is known. The expression therefore contains only one parameter, the Henry's Law constant, and this may be readily determined from the initial slope of the low concentration region of the isotherm.

Although the approximations from which it is derived are severe, this expression has been found to provide a good representation of the isotherms for several light hydrocarbons in 5A sieve$^{(32,33)}$ as may be seen from figure 3. More recently the model has been sucessfully used to correlate equilibrium data for CO_2 on a range of different zeolites$^{(117,118)}$. However, this model does

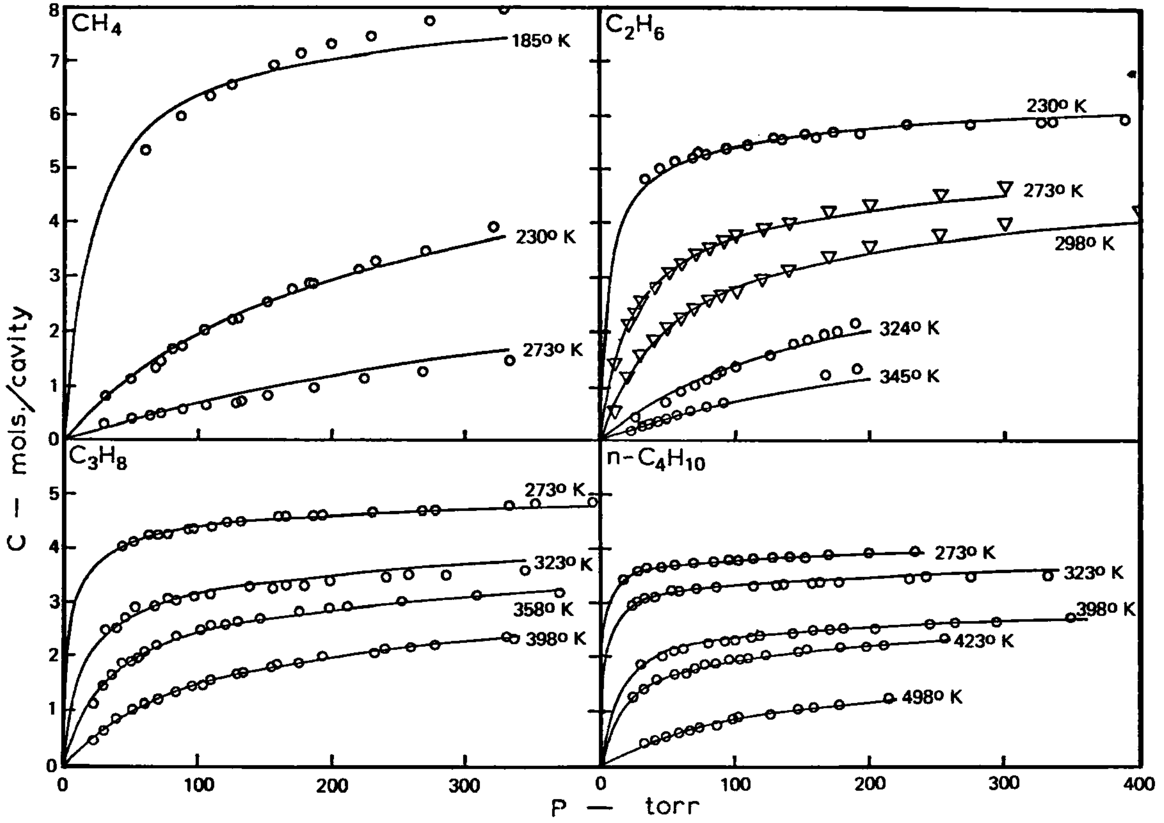


FIGURE 3. Comparison of experimental equilibrium isotherms for light paraffins in 5A zeolite and theoretical curves calculated from equation 7 with Henry constants from Table I. (From reference (32) with permission of the Faraday Society.)

not fit the equilibrium data for the inert gases in this sieve, neither does it fit the isotherms for polar molecules. For a linear molecule the effect of molecular rotation is to average the potential field over an appreciable region of space. The assumption of a uniform field within a cavity is therefore likely to be a better approximation for a non-polar polyatomic molecule such as a hydrocarbon. Monatomic molecules and small polar molecules are much more likely to be adsorbed at localized sites so that, for such adsorbates, the model is inappropriate.

In the original formulation of this statistical thermodynamic model, exponential factors were included to account for attractive intermolecular forces. The magnitude of the intermolecular forces was estimated from Lennard-Jones force constants. The difference between the isotherms calculated with and without the attractive forces was found to be small and it was shown that the main features of the adsorption equilibrium behaviour, including the variation of isosteric heat with concentration, could be accounted for entirely by the effect of the finite size of the molecules alone (equations 6 and 7) suggesting that the effect of molecular attraction is secondary.

Generalized Correlations

Because of the limited applicability of model isotherms various generalized thermodynamic correlations have been developed which do not depend on the assumption of a particular physical model. One example of this approach is the Polanyi potential theory(34) which has been extended and applied to zeolitic adsorbents by Dubinin and his co-workers(29,30,35-37).

It is assumed that the adsorbed fluid is similar to the saturated liquid sorbate and the equilibrium data are correlated in terms of the "adsorption potential" (ε) which is defined as the difference in free energy between the adsorbed fluid and the pure saturated liquid sorbate:

$$\varepsilon = RT \ln (f/f_s) \approx RT \ln(p/f_s) \qquad (8)$$

According to the potential theory, for any particular adsorbate-adsorbent system, a plot of the volume of fluid adsorbed against the adsorption potential should yield a temperature invariant characteristic curve. For many systems the form of the characteristic curve can be adequately represented by the Dubinin-Radushkevich equation:

$$\frac{W}{W_0} = \frac{c}{c_s} = \exp\left[-\left(\frac{\varepsilon}{\varepsilon'}\right)^2\right] \qquad (9)$$

where ε' is a constant, characteristic of the particular system. The total specific micropore volume W_0 may be determined either from the saturation limit ($W_0 = c_s\beta$) or by calculation from the crystal structure. Once the characteristic curve has been established, either from a single isotherm covering a wide range of pressure or from isotherms at several temperatures, the isotherm for any other temperature may be obtained directly. The equilibrium data of figure 3 are plotted in the form of characteristic curves in figure 4(42). Similar curves for other zeolitic systems have been reported in the literature(33,38-41).

The original Polanyi theory and the principle of temperature invariance of the characteristic curve were based on the nature of dispersion-repulsion forces, which are independent of temperature. Electrostatic forces (dipole and quadrupole interactions) are temperature dependent and for systems in which these forces make an appreciable contribution to the sorption potential the principle of temperature invariance will not be strictly valid. However, over the temperature range 25-125°C, equilibrium data for NH_3, H_2S, SO_2, CO_2 and H_2O in 4A and 13X zeolites have been shown to follow characteristic curves quite closely despite the appreciable electrostatic contributions which are expected for these systems(40).

A major problem in the practical application of the Polanyi theory is the difficulty of estimating the molecular volume of the sorbate with sufficient accuracy. At temperatures below the normal boiling point the difficulty is not severe as the molecular volume of the saturated liquid provides a good approximation to the molec-

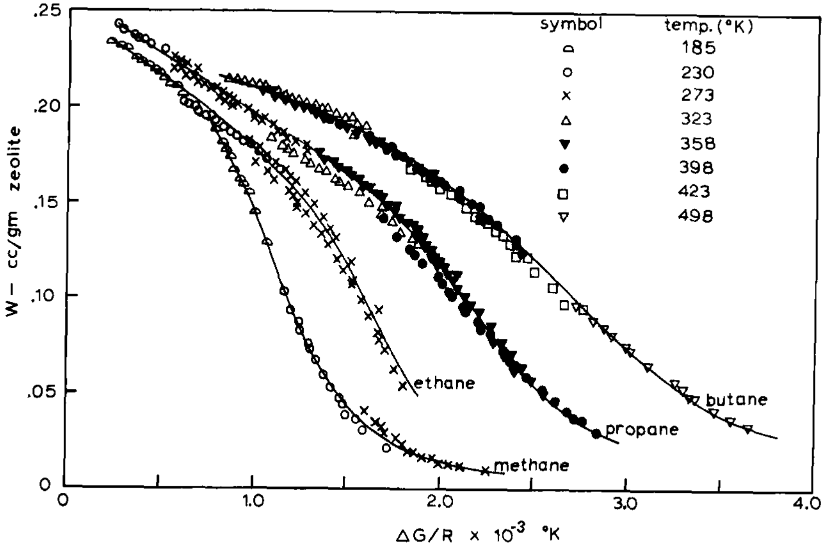


FIGURE 4

Characteristic curve for light paraffins in 5A Zeolite. The experimental data points are the same as those in figure II. (From reference (42) with permission of Academic Press).

ular volume of the sorbate fluid. Above the boiling point methods of extrapolation are required and this inevitably introduces uncertainty. The Polanyi theory also suffers from the disadvantage that it does not reduce, automatically, to Henry's Law in the low concentration limit. This severely limits its value as a basis for the development of more detailed theoretical models. The main value of this theory lies in the usefulness of the characteristic curve as a concise correlation of equilibrium data and a basis for (modest) extrapolation of isotherms.

