Theory of Gas Diffusion and Permeation in Inorganic Molecular-Sieve Membranes

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Theoretical models of gas diffusion and permeation in microporous molecular-sieve membranes are presented. The effect of the adsorbed diffusant on the total transmembrane flow is insignificant for permanent gases. For highly adsorbable gases the effect of the adsorbed molecules on the total transmembrane flux may be high at low temperatures. The activation energy of diffusion increases when the kinetic diameter of the diffusant increases. The activation energy of gas diffusion compares well with the values calculated based on the Lennard-Jones potential. Maximum possible permeability coefficients calculated for He in the molecular-sieve membranes do not exceed ~30,000 Barrer at room temperature. The experimentally observed value for He permeability is ~1,000 Barrer ($T=30°C$) because of the high tortuosity ($\tau \approx 25$) and low porosity ($\theta = 0.22$) of the membrane porous structure.

Introduction

Gas separation processes with microporous inorganic membranes (pore diameter less than 2 nm) are seen as a very promising technology. Usually, they are aimed to fill the technological niche of high-temperature gas separation ($T > 100°C$). Inorganic membranes may also provide selectivity factors different from the ones in polymeric membranes, as the principle of gas separation is based mostly on the differences in the molecular sizes of the diffusants (Koresh and Soffer, 1987). In addition, porous inorganic membranes are usually chemically resistant. It is difficult to estimate the potential market for such types of membranes as the number of them described in the literature is limited. Information on the gas transport properties in these membranes is also scarce and sometimes contradictory. Commercial feasibility tests of these membranes are not available at this time, and it is not yet clear if inorganic membranes will be competitive with alternative gas separation processes. There are two main reasons for the absence of commercial appraisals: lack of commercial molecular-sieve membranes with reproducible gas permeability properties, and lack of a quantitative theory of gas diffusion and permeation in such membranes.

In recent years, however, a microporous glass membrane with very good thermal stability (up to 300°C) and very high selectivity ($\alpha_{He/CH_4} > 10{,}000$) has been prepared and patented by PPG Industries Inc. (Hammel, 1989; Hammel et al., 1989). It was manufactured in limited quantities with relatively good reproducibility of its gas separation properties. Detailed experimental investigations of gas transport properties in this type of molecular-sieve inorganic glass membrane were carried out by Way and Roberts (1992), Roberts et al. (1992), Bhandarkar et al. (1992), and Shelekhin et al. (1992, 1993).

This article proposes a mathematical model to describe diffusion, permeation and separation of gases in microporous molecular-sieve membranes. Dependencies of diffusion and permeability coefficients on the temperature, pressure and kinetic diameter of the diffusant in the molecular-sieve membranes are presented. The theoretical predictions are compared with the experimental observations for a molecular-sieve glass membrane. In addition, similarities between diffusion in the molecular-sieve membrane and diffusion in zeolites are discussed. The theory developed here is applied to the prediction of the upper limit of gas permeability in molecular-sieve membranes. These assessments can be used for the analysis of the future commercial potential of molecular-sieve membranes.

Theory

This work focuses on the development of a theory describing the diffusion of the permanent gases, in pores with diameter

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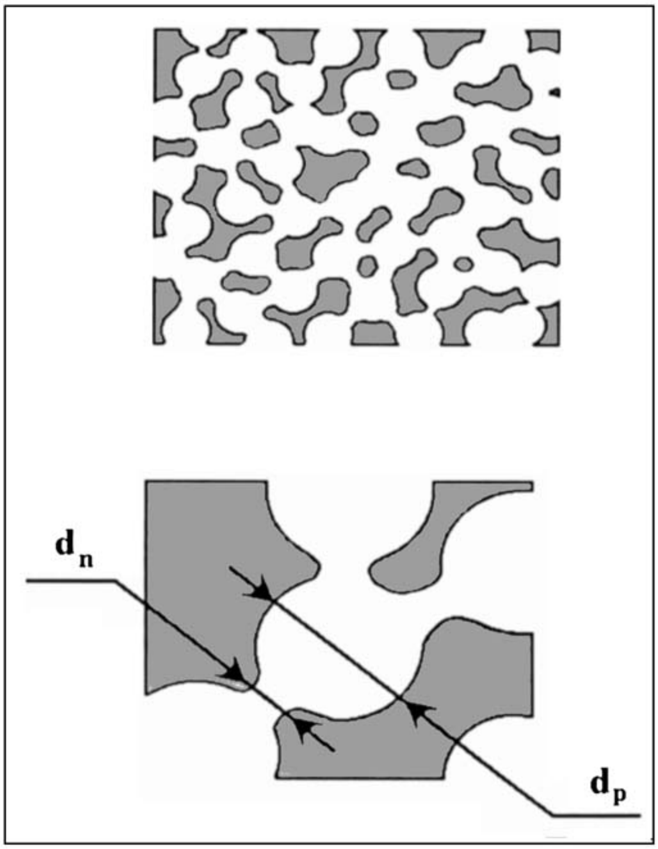