An alternative approach to the correlation of equilibrium data, which also avoids the need for a particular model, is the virial isotherm which was developed independently by Barrer(43,44) and Kiselev(45). It is assumed that the equation of state of the adsorbed fluid expressed in terms of the osmotic pressure Π can be represented by a virial series:

$$\frac{\Pi}{cRT} = 1 + A_1c + A_2c^2 + \ldots. \tag{10}$$

The adsorbed phase is considered as a two component mixture of zeolite and sorbate. For the sorbate, the differential change in chemical potential corresponding to a change in pressure is given by:

$$d\mu_S = RTd(\ln p) = \frac{RTdp}{p} \tag{11}$$

Making use of the Gibbs-Duhem equation, one has, for the difference in chemical potential of the solid in the solution and in the sorbate free state:

$$\Delta\mu_Z = \int_0^p Vdp - \frac{RTM_Z}{M_S}\int_0^p \frac{xdp}{p} = -\Pi V \tag{12}$$

The first term in this expression is generally negligible and $M_Z/V = \rho$, the density of the outgassed zeolite, so that

$$\frac{\Pi}{cRT} = \frac{\rho}{M_Sc}\int_0^p \frac{xdp}{p} \tag{13}$$

whence, from equation 10, the expression for the isotherm is obtained as:

$$Kp = c\ \exp(2A_1c + \tfrac{3}{2}A_2{}^2 + \ldots.) \tag{14}$$

This expression is equivalent to representing the deviation from ideal Henry's Law behaviour in terms of an activity coefficient γ given by:

$$\gamma = \exp(2A_1c + \tfrac{3}{2}A_2c^2 + \ldots.) \tag{15}$$

The main disadvantage of the virial isotherm is the need for several coefficients, all of which are temperature dependent, in order to correlate the isotherm data. The equation is however useful as a method of extracting Henry's Law constants from experimental data at higher sorbate concentrations outside the linear region since it shows that a plot of log(p/c) vs c should extrapolate linearly to zero concentration and the intercept of such a plot gives, immediately, the value of K.

Enthalpy and Entropy of Sorption

The difference in free energy between the adsorbed phase and the free gaseous phase at a reference pressure p_o is given by:

$$\Delta G = \Delta H - T\Delta S = RT\ln(p/p_o) \tag{16}$$

By differentiation it follows that the isosteric heat of sorption ($q = -\Delta H$) is given by:

$$\left(\frac{\partial \ln p}{\partial T}\right)_c = \frac{q}{RT^2} \tag{17}$$

and the partial molar entropy of the adsorbed species ($\bar{S}_z$) is given by:

$$\Delta S = \bar{S}_z - S_g^o = R\ln(p_o/p) - q/T \tag{18}$$

The partial molar entropy may be regarded as the sum of thermal and configurational contributions:

$$\bar{S}_z = \bar{S}_{th} + \bar{S}_c \tag{19}$$

For ideal localized sorption:

$$\bar{S}_z = R\ln[(1-\theta)/\theta] \tag{20}$$

and $\bar{S}_{th} = S_g^o + R\ln b_o$ (independent of c). Analysis of the thermal entropy has been used to gain evidence concerning the physical state of the adsorbed molecule$^{(21,27)}$ but since the assumption of localized sorption is not always valid such evidence is seldom unequivocal.

Experimental values of q_o, the initial heat of sorption, for a range of different sorbates in several zeolites are summarized in Table I. For non-polar sorbates the initial heat of sorption

TABLE I

Experimental Values of K_o and q_o giving Temperature Dependence of Henry Constants according to Equation 3

	Systems	$K_o \times 10^8$ (mmole/gm.torr)	q_o (Kcal)
Monatomic	Ar-5A	58.5	3.35
	Ar-Chab.	67	3.34
	Kr-4A/5A	71	4.24
	Kr-Chab.	62	4.35
	Xe-5A	73	5.38
	Xe-Chab.	55	5.9
Diatomic	O_2-4A	69	3.2
	O_2-5A	83	3.3
	O_2-Chab.	71	3.43
High Quadrupole	N_2-4A	36	4.4
	N_2-5A	20	5.0
	N_2-Chab.	7	4.8
	CO_2-5A	8	10.8
	CO_2-Chab.	1.2	9.1
Saturated Hydrocarbons	CF_4-5A	29	5.9
	CH_4-5A	107	4.5
	CH_4-Chab.	42	4.9
	C_2H_6-5A	43	6.6
	C_2H_6-Chab.	24	7.4
	C_2H_6-Erion.	36	8.7
	C_3H_8-5A	70	8.1
	C_3H_8-Chab.	34	8.9
	nC_4H_{10}-5A	48	10.2
	nC_4H_{10}-Chab.	13	10.9
	nC_7H_{16}-5A	1.23	17.0
	nC_7H_{16}-13X	4.2	15.2
Unsaturated Hydrocarbons	C_2H_4-4A	1.6	10.0
	C_2H_4-5A	10	9.7
	C_2H_4-Erion.	3.7	11.1
	C_3H_6-5A	43	10.0
	cyclo C_3H_6-5A	143	8.1
	1-C_4H_8-5A	1.74	14.2
	tr · 2-C_4H_8-5A	3.9	13.2
	SF_6-13X	49	6.9
Cyclic Hydrocarbons	C_2H_6-13X	0.27	17.5
	C_6H_{12}-13X	4.65	13.4
	$C_6H_5 \cdot CH_3$-13X	0.36	21.0

The values for 4A, 5A, and erionite (Rome, Ore) are from Ruthven, Loughlin, Derrah and Doetsch(13,32,33,55-58). The values for H-chabazite are from Barrer and Davies(25). The values for 13X are from unpublished data obtained by I.H. Doetsch in this laboratory.

1m mole/gm = 1.78 molecule/cavity·(4A/5A), 1.68 molecule/cavity (13X), 1.22 molecule/cavity (erionite) and 0.81 molecule/cavity (H-chabazite). These figures are based on actual sample densities and for the erionite and chabazite corrections have been applied to account for inert impurities present in the original samples. The is determined mainly by the dispersion energy. This is larger for the zeolites with the smaller cavities (chabazite and erionite) due to the greater proximity of the framework to the adsorbed molecules. The effect of the exchangeable cation is minor. Thus, for the inert gases and saturated hydrocarbons $q_{chabazite} > q_{5A} \sim q_{4A} > q_{13X}$. By contrast, for N_2 and CO_2, molecules with large quadrupole moments, the effect of the increased electrostatic contribution arising from the divalent Ca^{++} ion in 5A more than makes up for the greater dispersion energy in chabazite so that $q_{5A} > q_{chabazite} > q_{4A}$.

For a system which obeys the Langmuir isotherm the isosteric heat is independent of sorbate concentration but, for most zeolitic systems, there is an appreciable concentration dependence. The pattern of this variation shows characteristic differences for different classes of sorbate. For non-polar species such as the hydrocarbon(32,33,46), fluorocarbons(21) and inert gases(13) the isosteric heat generally increases somewhat with sorbate concentration. This trend has frequently been attributed to the effect of intermolecular attraction between sorbate molecules but it has been shown that the effect can arise simply from repulsive forces as a consequence of the temperature dependence of the molecular volume(32). Species such as H_2O, NH_3 and CO_2 for which there is an appreciable electrostatic contribution to the energy of adsorption (either dipole or quadrupole) generally show the opposite trend with the isosteric heat decreasing with sorbate concentration(8,47-50). For such species adsorption is probably localized and the variation in isosteric heat probably arises from the selective occupation of sites in order of decreasing energy, the most favourable sites being those adjacent to the cations. Thus it is that, for polar sorbates, the initial isosteric heat is very sensitive to the cationic form of the zeolite but this difference disappears as the sorbate concentration increases. These trends which are discussed in detail in references (52-54) are illustrated by the experimental data shown in figure 5.

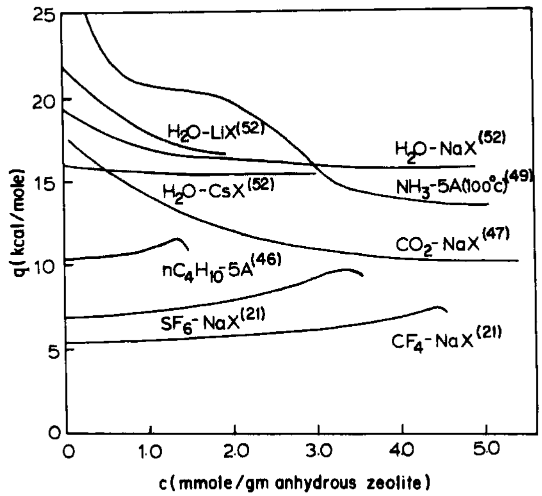


FIGURE 5

Variation of isosteric heat of sorption (q) with sorbate concentration for various sorbates in A and X zeolites.

In homologous series such as the n-paraffins the initial heat of sorption (q_0) increases regularly with increasing chain length as(8,51,52) illustrated in figure 6. It is thus possible to assign contributions to the $-CH_3$ and $>CH_2$ groups and these values may be used to provide an approximate estimate of the heat of sorption of higher homologs. This concept of group contributions has been extended to more complex molecules(8,48,59) and approximate values for some of the more important groups are given in Table II.

Physical State of Adsorbed Molecules

At low concentrations, within the Henry's Law region, information as to the state of the adsorded molecules may be deduced from the Henry constants. If the molecules are confined within particular cavities, but not adsorbed at specific localized sites

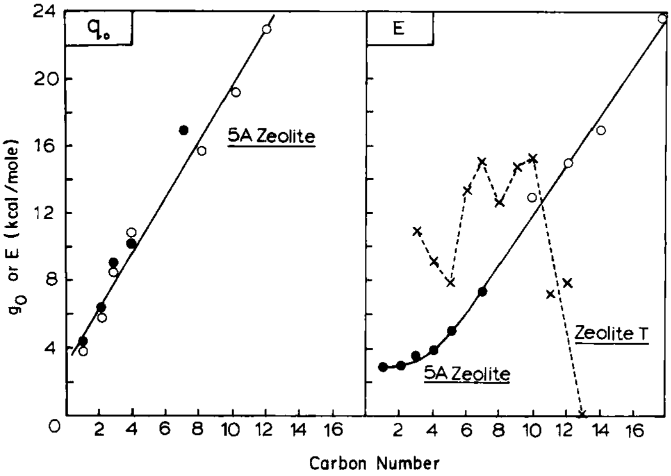


FIGURE 6

Variation of limiting heat of sorption (q_0) and diffusional activation energy (E) with hydrocarbon chain length for n-paraffins in 5A zeolite and zeolite T. (Data from Schirmer et al.(8), o; data from this laboratory, ●; data of Gorring for zeolite T,(91) x).

TABLE II

Group Contributions to Initial Heat of Sorption (Kcal)

Group	5A(8)	13X(59)
$-CH_3$	3.0	2.7
$>CH_2$	2.5	2.4
$-CH_2 = CH_2-$	8.4	8.9
-OH(alcohols)	-	14.6
$-NH_2$(amines)	16.0	16.3

within the cavities and if they retain the same rotational and internal freedom as in the gas phase the ratio of partition functions and heat of sorption will be given by:

$$\frac{f_z}{f'_g} = \frac{\phi}{e} \ ; \quad q_o = u_g - u_z + RT \qquad (21)$$

where ϕ is the free volume of the cavity. From equations 1 and 3 it follows that:

$$K_o = \phi/kTe^2 \qquad (22)$$

The values of K_o for the light hydrocarbons in 5A zeolite are approximately consistent with this expression(58) suggesting that the model of a freely rotating, freely translating molecule confined within a particular cavity but not adsorbed at a specific localized site within the cavity, may not be unrealistic. For the longer chain hydrocarbon the values of K_o calculated from equation 22 are greater than the experimental values indicating either a restriction of rotational freedom or localized adsorption. It may be seen from table 1 that the values of K_o for H-chabazite are consistently smaller than the values for the same sorbate in 4A/5A reflecting greater localization of the sorbate due to the smaller size of the chabazite cavity. The values of K_o for N_2 are consistently smaller than the values for O_2 and the values for benzene/toluene are also smaller than those for cyclohexane. This is probably due to either greater localization or restricted rotation resulting from the electrostatic forces.

For molecules such as O_2 and CH_4 in 5A sieve more direct evidence of the rotational freedom is available(60). These molecules have about the same size and polarizability as Ar and Kr respectively and the values of both K_o and q_o for O_2 and Ar and for CH_4 and Kr are very nearly the same. This is the expected result if the polyatomic molecules are freely rotating in the adsorbed phase whereas if the rotational freedom were restricted the value of K_o would be smaller by the factor f_{rot} (15 for CH_4 and 20 for O_2 at 298°K).

Sorption of Mixtures

The problem of predicting equilibrium data for multicomponent systems from the pure component isotherms is of considerable practical importance and it has attracted the attention of a number of investigators. The statistical thermodynamic model, represented by equation 7 can be readily extended to multicomponent sorbates(61) and it has been shown that for simple mixtures of similar sorbates (e.g. propane-cyclopropane) the mixture isotherms are satisfactorily predicted by the model using the Henry constants for the pure components(62). The model is less satisfactory for mixtures such as C_2H_4-C_3H_8 or C_2H_4-CO_2(62).

The extension of the Dubinin-Polanyi theory to mixed sorbates and other methods of estimating mixture isotherms from single component data have been discussed by Schirmer et al.(63,64). The most general method yet proposed is the ideal adsorbed solution theory of Myers and Prausnitz(65). This theory has been found very satisfactory for adsorbents such as silica gel but it is less satisfactory for zeolites. Implicit in the formulation of this theory is the assumption that the sorbate is thermodynamically inert and acts merely as a container for the adsorbed phase. For many zeolitic systems this is unlikely to be true. Some further difficulties in the practical application of this theory have been pointed out by Danner and Wenzel(66).

KINETICS OF SORPTION

Commercial molecular sieve pellets consist of small crystals of zeolite formed into a macroporous pellet with the aid of a day binder. In addition to the mass transfer resistance of the external fluid film there are therefore two distinct diffusional resistances; the macropore resistance of the pellet and the micropore resistance of the actual zeolite crystals. In principle there is also the possibility of a rate process associated with the adsorption/desorption step at the crystal surface but for most zeolitic systems this step is rapid, so that the assumption of local equilibrium at the crystal surface is a good approximation. External film resistance may be minimized by maintaining a sufficiently high fluid velocity and in most industrial adsorbers the rate of mass transfer is controlled either by macropore or by micropore diffusion or by a combination of these processes. Variationof the gross pellet size provides a simple and convenient experimental test for macropore resistance. Macropore diffusion may occur by either Knudsen flow or by molecular diffusion but in either case the process is fairly well understood and the diffusional time constant can be estimated with some confidence.

For the diffusion of ethane and butane in 5A sieve it has been shown that the intrinsic rate of micropore diffusion within the zeolite crystals is not significantly affected by pelletization. Under properly selected conditions of micropore diffusion control uptake rates in commercial pelleted sieve were found to be essentially the same as for the unaggregated crystals(119,120). By contrast, for the 4A sieve, diffusion rates in the pelleted sieve were considerably lower than in the pure crystals. This difference appears to be due to the somewhat lower thermal stability of the 4A sieve. From a detailed study of the pellization process Kondis and Dranoff(121) concluded that the reduction in diffusivity arises from partial disintegration of the zeolite crystal surfaces as a result of high temperature steam treatment during the pelletization process. It is therefore evident that comparisons between kinetic data obtained with crystals and pellets may not always be valid, particularly for the 4A sieve.

Diffusion within the micropores of the zeolite crystal is less well understood than macropore diffusion although in recent years the phenomenon has been widely studied. Zeolitic diffusion differs fundamentally from both Knudsen and molecular diffusion since the diffusing molecules never escape from the force field of the surrounding crystal. Zeolitic diffusivities are in general strongly concentration dependent and they show also the strong exponential temperature dependence characteristic of an activated rate process.

The true driving force for a diffusive transport process is the gradient of chemical potential rather than the concentration gradient(122) and the Fickian diffusivity (D) is therefore related to the corrected diffusivity (D_o) by:

$$D = D_o(d\ln a/d\ln c) = D_o(d\ln p/d\ln c)$$

In an adsorbed phase, ideal behaviour ($d\ln p/d\ln c = 1$) is approached only in the low concentration limit (Henry's Law region) and at higher concentrations the activity correction term $d\ln p/d\ln c$ is a strong function of concentration. Although both D and D_o are in principle concentration dependent it is evident that the concentration dependence of D_o will in general be less pronounced as a consequence of elimination of the thermodynamic factor. Corrected diffusivities show a clear correlation with the size of the zeolite window and the diameter of the diffusing molecule. However, in much of the early work these regularities of behaviour were overlooked because the importance of the thermodynamic factor was not recognized.

Experimental Measurement of Zeolitic Diffusivities

The simplest method of determining the zeolitic diffusivity depends on the analysis of experimental transient adsorption or desorption curves. Such curves may be measured either volumetrically or gravimetrically but the gravimetric technique has been found to be particularly convenient. For a system of uniform spherical particles subjected to a step change in surface concentration at time zero, the uptake curve will be given by the familiar solution of the diffusion equation:

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot \exp(-n^2\pi^2 Dt/r^2) \qquad (23)$$

or, in the initial region:

$$\frac{m_t}{m_\infty} = \frac{2A}{V} \sqrt{\frac{Dt}{\pi}} \qquad \text{(valid for } m_t/m_\infty < \sim 0.25) \qquad (24)$$

where, for spherical particles, $A/v = 3/r$. Thus, by matching the experimental uptake curve to equation 23 or equation 24, the diffusional time constant (r^2/D), and hence the diffusivity may be determined.

In order to obtain reliable data by this method several precautions are necessary(67,68).

(i) It is necessary to ensure that, under the experimental conditions, the sorption rate is determined by zeolitic diffusion and not by other rate processes. With a single component adsorbate there is no external film resistance but macropore diffusional resistance may be significant. If the adsorbent is in pelleted form the particle size should be varied to confirm the absence of significant macropore resistance. This difficulty can be minimized by the use of unaggregated crystals rather than pellets but even then, for rapid sorption processes, the bed of crystals may offer some diffusional resistance and it is therefore desirable to make replicate experiments with different depths of adsorbent sample.

(ii) In the derivation of equation 23 it is assumed that the surface concentration remains constant after the initial step change. The system must therefore be sufficiently large to ensure that the pressure does not vary significantly as a result of the material adsorbed or desorbed during the course of the experiment. Changing the total weight of the zeolite sample provides a convenient test of this approximation.

(iii) Since both the zeolitic diffusivity and the final position of equilibrium are strongly temperature dependent it is important that isothermal conditions be maintained(69). Because of the large heat of adsorption this can prove difficult to achieve.

(iv) Zeolitic diffusivities are, in general, strongly concentration dependent. The rate of uptake in an integral sorption measurement therefore depends on the interval over which the sorption curve is measured and, for the same interval, is different for adsorption and desorption steps. When the interval is sufficiently small that it can be considered as a differential measurement the rate of sorption becomes independent of the step size and the same for adsorption and desorption. Varying the step size and measuring both adsorption and desorption rates therefore provides a convenient means of verifying that the true differential diffusivity is indeed being measured. This test also confirms the absence of significant thermal effects and the absence of any significant surface adsorption rate process since in a surface controlled adsorption process the rates of adsorption and desorption will generally be different.

The requirement for differential measurements makes it necessary to use an accurate microbalance system. Most of the earlier diffusivity data reported in the literature were derived from integral measurements and the interpretation of these data is therefore often ambiguous. Variation of the step size in an <u>integral</u> measurement does not provide a sensitive test for concentration dependence of the <u>differential</u> diffusivity. For the forms of concentration dependence commonly encountered in zeolitic systems, it may be shown that, when the step change is large, the integral diffusivity becomes insensitive to the size of this step although the magnitude of the integral diffusivity may still be much larger than the true differential diffusivity at the average concentration.

(v) Since zeolitic diffusivities are strongly influenced by traces of moisture(70), or other strongly adsorbed species, it is necessary to pay particular attention to the degassing procedure and the purification of adsorbates. For types A and X zeolites a minimum period of 12 hours at 10^{-5} torr, 400°C seems adequate for initial degassing. Somewhat shorter periods are adequate for subsequent experiments.

(vi) It is necessary to use crystals of high quality since strucural defects and grain boundaries can have a significant effect on the uptake rate(70). This problem is more severe with natural zeolites since the crystals of the synthetic zeolites are generally smaller with fewer imperfections.