Figure 1. Porous structure of the molecular-sieve glass membrane.

less than 2 nm, at temperatures higher than 300 K. With these assumptions, the transport processes in microporous membranes may be represented by the Knudsen and/or configurational diffusion mechanisms, possibly combined with surface flow.

Experimental measurements on the microporous glass membranes suggest that pores with approximate diameter equal to 15±5 Å are formed (Hammel, 1989; Hammel et al., 1989; Bhandarkar et al., 1992; Shelekhin et al., 1993) due to the specifics of the membrane preparation technique. Large pores inside the membrane (~15 Å) are interconnected by pore necks which are smaller in diameter (Figure 1). The interconnected pores create a tortuous diffusion path. The difference in size between these connections and the pores creates an activation barrier for gas diffusion. It is well known that the size of the necks is crucial in determining the magnitude of the energy barrier for diffusion between zeolite cages (Ruthven, 1984; Xiao and Wei, 1992a,b). In turn, knowledge of the activation energy may help determine the size of the necks in other molecular-sieve membranes.

The permeability of membranes is a function of both the diffusion coefficient and the concentration of the penetrant. There are two possible states for the diffusant molecule inside the porous structure of the membrane if the pore is sufficiently large ($10 < d_p < 20$ Å). A certain fraction of the gas molecules moves inside the pore, while the rest of them reside on the pore walls. Therefore, the total concentration of the gas molecules inside the membrane is determined as

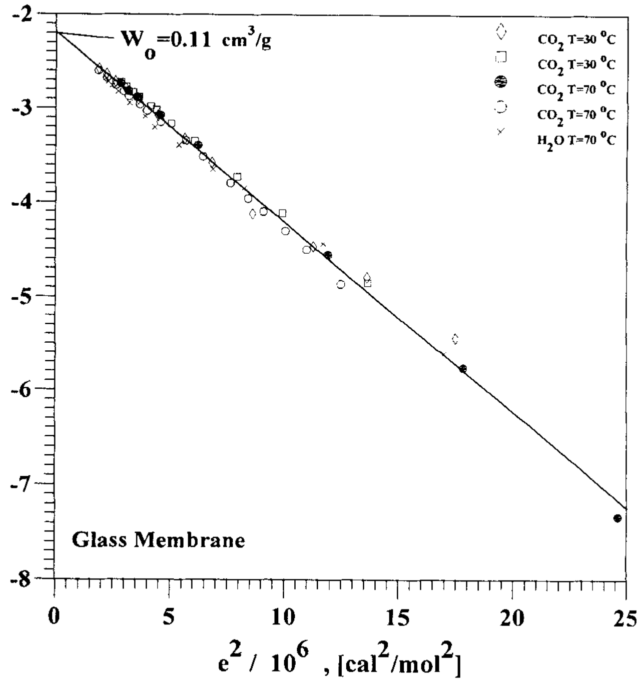

Figure 2. Adsorption in the molecular-sieve glass membrane vs. adsorption potential.

$$C_T = C_g + C_a \tag{1}$$

where C_T, C_g, and C_a are the total, the gas-phase and the adsorbed-phase concentrations, respectively [mol/m^3 (membrane)].

The adsorption phenomena in the porous glass membrane may be adequately described by the Dubinin-Radushkevich isotherm (Dubinin, 1987; Bhandarkar et al., 1992):

$$W = W_o \exp\left(-A\,\frac{e^2}{\beta^2}\right) \tag{2}$$

where W_o is the limiting adsorption volume (m^3/kg), β is the empirical factor or affinity coefficient (J/mol), $e = RT \ln (p_o/p)$ is the adsorption potential (J/mol), which equals the free energy required to remove 1 mol of the adsorbate molecules from their location on the surface to the gas phase, and W is the adsorbate volume (m^3/kg) at temperature T (K) and at relative pressure p/p_c. Dubinin-Radushkevich isotherm allows calculation of the adsorption isotherms at different temperatures and pressures if the coefficients W_o, A, and β are known for a given gas.