(vii) Equation 24 is applicable to particles of any shape and size distribution and if the diffusion process is sufficiently slow so that the initial portion of the uptake curve can be measured, this equation provides a simple and useful method of analysis. For many systems the uptake is too rapid for the initial portion of the curve to be measured with any accuracy and in such cases it is necessary to analyse the later portion of the curve using equation 23 or equivalent. The later portion of the curve is quite sensitive to particle shape and size distribution and the assumption of a single mean equivalent spherical radius can cause significant error. To obtain reliable diffusivities for the faster sorption processes it is therefore necessary to use, in place of equation 23, a more complex equation based on the appropriate crystal shape and including a correction for the distribution of crystal size(67).

As an alternative to the conventional gravimetric or volumetric methods, various chromatographic techniques for measuring zeolitic diffusivities have been developed. These methods depend on the fact that the spread of a chromatographic peak is determined by the mass transfer resistance. To avoid excessive pressure drop it is necessary to pack the column with pelleted molecular sieve, of small particle size, rather than with unaggregated crystals. In order to estimate zeolitic diffusivities the contributions to the mass transfer resistance from external film and macropore resistance must therefore either be eliminated by the experimental technique or allowed for in the analysis. This may be achieved by making measurements over a range of carrier gas velocities either with two different carrier gases or with particles of different size.

The resulting experimental data may be analyzed in either of two different but equivalent ways. The method used by Eberly(71) depends on the use of the van Deemter equation(72) relating the HETP to the gas velocity:

$$\text{HETP} = A + \frac{B}{u} + Cu \qquad (25)$$

The constant C, which may be found from the limiting slope of the plot of HETP vs u as $u \to \infty$, is related to the diffusional time constants for both macropore and micropore diffusion processes. A variant of this method involving the use of two different carrier gases to eliminate the macropore contribution was used by MacDonald and Habgood(73). The alternative method of moments analysis has been used by several different groups of workers(74-76).

The chromatographic method is based on the assumptions of a linear isotherm and a constant diffusivity. It is generally assumed that these assumptions will be fulfilled provided that the pulse of sorbate is sufficiently small relative to the carrier gas flowrate. However, for certain zeolitic systems the diffusivity is strongly concentration dependent even within the Henry's Law region and, for such systems, the diffusivity determined from a chromatographic experiment will be an integral value which depends on the size of the pulse and the carrier flowrate. There are several systems for which diffusivities have been measured, under comparable conditions, by both chromatographic and gravimetric methods but the agreement is generally poor. For the systems studied by Eberly(71) (Ar-5A, Kr-5A, SF_6-13X) the discrepancy is attributable to the concentration dependence of the diffusivity. For these systems measurements of the differential diffusivity by the gravimetric method show that, within the Henry's Law region(57):

$$D_o = \frac{D'_o}{c} \qquad (26)$$

where D'_o is a constant which varies with temperature according to an Arrhenius equation:

$$D'_o = D'_* e^{-E/RT} \qquad (27)$$

Within the Henry's Law region c = Kp and K varies with temperature according to equation 3 so that:

$$D = \frac{D'_*}{K_o p} \cdot e^{-(E + q_o)/RT} \qquad (28)$$

The precise value of the integral diffusivity determined in a chromatographic experiment will depend on the pulse size but it is clear from equation 28 that if the pulse size is kept constant and the temperature varied the apparent energy of activation (E_a) will be given by $E_a = E + q_o$. The values of E_a determined by Eberly agree well with the values of $E + q_o$ from the gravimetric measurements as may be seen from table III.

When the assumptions of a linear isotherm and a constant diffusivity are fulfilled and provided the experimental conditions are such that the major contribution to the mass transfer resistance arises from intracrystalline diffusion, the diffusivities obtained by the chromatographic method should agree with the values determined directly from transient sorption curves. These conditions are fulfilled for the diffusion of Ar in 4A sieve at room temperature and for this system the chromatographic diffusivities reported by Sarma and Haynes(123) are in reasonable agreement with the gravimetric data of Ruthven and Derrah(57). These conditions

TABLE III

Comparison of Values of $E + q_o$ with Apparent Activation Energies from Chromatographic Data

System	q^*_o (Kcal)	$E^\dagger$ (kcal)	$E + q_o$ (kcal)	$E_a^\ddagger$ (kcal)
Ar-5A	3.3	<<1	3.4	3.5
Kr-5A	3.6	2.0	5.6	5.9
SF_6-13X	5.0	2.8	7.8	7.5

* Values of q_o from Eberly(71) at high temperatures.

† Values of E calculated according to equation 26 and 27 from gravimetric data.

‡ Apparent activation energy from chromatographic measurements(71).

should also be fulfilled for the nC_4H_{10}-5A system at low concentrations but, for this system, the diffusivity data obtained chromatographically by Hashimoto and Smith$^{(76)}$ are very much larger than the gravimetric values of Ruthven and Loughlin$^{(77)}$. The origin of this discrepancy is not clear but it may be related to the difficulty of correctly evaluating the second moments of the chromatographic peaks which, exhibit considerable tailing when micropore diffusion resistance is significant. For the butane-5A system this problem is compounded by the need to extrapolate the second moment values in order to eliminate contributions from macropore resistance.

The analysis of breakthrough curves for a packed column subjected to a step change in feed concentration is, in principle, a variant of the chromatographic method. For systems in which the mass transfer rate is essentially controlled by zeolitic diffusion it has been shown that diffusivities calculated from the uptake curves agree well with the gravimetrically measured values$^{(78)}$.

The advantages of the chromatographic method lie in the simplicity of the apparatus and the rapidity with which measurements can be made. This makes the method useful for the approximate determination of overall mass transfer coefficients and difficulties only arise when one attempts to separate out the individual contributions from film, macropore and micropore resistance. Macropore diffusivities can be determined with some accuracy since variation of the particle size or carrier gas provides a simple method of varying this contribution. However it appears that for the determination of zeolitic diffusivities the chromatographic methods are in general less reliable and convenient than conventional gravimetric methods.

Tracer Diffusivities

The relationship between the diffusivity measured in a sorption experiment (D) and the tracer self diffusivity $\mathcal{D}$ has been derived by Ash and Barrer$^{(79)}$ and Kärger$^{(80)}$ from the principles of irreversible thermodynamics:

$$D = \frac{\mathcal{D}}{\left(1 - \dfrac{c_A L_{A*A}}{c_{A*} L_{AA}}\right)} \cdot \frac{\partial \ln a_A}{\partial \ln c_A} \qquad (29)$$

or, for an ideal vapour phase:

$$D = \frac{\mathcal{D}}{\left(1 - \dfrac{c_A}{c_{A*}} \dfrac{L_{A*A}}{L_{AA}}\right)} \cdot \frac{\partial \ln p}{\partial \ln c} \qquad (30)$$

where the derivative $\partial \ln p/\partial \ln c$ represents the gradient of the equilibrium isotherm, plotted in logarithmic coordinates. At sufficiently low sorbate concentrations the isotherm becomes linear ($\partial \ln p/\partial \ln c \rightarrow 1.0$) and encounters between the diffusing molecules become increasingly infrequent so that $L_{A*A} \rightarrow 0$. As the sorbate concentration approaches zero the limiting diffusivity (D_o) therefore becomes identical with the tracer self diffusivity ($\mathcal{D}$). For many zeolitic systems it appears that the cross coefficient L_{A*A} is quite small, even at relatively high sorbate concentrations. For such systems, equation 30 reduces simply to Darken's equation(81):

$$D = \mathcal{D} \cdot \frac{\partial \ln a}{\partial \ln c} = D_o \frac{\partial \ln p}{\partial \ln c} \qquad (31)$$

which was originally derived for interdiffusion in binary alloys. This equation may also be obtained directly if it is assumed that the driving force for the zeolitic transport process is the gradient of chemical potential, rather than the concentration gradient(82,83). For most common shapes of isotherm the activity correction term $\partial \ln p/\partial \ln c$ increases rapidly as the sorbate concentration approaches saturation. Thus if D_o (or $\mathcal{D}$) is independent of concentration equation 31 predicts a monotonic increase at the diffusivity D with increasing sorbate concentration. Such behaviour has been observed experimentally for several systems (see below).

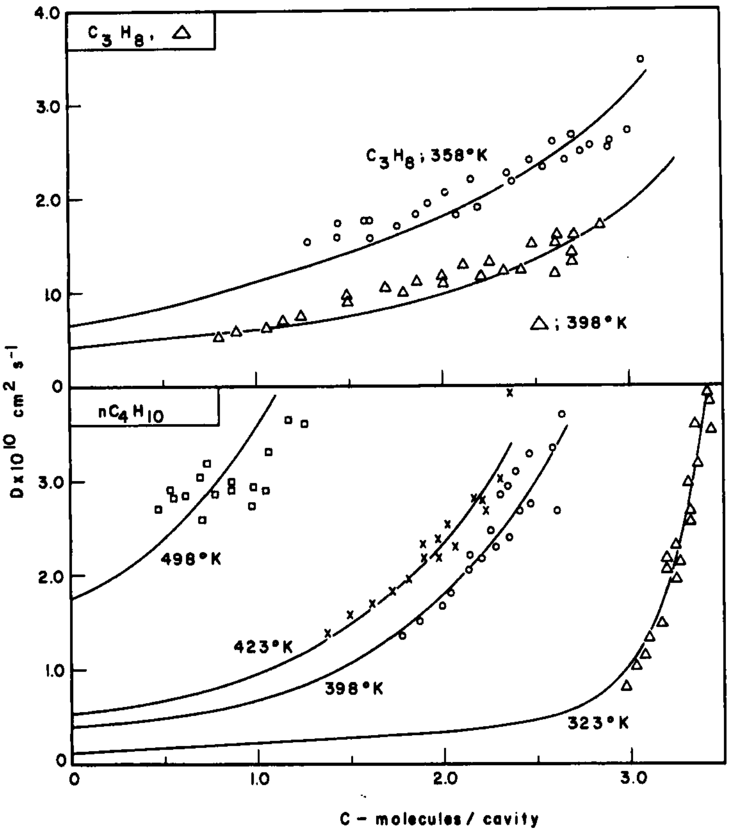
There are only a few systems for which both differential diffusivities and tracer self diffusivities have been determined under comparable conditions. For the diffusion of water in various natural zeolites Barrer and Fender(84) showed that the concentration dependence of the diffusivity could be largely accounted for by the activity correction term and that the limiting diffusivity was essentially equal to the tracer self diffusivity. These data were later re-analyzed by Barrer(5) who suggested that there was evidence of a small additional concentration dependence arising from the term $c_A L_{A*A}/c_{A*} \cdot L_{AA}$ in the denominator of equation 30. Tracer diffusivities ($\mathcal{D}$) for CO_2 in 4A and 5A sieves have been determined by Rees(85) and Sargent and Whitford(86). These values are in order of magnitude agreement with the limiting diffusivities (D_o) determined in this laboratory. However, the limiting diffusivities are concentration dependent so detailed comparisons are not possible without additional tracer data.

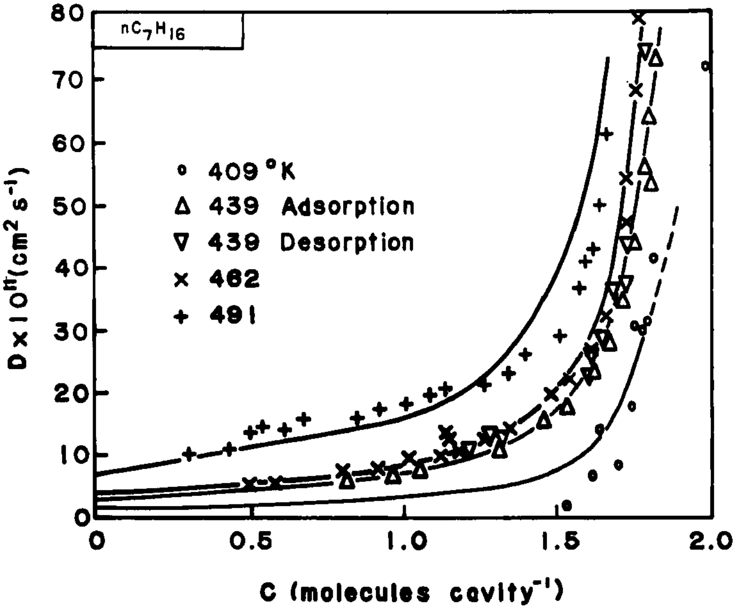
Although both D and $\mathcal{D}$ are, in principle, concentration dependent it may be seen from equation 30 that the concentration dependence of D will be the more complex since it arises from the combined effect of three separate terms. For fundamental analysis of the transport process the self diffusivity $\mathcal{D}$ or the limiting diffusivity D_o are clearly the more important parameters.

Diffusion of Hydrocarbons in Small Port Zeolites (Type A, Erionite and H-Chabazite)

The diffusivities of the light hydrocarbons in 5A zeolite are strongly concentration dependent, increasing rapidly as saturation is approached. Representative data are shown in figure 7(87). The concentration dependence of the differential diffusivity can be quantitatively accounted for by equation 31 with a constant value of D_o. The temperature dependence of D_o follows the usual Eyring equation:

$$D_o = D_* e^{-E/RT} \qquad (32)$$


C_3H_8, △
C_3H_8; 358°K
△; 398°K
nC_4H_{10}
498°K
423°K
398°K
323°K
$D \times 10^{10}$ cm^2 s^{-1}
4.0
3.0
2.0
1.0
0
0
1.0
2.0
3.0
C – molecules / cavity


nC_7H_{16}
○ 409 °K
△ 439 Adsorption
▽ 439 Desorption
× 462
+ 491
$D \times 10^{11}$ (cm^2 s^{-1})
80
70
60
50
40
30
20
10
0
0
0.5
1.0
1.5
2.0
C (molecules cavity^{-1})

The diffusional activation energies may be correlated with the critical diameter of the sorbate molecules, as may be seen from Table IV, suggesting that the rate limiting step in the transport process is the passage of the sorbate molecules through the relatively small windows between adjacent cavities. The data for the isomeric butenes are of particular interest since 1-butene and trans-2-butene have the same critical diameter and the same activation energy as propylene. The critical diameter of the isomeric cis-2-butene is appreciably larger and this is reflected in the much larger activation energy. However, the critical diameter is not the only important parameter. For the longer chain species there is also an effect of chain length as shown in figure 6. The simple monotonic increase in activation energy with hydrocarbon chain length is in marked contrast with the complex behaviour reported by Gorring(91) for diffusion in zeolite T, a synthetic intergrowth of erionite and offretite. The limited data available for diffusion in erionite and chabazite conform to the general trend of the 5A data. It thus seems possible that Gorring's results may have been complicated by the effects of a concentration dependent diffusivity. Clearly, if the diffusivity is concentration dependent (according to equation 31) the apparent energy of activation of D will arise from the combined effects of the temperature dependence of D_0 and $\partial \ln p/\partial \ln c$. The apparent activation energy of an integral diffusivity will be even more complex.

FIGURE 7

Variation of diffusivity with sorbate concentration for light hydrocarbons in 5A zeolite. The points are experimental values while the lines are calculated according to equation 31 with constant values of D_0 using the activity correction factors ($\partial \ln p/\partial \ln c$) calculated from the experimental equilibrium isotherms. ($\Delta \equiv$ cyclopropane; from references (55, 87), with permission of Canadian Journal of Chemistry).

TABLE IV

Systems in which Critical Molecular Diameter is Greater than or Equal to Window Aperture: Parameters E and D* giving Temperatures Dependence of Limiting Diffusivity D_0

System	σ (Å)	E (kcal)	Experimental $D_* \times 10^8$ ($cm^2.sec^{-1}$)	Theoretical Values Rotating $D_* \times 10^8$ ($cm^2.sec^{-1}$)	Theoretical Values Non-Rotating $D_* \times 10^8$ ($cm^2.sec^{-1}$)
Ar-4A	3.4	5.8	122	-	103
O_2-4A	3.5	4.53	660	132	2.4
Kr-4A	3.6	8.1	9.7	-	13
N_2-4A	3.7	6.1	96	266	7.0
C_2H_4-4A	4.08	8.5	61	3550	5.0
C_2H_4-5A	4.08	2.75	0.198	132	0.24
C_2H_4-Erion.	4.08	2.34	0.36	830	1.26
CH_4-4A	4.08	7.4	5.8	(172)	(6.22)
CH_4-5A	4.08	2.98	7.2	172	6.22
C_2H_6-4A	4.36	6.24	5.66	-	-
C_2H_6-5A	4.36	1.28	3.02	332	1.01
C_2H_6-Erion.	4.36	4.3	6.6	1100	3.1
C_3H_6-5A	4.95	3.46	0.25	96	0.008
1-C_4H_8-5A	4.95	3.44	0.18	1660	0.062
tr-2C_4H_8-5A	4.95	3.46	0.26	750	0.028
C_3H_8-4A	5.1	8.7	1.24	(90)	(0.014)
C_3H_8-5A	5.1	3.5	0.82	90	0.014
*C_3H_8-Chab.	5.1	4.04	-	-	-
nC_4H_{10}-4A	5.1	8.5	0.42	(57)	(0.0021)
nC_4H_{10}-5A	5.1	4.0	0.73	57	0.0021
nC_4H_{10}-Chab.	5.1	4.16	-	-	-
nC_5H_{12}-5A	5.1	4.6	0.63	-	-
nC_5H_{12}-Erion	5.1	5.0	0.09	-	-
nC_5H_{12}-Chabz	5.1	4.95	-	-	-
nC_7H_{16}-5A	5.1	7.5	15.0	1000	0.0025
cyclo-C_3H_6-5A	5.2	4.34	1.06	25	0.015
CF_4-5A	5.44	9.15	250	192	0.034
cis-2-C_4H_8-5A	5.58	9.2	151	-	-

The data are correlated according to equations 31 and 32 (D_0 independent of c). The critical diameter σ is defined as the radius of the smallest cylinder which can circumscribe the molecule in its most favourable equilibrium conformation. Window aperatures are about 3.4Å for 4A sieve and 4.3Å for 5A. Values for 4A, 5A and erionite are from data obtained in these laboratories(55-58,87,88). Values for H-chabazite are from Barrer and Davies(25). The calculation of the theoretical values of D_* for CH_4 and CF_4 is discussed in detail by Ruthven and Derrah(88).

From transition state theory it follows that the limiting diffusivity is given by$^{(88)}$:

$$D_o = \left(\frac{\delta^2}{6h}\right) \frac{1}{K_o} \left(\frac{f^*_z}{f'_g}\right) \exp\left(-\frac{(u' + q_o)}{RT}\right) \qquad (33)$$

or

$$D_* = \frac{\delta^2}{6hK_o} \frac{f^*_z}{f'_g} \quad ; \quad E = u' + q_o \qquad (34)$$

where f^*_z/f'_g is the ratio of the partition function for the transition state to the partition function per unit volume for the free gaseous species. If the internal freedom of the molecule is not significantly altered in the transition state and if there is no significant freedom of motion in the plane of the window, which is a valid assumption for molecules with critical diameters greater than or equal to the window aperature, then, for the extreme cases of a freely rotating and a non-rotating transition state, we have:

<u>free rotation</u>

$$\frac{f^*_z}{f'_g} = \frac{1}{f'_{trans}} = \frac{1}{(2\pi mkT/h^2)^{3/2} e} \qquad (35)$$

<u>no rotation</u>

$$\frac{f^*_z}{f'_g} = \frac{1}{f'_{trans} f_{rot}} = \frac{1}{(2\pi mkT/h^2)^{3/2} e \; (8\pi IkT/h^2)^{3/2} \sqrt{\pi}/\sigma} \qquad (36)$$

Equation 34 and 35 or 36 may be used to calculate values of D_* for these two extreme cases and the values so obtained are given in Table IV. It may be seen that for the small hydrocarbon molecules (CH_4, C_2H_6, C_2H_4) the experimental values are close to the theoretical values for a non-rotating transition state while for the longer chain molecules the experimental values are intermediate between the rotating and non-rotating values. This suggests that the repulsive interaction with the oxygen ions of the window is sufficient to suppress the rotation of the smaller molecules but with the larger molecules a significant contribution from rocking vibration is to be expected. Whereas the data for CH_4 suggest a non-rotating transition state, it appears that CF_4 is freely rotating. This difference is understandable in view of the very much larger moment of inertia and the correspondingly greater rotational partition function(88).