Figure 2 (Bhandarkar et al., 1992) represents the dependence of the micropore filling on the adsorption potential. It is notable that the amounts of adsorbed CO$_2$ at two different temperatures, as well as the adsorption data for H$_2$O, lie on the same straight line in accordance with the isotherm. This agreement enables one to predict the adsorption of different gases at different temperatures and pressures.

Based on Eq. 2 and experimental data of Bhandarkar et al. (1992), the amounts of He, H$_2$, N$_2$, O$_2$, CH$_4$ and CO$_2$ adsorbed on the internal surface of the membrane were calculated at pressure $p = 5$ atm (Figure 3). Concentration in the gas phase

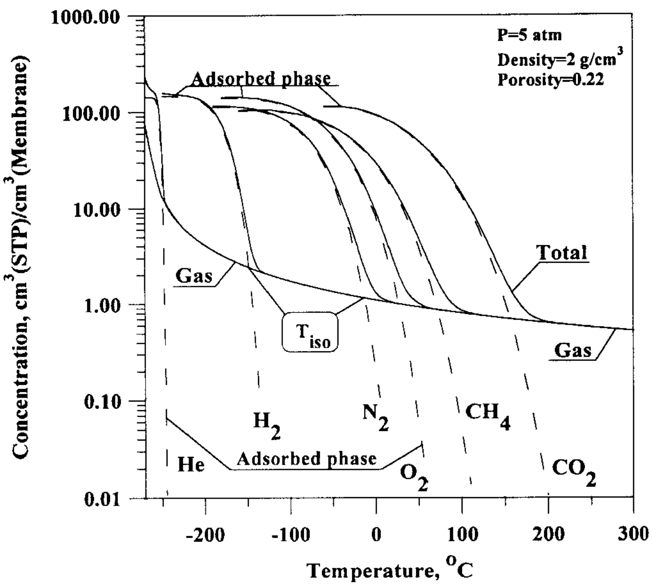

Figure 3. Total, gas-phase, and adsorbed-phase concentrations in molecular-sieve glass membranes vs. temperature.

vs. temperature is also presented in Figure 3, together with adsorption of He and H_2 which is negligible at temperatures higher than ambient. For N_2, O_2, and CH_4, temperatures at which the diffusant concentration inside the porous structure is determined equally by the concentration in the gas phase and the concentration in the adsorbed phase are −20, 30 and 70°C, respectively. For highly adsorbable gases such as CO_2, this temperature may be as high as 160°C. If the temperature increased even 20°C above this point of equal concentrations, the amount of the adsorbed gas fell by 1 order of magnitude in comparison to the concentration in the gas phase. Therefore, for each diffusant a temperature exists at which the amount of the adsorbed phase inside the pores equals the gas amount in the mobile or nonadsorbed gas phase. This temperature will be referred to as the "isoconcentration point."

If the concentration of the diffusant molecules inside the porous structure is determined only by the gas phase inside the membrane porous structure, then

$$C_T \approx C_g = \frac{p\theta}{RT} \quad T > T_{\text{iso}} + \Delta T \tag{3}$$

where θ is the porosity of the membrane. Below the isoconcentration point, the total concentration of the diffusant is determined primarily by the concentration of the adsorbed phase,

$$C_T \approx C_a = \frac{W\xi}{V_m} \quad T < T_{\text{iso}} - \Delta T \tag{4}$$

where V_m is the molar volume of the adsorbate in the adsorbed state (m³/mol, ξ is the density of the porous medium (kg/m³). The value of ΔT can be as small as 10-20°C.