Diffusion in 4A zeolite is very much slower due to the smaller effective diameter of the window. This difference is reflected in a higher diffusional activation energy and the pre-exponential factors are essentially the same, as is to be expected from equation 33 since the values of K_0 are similar.

Diffusion in the partially ion exchanged forms of the A zeolite (intermediate between 4A and 5A) has also been investigated(111-113). The diffusivities show an abrupt increase when about 33% of the original Na^+ ions have been replaced by Ca^{++}. This corresponds to the composition at which the obstructing Na^+ cations are removed from one third of the windows so that each cell has, on average, two unobstructed windows. When more than 67% of the Na^+ ions are replaced all windows are unobstructed and the diffusional properties become essentially the same as those of the pure CaA (5A) sieve. The changeover from 4A to 5A sieve therefore occurs almost entirely over the range 33-67% Na^+ exchange(113).

Diffusion in erionite has been studied less extensively(56) but the limited data available (figure 8 and table IV) indicate that the behaviour is essentially similar to that of the type A zeolites, as is to be expected from simple structural considerations. The concentration dependence of the diffusivity for light hydrocarbons (C_2H_6, C_2H_4, nC_5H_{12}) follows equation 31 with a constant value of D_0. The diffusional activation energy for ethane in erionite is somewhat larger than in 5A whereas for ethylene the activation energies are almost the same. This may be explained by the difference in the shape of these molecules. The three

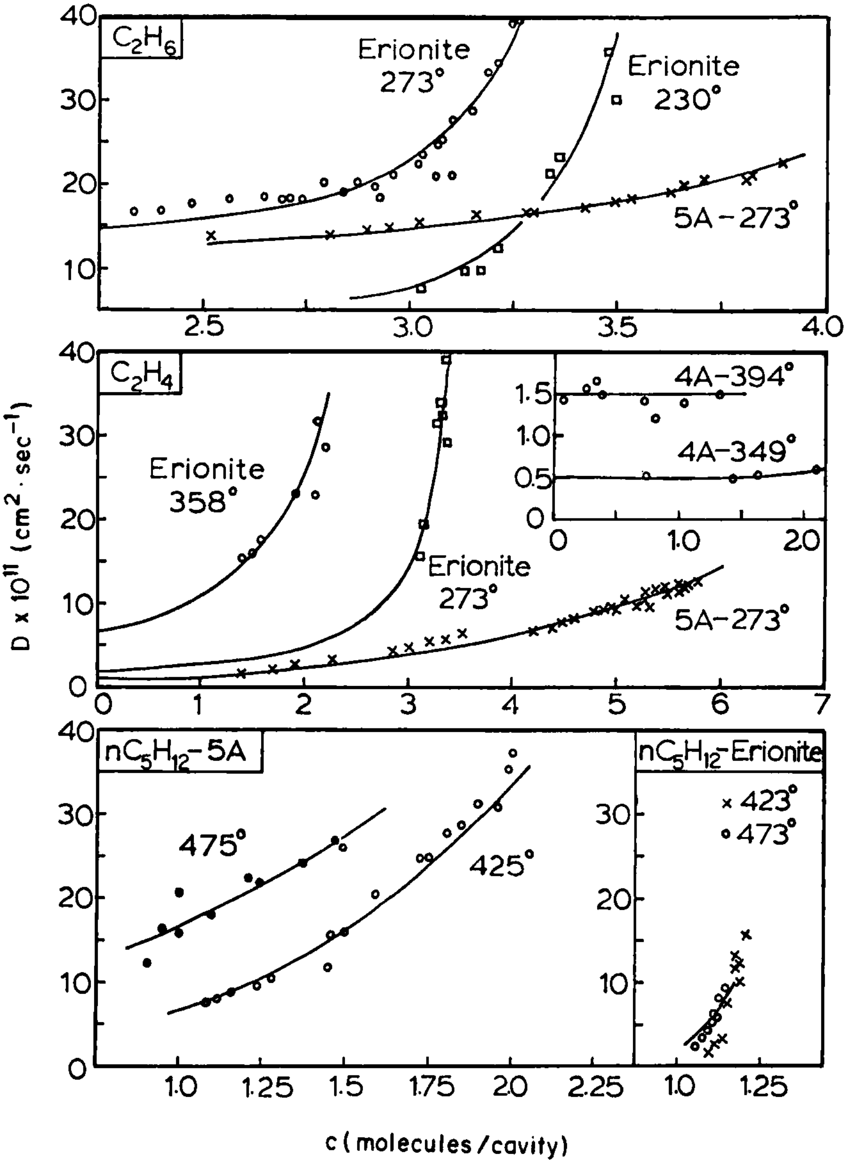


FIGURE 8

Comparison of diffusivity data for light hydrocarbons in erionite and in type A zeolites. The points are experimental values while the lines are calculated according to equation 31 with constant values of D_0, using the activity correction factors ($\partial \ln p/\partial \ln c$) calculated from the equilibrium isotherms. (From reference (56) with permission of Journal of Colloid and Interface Science).

dimensional ethane molecule will encounter a higher energy of repulsion in passing through the distorted octagonal window of erionite, as compared with the symmetric window of the A type zeolite whereas the repulsion energy for the planar ethylene molecule will be about the same for both windows.

Diffusion of light paraffins in H-chabazite was studied by Barrer and Davies(25) who observed a similar pattern of behaviour to that observed for 5A and erionite. The concentration dependence of the diffusivity could be adequately correlated by equation 31 and the diffusional activation energies are similar to the values for 5A and erionite. Since the windows of the chabazite structure are essentially similar to those of erionite and 5A (8-membered oxygen rings) such similarity of behaviour is not unexpected.

Diffusion of Monatomic and Diatomic Gases in Type A Zeolites

In 4A zeolite the monatomic and diatomic gases (Ar, Kr, O_2, N_2) show a very similar pattern of behaviour to that which is observed for the hydrocarbons in 5A(57). The diffusivities are constant within the Henry's Law region and increase monotonically according to equation 31 at higher sorbate concentrations. The magnitude of the observed diffusivities can be satisfactorily accounted for by transition state theory as may be seen from Table IV. For the monatomic species there is no possibility of molecular rotation. The values of D_* for O_2 and N_2 suggest a freely rotating transition state (particularly for O_2) but the difference between the values for rotating and non-rotating cases is smaller than for the larger hydrocarbon molecules so the evidence is less conclusive.

By contrast, in the 5A zeolite, an entirely different pattern of concentration dependence is observed as illustrated in figure 9. At low concentrations, within the Herny's Law region, the diffusivity decreases rapidly with increasing concentration passing through a minimum at about one third of saturation and increasing again at high concentrations. This profound difference in the

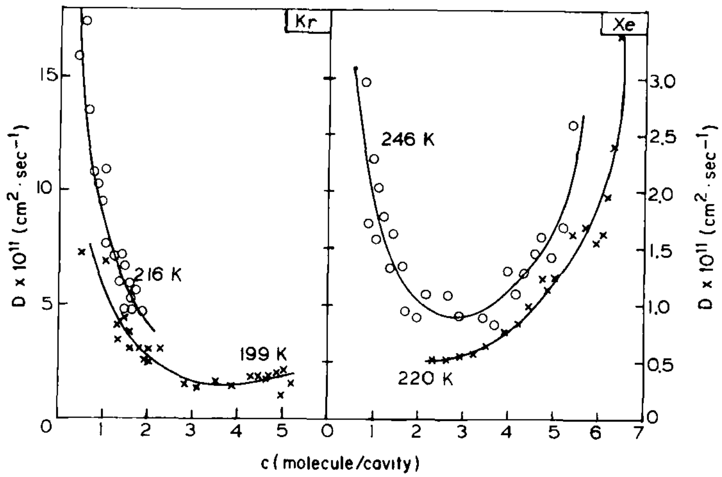


FIGURE 9

Variation of diffusivity with sorbate concentration for Kr and Xe in 5A zeolite.

pattern of concentration dependence suggests a difference in the transport mechanism. For all species studied (Ar, Kr, Xe, O_2, N_2) the corrected diffusivities (D_0), calculated according to equation 31, were found to be inversely proportional to sorbate concentration (equation 26 and 27). This type of behaviour is illustrated in figure 10 which shows a log-log plot of D_0 vs c and in figure 11 in which the behaviour of O_2 in 4A and 5A zeolites is compared. This is the form of concentration dependence which is observed for ordinary molecular diffusion in the gas phase and it is therefore suggestive of a collisional diffusion mechanism in which the mean free path of the diffusing molecule is determined by intermolecular collisions. It has been shown that both the form of the concentration dependence of D_0 and the orders of magnitude of D'_* and the diffusional activation energy can be accounted for in terms of a simple mechanism in which it is assumed that transport is due primarily to the small fraction of adsorbed molecules which are moving

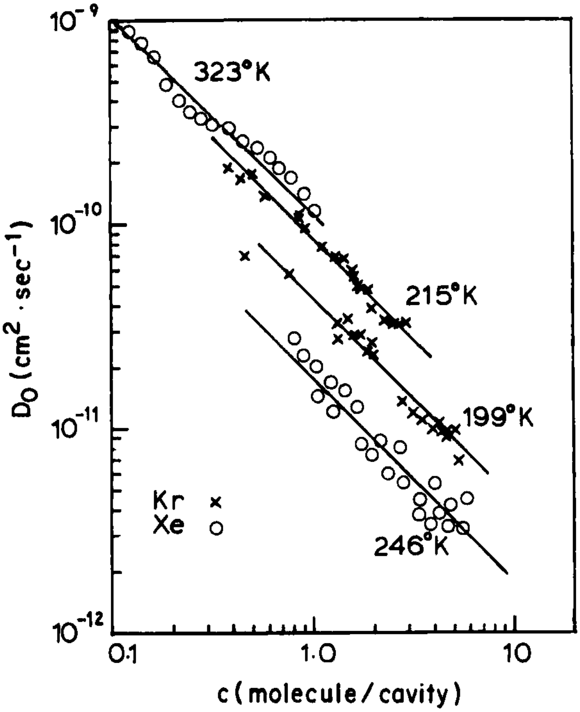


FIGURE 10

Log-Log plot showing variation of corrected diffusivity (D_O) with sorbate concentration for Kr and Xe in 5A zeolite. Values of D_O are calculated according to equation 31 using the values of the activity correction factor ($\partial \ln p/\partial \ln c$) from the equilibrium isotherms. The solid lines have slope -1.0 in accordance with equation 26. (The data for Kr at 199°K and 215°K and for Xe at 246°K are the same as the points shown in figure 9).

rapidly along the axes through the centres of successive windows with a mean free path inversely proportional to the fraction of occupied cavities(57).

The essential factor which governs the nature of the diffusion mechanism is the size of the sorbate molecule relative to the window aperature since it is this which determines the magnitude of the energy barrier between cavities. When the diffusing molecule

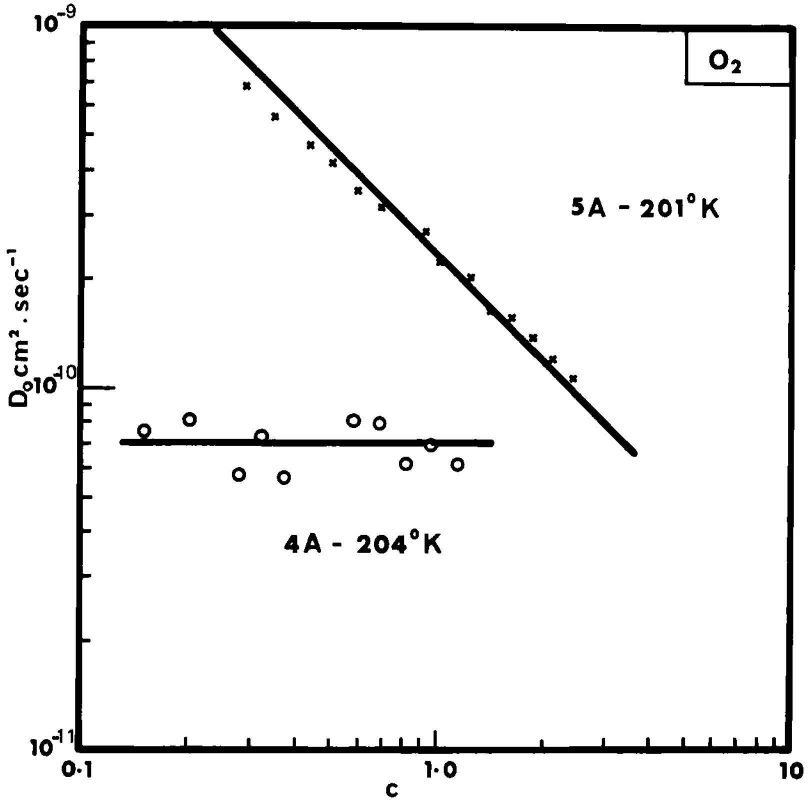


FIGURE 11

Comparison of diffusivity of O_2 in 4A and 5A zeolites. The ordinate is the corrected diffusivity calculated according to equation 31 but at concentrations below 1 molecule per cavity the activity correction factor $\partial \ln p / \partial \ln c$ is always close to 1.0. The data show the corrected diffusivity to be essentially constant for 4A and to vary according to equation 26 for 5A.

is relatively large (monatomic and diatomic species in 4A or hydrocarbons etc. in 5A) only a small fraction of the molecules striking a window will pass successfully to the next cavity and the critical assumption of transition state theory (equilibrium with the transition state) is thus fulfilled. When the diffusing molecule is small relative to the window aperature, as is the case for the monatomic and diatomic species in 5A zeolite, the molecules can pass with relative ease between cavities. Under these conditions the molecule in the window can no longer be identified with the transition state and it appears that a collisional diffusion mechanism becomes dominant.

Diffusion in 13X Zeolite

The microporesof the X and Y zeolites, which contain only 12-membered oxygen windows (free diameter ∿ 7.4Å), are much larger than those of the type A zeolites and erionite which are interrupted by 8-membered windows. This difference is reflected in the ability to adsorb much larger molecules, including branched chain, aromatic and cyclic hydrocarbons, and in generally faster diffusion rates. The commercial X and Y zeolites are available only as very small crystals (∿ 1 micron) and the diffusional time constants (r^2/D) for most species are too small to measure by the gravimetric method. In order to determine reliable values for zeolitic diffusivities in these adsorbents it is therefore necessary to use specially prepared crystals of larger size.

In this laboratory diffusivities have been determined for several hydrocarbons(124) and SF_6(125) in a specially prepared 13X zeolite. The results are summarized in Table V. The critical diameters of all these species are less than 7.4Å and the diffusivities show the same type of concentration dependence as for the monatomic and diatomic molecules in 5A zeolite (equations 31, 26, 27). Representative data are shown in figures 12 and 13. Only the data for SF_6 have so far been analyzed in detail. It appears that these data can be interpreted in terms of the same theoretical model as for the monatomic and diatomic molecules in 5A on the assumption that the SF_6 molecule is freely rotating. For the hydrocarbons however it seems that molecular rotation must be to some extent restricted but this makes a quantitative analysis of the data more difficult.

TABLE V

Systems in which Critical Molecular Diameter is Smaller than Window Aperture: Parameters E and D'_* giving Temperature Dependence of D'_o.

System	σ (Å)	E (kcal)	$D'_* \times 10^7$ (molecule·cm^2/cavity·sec)
Ar-5A	3.4	<<1.0	0.01
Kr-5A	3.6	2.0	0.077
Xe-5A	4.0	3.0	0.15
O_2-5A	3.5	1.0	0.026
N_2-5A	3.7	1.5	0.052
SF_6-13X	6.1	2.77	2.98
nC_7H_{16}-13X	5.1	6.2	22
C_6H_{12}-13X	6.5	4.96	10.2
C_6H_6-13X	6.5	4.9	4.9
$C_6H_5CH_3$-13X	6.5	6.6	6.6

The data are correlated according to equation 31, 26, 27 ($D_o = D'_o/c$; $D'_o = D'_* e^{-E/RT}$.

Free aperture of 5A sieve = 4.3Å and of 13X sieve = 7.4Å.

Data for 5A are from Ruthven and Derrah(57).

Data for 13X are unpublished results obtained by I.H. Doetsch in this laboratory

NMR Measurements

Nuclear magnetic resonance methods of studying the motion of adsorbed molecules have recently been applied to several zeolitic systems. The subject has been discussed by Resing and Murday(92) and by Pfeifer et al.(93). The experimental techniques are of two distinct kinds: the measurement of relaxation times and the direct

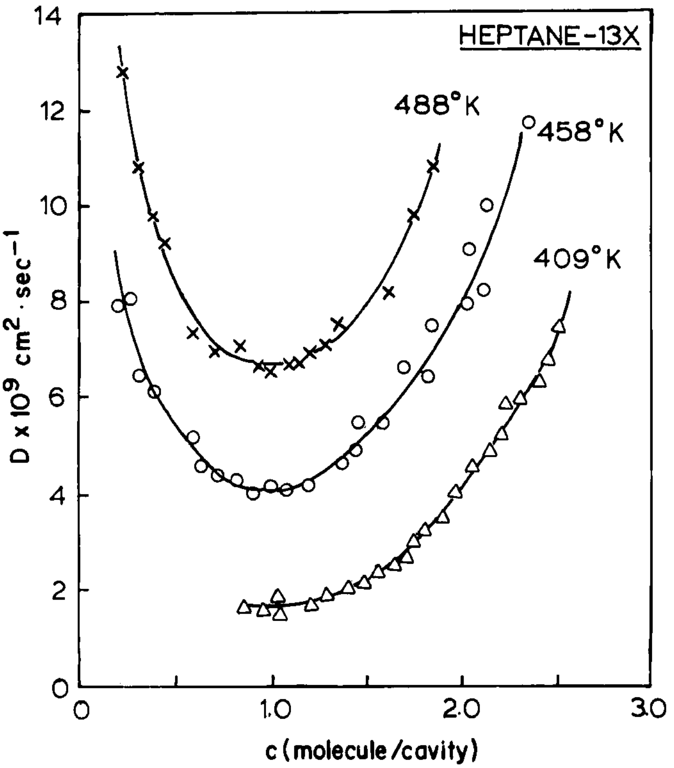


FIGURE 12

Variation of diffusivity for n-heptane in 13X zeolite with sorbate concentration.

measurement of the self diffusivity by the pulsed field gradient spin-echo method. The first of these methods depends on extracting from the relaxation time measurements the average time interval between successive translational jumps of the adsorbed species (τ). The self diffusivity is then calculated on the basis on an assumed mean jump distance λ:

$$\mathcal{D} = \frac{1}{6}\frac{\lambda^2}{\tau} \qquad (37)$$

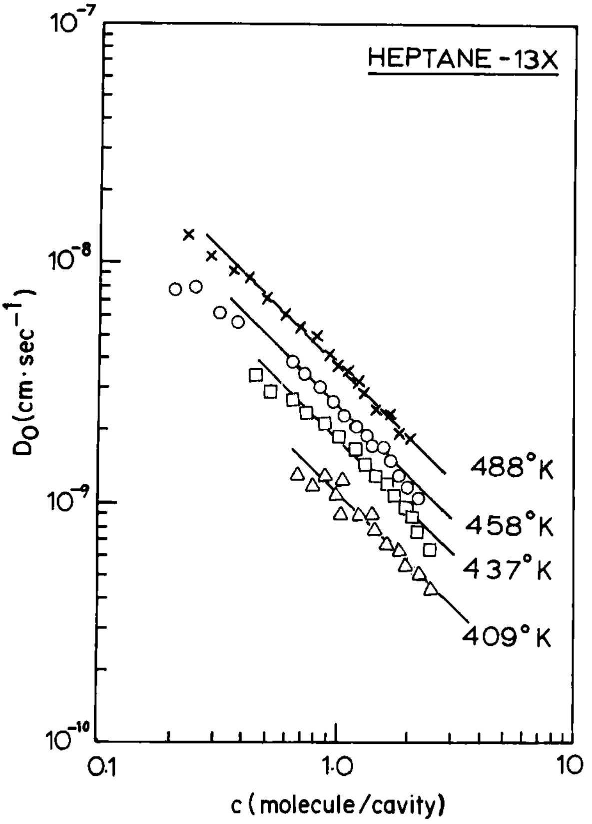


FIGURE 13

Log-Log plot showing the variation of corrected diffusivity D_0 with sorbate concentration for n-heptane in 13X zeolite. Values of D_0 are calculated according to equation 31 using the values of the activity correction factor ($\partial \ln p/\partial \ln c$) calculated from the equilibrium isotherms. The data points are the experimental points from figure 12 while the lines are drawn with slope -1.0 in accordance with equation 26.