Diffusion coefficient

If the diffusion proceeds in a medium with some spatial restrictions such as the pore walls and pore openings, the equation for the diffusion coefficient is

$$D = \lambda \rho \bar{u} \tag{5}$$

where ρ is the probability that the diffusant makes a jump, whose length is λ. This probability is governed by geometrical and energetical factors and can be represented in the form

$$\rho = \rho_g \rho_E = \rho_g \exp\left(-\frac{\Delta E}{RT}\right) \tag{6}$$

where ρ_g is the probability that the gas molecule jumps in the desired direction or the geometrical probability, ρ_E is the probability that the molecule has kinetic energy sufficient to surmount the energy barrier ΔE. If the obstruction in the way of the diffusant molecule is rigid so that the diffusant will bounce off during the collision, then ρ_g can be calculated from

$$\rho_g = \frac{1}{3}\frac{S_n}{S_p} \tag{7}$$

where S_n is the area of the pore opening that leads to another pore (cross section of the neck), and S_p is the cross-sectional area of the pore. For example, if the diffusant is moving inside a spherical cavity of pore diameter d_p (m) with a hole on it having pore neck diameter d_n (m), then the probability that the particle will jump through the hole, ρ_g, is

$$\rho_g = \frac{1}{3}\frac{(\pi d_n^2/4)}{(\pi d_p^2/4)} = \frac{1}{3}\frac{d_n^2}{d_p^2}, \quad d_n < d_p \tag{8}$$

If the diffusant moves in 3-D space without spatial obstructions, then the geometrical probability is $\rho_g = 1/3$. For nonspherical molecules, more complex expressions, not Eq. 8, should be used, taking into account the probability that the nonspherical gas molecule will be oriented in the right way before entering the hole. This phenomenon is known as the shape selectivity of the molecular sieves.

Substituting expressions for the energetical probability ρ_E and the mean free velocity $\bar{u}$ into Eq. 5 and taking $\lambda = d_p$, one gets an expression for the diffusion coefficient

$$D = \rho_g d_p \left(\frac{8RT}{\pi M}\right)^{1/2} e^{-\frac{\Delta E}{RT}} \tag{9}$$

For configurational diffusion, the diffusion coefficient depends not only on the size of the diffusant but on its shape. In principle, configurational diffusion is simply an activated process where the geometrical probability and the activation energy are determined by the geometry of the pore opening. It is also important to note that it is erroneous to represent the experimental results for the gas diffusion coefficient in the simplified Arrhenius form

$$D = D_o e^{-\frac{\Delta E}{RT}} \tag{10}$$

which should only be regarded as an empirical fit of experimental data.

Permeability coefficient

The permeability coefficient in straight pores is defined as

$$P_s = \frac{J_s \cdot L}{\Delta p} \tag{11}$$

where P_s and J_s are the permeability coefficient and the transmembrane flux, respectively, in straight pores. For any transport process, the driving force is the gradient of the chemical potential

$$J_s = -Bc\frac{\partial \mu}{\partial x} \tag{12}$$

where B is the mobility (mol·m^2/J·s), c is the concentration, and μ is the chemical potential (J/mol). Then, the diffusion coefficient is determined by (taking $\mu = \mu^o + RT\ \ln p$)

$$D_F = BRT\frac{d\ln(p)}{d\ln(c)} = D_c\frac{d\ln(p)}{d\ln(c)} \tag{13}$$

where D_c is the corrected diffusivity that may or may not depend on the concentration, and D_F is the Fickian diffusivity.

For the adsorbed phase, the derivative is

$$\frac{d\ln(p)}{d\ln(c)} = \frac{1}{2A/\beta^2(RT)^2\ln(p_0/p)} \tag{14}$$

and the corrected diffusivity in the adsorbed phase is given by

$$D_{\text{ads}} = \frac{D_{c,\text{ads}}}{[2A/\beta^2(RT)^2\ln(p_0/p)]} \tag{15}$$

For the gas phase, the derivative is

$$\frac{d\ln(p)}{d\ln(c)} = 1 \tag{16}$$

and the corrected diffusivity is independent of the pressure ($D_{c,\text{gas}} = D_{\text{gas}}$). Additionally, a correction coefficient, accounting for the differences between the transmembrane flux in membranes with random porous structures and the flux in straight channels should be included in Eq. 11. According to Shelekhin et al. (1993), the flux in the porous medium is

$$\frac{J_s}{J} = \frac{\tau}{\theta} \tag{17}$$

where θ is the porosity, and τ is the tortuosity.

An expression for the total transmembrane flux can be written as

$$J = -\left(D_{\text{ads}}\frac{dC_{\text{ads}}}{dp} + D_{\text{gas}}\frac{dC_{\text{gas}}}{dp}\right)\frac{\theta}{\tau}\frac{dp}{dx}$$
$$= -\left(D_{c,\text{ads}}\frac{d\ln(p)}{d\ln(C_{\text{ads}})}\frac{dC_{\text{ads}}}{dp} + \frac{D_{c,\text{gas}}}{RT}\right)\frac{\theta}{\tau}\frac{\Delta p}{L} \tag{18}$$

where $D_{c,\text{ads}}$ and $D_{c,\text{gas}}$ are the corrected diffusion coefficients (m^2/s) in the adsorbed and gas phases, respectively, and J is the transmembrane flux across the membrane. The structure of the porous medium need not be defined in Eq. 18, because it is being accounted for by the porosity and the tortuosity factor. For example, if the diffusion channels are straight and closely packed, then $\tau = 1$ while $\theta = 0.95$. Similarly, in the microporous glass membrane with $\theta = 0.22$, the tortuosity factor is $\tau = 25 \pm 5$ (Shelekhin et al., 1993). In the Vycor glass membrane with $\theta = 0.3$, the tortuosity factor is $\tau = 5.9 \pm 0.3$ (Satterfield and Sherwood, 1963).

Both of the diffusion coefficients, $D_{c,\text{ads}}$ and $D_{c,\text{gas}}$, are governed by the geometrical and energetical probabilities. Taking this into account, the permeability coefficient can be presented as

$$P = D_{c,\text{ads}}\frac{d\ln(p)}{d\ln(C_{\text{ads}})}\frac{\theta}{\tau}\frac{dC_{\text{ads}}}{dp} + \frac{\theta}{\tau}\frac{D_{c,\text{gas}}}{RT} \tag{19}$$

$$D_{c,\text{ads}} = \rho_g d_p\left(\frac{8RT}{\pi M}\right)^{1/2} e^{-\frac{\Delta E_{\text{ads}}}{RT}} \tag{20}$$

$$D_{c,\text{gas}} = \rho_g d_p\left(\frac{8RT}{\pi M}\right)^{1/2} e^{-\frac{\Delta E_{\text{gas}}}{RT}} \tag{21}$$

The terms dC_{ads}/dp and $1/RT$ are analogous to the "solubility" coefficient, which is commonly used to describe the permeability of polymeric membranes. The term $1/RT$ at 0°C equals 1 m^3(STP)/m^3(pore)·atm or θ m^3(STP)/m^3(membrane)·atm. As the temperature increases, the "solubility" decreases. The "solubility coefficient" in the adsorbed phase may be of the order of 100 m^3(STP)/m^3(membrane)·atm in the glass membranes at temperatures below the isoconcentration point. Above the isoconcentration point, the first term in Eq. 19 is negligibly small, and the permeability coefficient is determined exclusively by the mass transport in the "gas phase." This is the case for the majority of permanent gases such as H_2, He, N_2, O_2, and Ar, where the permeability coefficient is simply

$$P = d_p\rho_g\left(\frac{8}{\pi MRT}\right)^{1/2}\frac{\theta}{\tau}e^{-\frac{\Delta E_{\text{gas}}}{RT}} \tag{22}$$

For big straight pores, $\Delta E_{\text{gas}} \rightarrow 0$, $\rho_g \rightarrow 1/3$, and Eq. 22 yields the classical Knudsen formula for the permeability coefficient.

Upper bound for the permeability coefficient

Based on Eq. 22, an upper bound for the permeability coefficients in the microporous molecular-sieve membranes can be estimated. The following assumptions were made to calculate the upper bound for the permeability coefficient. First, low adsorption of the diffusant was assumed. This is true for the