The pulsed field gradient spin-echo method is more direct in that the self diffusivity is obtained from measurements of the loss of phase coherence in the transverse magnetization of the molecular nuclei due to the random translational motion of the molecules. These measurements yield directly the mean square distance travelled during the time interval of the experiment so that assumptions about the jump distance are not required.

The relaxation method has been used by Resing and Thompson to study the diffusion of SF_6(94,95) and H_2O(96) in 13X zeolite and by Pfeifer and co-workers at the University of Leipzig to study the diffusion of C_4 hydrocarbons in type A zeolites and cyclic and aromatic hydrocarbons in 13Y(97-100). The pulsed field gradient spin-echo method has been developed mainly by Kärger who has studied the systems H_2O-13X, 13Y, 5A(101,102); nC_4H_{10}-nC_7H_{16}-13X(103-104); C_6H_{12}-13X(105); CH_4-5A(106,107). Several of these sytems have been studied in this laboratory by the conventional gravimetric technique. The self diffusivities obtained by both the NMR techniques are self consistent but they are in general three to four orders of magnitude larger than the values of D_0 obtained, under similar conditions, by the gravimetric method. Despite this very large difference in the numerical values both the NMR data and the gravimetric data show similar trends. The relative values of the diffusivities for different species in the same zeolite, as determined both NMR and gravimetric methods, lie in the same sequence and the relative variation of NMR and gravimetric diffusivities with degree of ion exchange in the Na-Ca A zeolites is quantitatively similar(126). Furthermore both the NMR and gravimetric methods show that for the hydrocarbons in 5A the self diffusivity is almost independent of sorbate concentration whereas with the 13X zeolite there is an inverse concentration dependence.

Similar large discrepancies between diffusivities determined by NMR and by other methods have been found for diffusion in molecular solids but the reasons for this difference are still quite uncertain(108-110). The suggestion that adsorption methods actually determine the rate of diffusion through a surface layer, which may be much slower than diffusion in the interior of the crystal, can be disproved by analysis of the form of the uptake curves. These are consistent with a diffusion mechanism and inconsistent with a surface resistance model. Furthermore, if the energy barrier at the surface was high one would expect an appreciable difference between the rates of adsorption and desorption. The models developed to explain the gravimetric diffusion data imply that most of the molecules are, at any given instant, confined within particular cavities. Transitions between cavities are relatively infrequent events. If the NMR methods respond only to the molecules which are moving between cavities and do not "see" the molecules which are confined within a cavity the large numerical difference in the diffusivity values and the qualitative agreement concerning the trends of the diffusivities with concentration and for different sorbates could be explained. However such an explanation is not supported by the intensity of the NMR signals which are such as to suggest that all adsorbed molecules are "seen"(111).

Counter Diffusion Studies

The diffusivity data discussed above refer exclusively to the diffusion of single molecular species either with a net flux, as in a sorption experiment, or with no net flux as in a tracer measurement. In many industrial processes however one is concerned with a counter diffusion situation in which one component is diffusing into a crystal while another component is simultaneously diffusing out. It has been shown that diffusivities measured in a counter diffusion situation may be very much smaller than the diffusivities of the individual components(114-116). However further study of this phenomenon is required since it is not yet certain to what extent such effects arise from the change in the activity correction term ($\partial \ln p/\partial \ln c$) and to what extent they reflect actual changes in the magnitude of the intrinsic diffusivity (D_0 or $\mathcal{D}$). From theoretical considerations one would expect that in systems in which the diffusivity is determined primarily by the crystal lattice (i.e. when the molecular diameter is large in relation to the window aperature) the intrinsic diffusivity should not be significantly different in a counter diffusion situation. However, when the collisional diffusion mechanism is dominant a significant difference between the intrinsic diffusivity in a counter diffusion situation, as compared with a single component system, is not unexpected. These hypotheses have not so far been tested experimentally.

CONCLUSIONS

The topics covered by this review include only some of the more recent work in this area. The kinetic data in the literature show many apparent anomalies and contradictions but in many cases this seems to be because the pronounced concentration dependence of zeolitic diffusivities and the consequent necessity of making differential rather than integral measurements were not appreciated in much of the earlier work. The more recent data show much greater regularity with a clear correlation between the diffusional behaviour and the relative sizes of the sorbate molecule and zeolite window. An improved understanding of these phenomena should lead eventually to improved technology in the design and operation of adsorption separation processes. We are however still far away from a situation in which the kinetic and equilibrium data required for process design can be predicted for first principles.

This review is based on a review paper presented at the 68th Annual Meeting of the American Institute of Chemical Engineers, Los Angeles, November 16-20th, 1975.

Notation

A	specific surface area of zeolite crystals (equation 24)
A_1, A_2, A_3	virial coefficients (equation 10)
a_A	activity of sorbate (equation 29)
B	constant (equation 25)
b	Langmuir equilibrium constant (equation 5)
b_0	pre-exponential factor in vant Hoff equation giving temperature dependence of b
C	constant (equation 25)
c	sorbate concentration (m.mole/gm or molecule/cavity)

c_A	concentration of species A
c_{A*}	concentration of isotopically labelled species A*.
c_s	saturation sorbate concentration $\equiv$ number of sites per cavity
D	zeolitic diffusivity ($cm^2.sec^{-1}$)
D_o	zeolitic diffusivity at zero concentration
D'_o	constant in equation 26 (molecules.cm^2/cavity sec.)
D_*	pre-exponential factor (equation 32)
D'_*	pre-exponential factor (equation 27)
$\mathcal{D}$	tracer self diffusivity ($cm^2.sec^{-1}$)
E	diffusional activation energy (equation 27 and 32)
e	base of natural logarithm
f	fugacity corresponding to sorbate equilibrium pressure p
f_s	fugacity of saturated liquid sorbate at isotherm temperature
f_z	partition function for adsorbed molecule
f'_g	partition function per unit volume for free gaseous molecule
f_{rot}	rotational partition function
f^*_z	partition function for molecule in transition state (<u>i.e.</u> at centre of window)
G	free energy
H	enthalpy
h	Planck's constant
I	moment of inertia of sorbate molecule
K	Henry's Law constant ($c = Kp$)
K_o	pre-exponential factor in equation 3 giving temperature dependence of K (in equations 33 and 34) K_o must be expressed in molecules/cavity·dyne cm^{-2})
k	Boltzmann's constant
L_{AA}	straight coefficient in the diffusion flux equation
L_{A*A}	cross coefficient in the diffusion flux equation
M_z	"molecular weight" of zeolite
M_s	molecular weight of sorbate
m	integer, defined by $m \leq v/\beta$ (equation 7)

m	mass of sorbate molecule (equations 35, 36)
m_t	mass of sorbate adsorbed or desorbed during time t (equations 23, 24)
m_∞	mass sorbate or desorbed as $t \to \infty$ (equation 23, 24)
p	equilibrium sorbate partial pressure
p_o	reference pressure (usually 1 atmosphere)
q	isosteric heat of sorption (equation 17)
q_o	limiting isosteric heat of sorption at zero sorbate concentration (equation 3)
R	gas constant
r	equivalent radius of zeolite crystal
$\underline{r}$	position vector
S	entropy
$\bar{S}_z$	partial molar entropy of adsorbed species
$\bar{S}_{th}$	partial molar thermal entropy of adsorbed species
$\bar{S}_c$	partial molar configurational entropy of adsorbed species
S_g^o	molar entropy of free gaseous sorbate at reference pressure p^o.
s	number of molecular in a cavity
δ	symmetry factor (equation 36)
T	temperature (Deg.K)
t	time (secs.)
u	fluid velocity (equation 25)
u_g	potential energy of free gaseous sorbate (zero)
u_z	potential energy of adsorbed molecule
$u(\underline{r})$	potential energy of adsorbed molecule, relative to gas phase, as function of position within the cavity.
u'	difference in potential energy between free gaseous molecule and molecule in the transition state at the centre of a window
V	volume of M_z gms of dehydrated zeolite
v	volume of zeolite cavity (776 Å^3 for type A, 406 Å^3 for erionite)
W	volume of intracrystalline fluid $(-W = \beta c)$
W_o	saturation adsorption volume $(W_o = \beta c_s \approx v)$

x	weight of sorbate per gm of dehydrated zeolite (equation 12)
Z_1	configuration integral for one molecule within a zeolite cavity
Z_s	configuration integral for s molecules confined within the same zeolite cavity
β	volume of a zeolite molecule
λ	activity coefficient (equation 15)
δ	lattice parameter (= distance between centres of neighbouring cavities)
ε	adsorption potential (equation 8)
ε'	characteristic energy (equation 9)
μ_s	chemical potential of sorbate
μ_z	chemical potential of zeolite
Π	osomotic pressure
ρ	density of dehydrated zeolite crystal
σ	critical diameter of sorbate molecule
θ	fraction of occupied sites (= c/c_s)
ϕ	free volume of zeolite cavity (smaller than v due to the finite size of the sorbate molecule)
λ	jump distance (equation 37)
τ	average time between molecular jumps (equation 37)

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