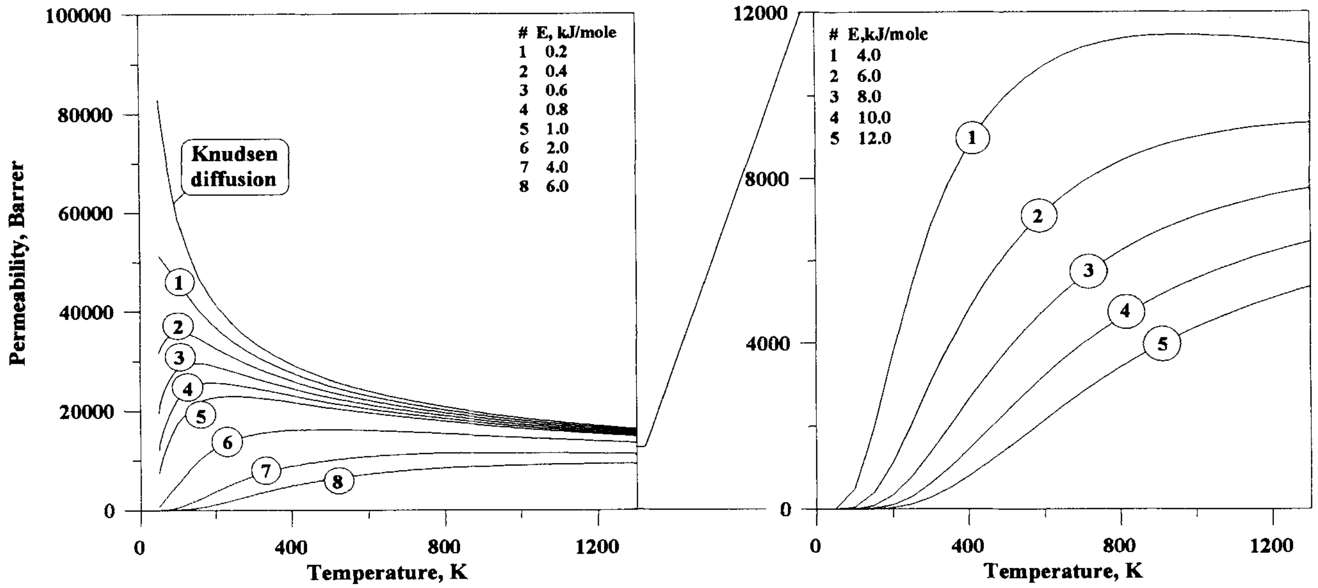

Figure 4. Temperature dependence of He permeability coefficient (theoretical predictions).

permanent gases or for temperatures somewhat higher than the isoconcentration point. Second, the porosity of the membrane was equal to 0.3, the tortuosity factor was equal to 2, the pore diameter was equal to 15 Å, and the geometrical factor was equal to 0.1. This set of assumptions corresponds to a membrane that might be prepared based on technology that could be developed in the near future.

The maximum permeability coefficient which can be accomplished in the molecular-sieve membrane with the characteristics listed above is approximately equal to 35,000 Barrer at room temperature and for $\Delta E = 0$ kJ/mol (Figure 4). Essentially, it is the limit for the permeability coefficient calculated based on the Knudsen diffusion mechanism. Note that for configurational diffusion the permeability coefficient is almost temperature-independent within the temperature range 30-1,000°C for $0.8 < \Delta E < 1.0$ kJ/mol. The permeability decreases very fast as the activation energy increases to 10 kJ/mol and is approximately 5,000 Barrer. However, increasing activation energy not only decreases the permeability, but also provides the selectivity of gas separation. Therefore, the upper bound for the permeability coefficient of He in the molecular-sieve membranes that could still exhibit selectivity different from the Knudsen selectivity can hardly exceed 30,000 Barrer.

Activation energy of diffusion as a function of the pore size

In membranes with pore diameters less than 1 nm, overlapping of the gas-solid interaction potential occurs. This interaction originates the potential barrier which is characterized by the activation energy required to overcome it. Several approaches have been proposed to calculate the activation energy in molecular sieves including transition state, molecular dynamics theories (June et al., 1990, 1991), and some simpler methods (Xiao and Wei, 1992a,b). Ambiguity of the internal porous structure of the molecular-sieve glass membrane is a strong incentive for employing the simpler methods for estimation of the activation energy of diffusion. One of the simple models for calculating the activation energy of diffusion was proposed by Roberts et al. (1992). Interactions between the diffusant and the pore are accounted for with the Lennard-Jones potential. Assuming that the perimeter of the pore neck consists of eight oxygen atoms, the potential is

$$E_D = 8\epsilon/k_{A-O_2}\left[\left(\frac{\sigma_{A-O_2}}{r_n}\right)^{12} - \left(\frac{\sigma_{A-O_2}}{r_n}\right)^{6}\right] \qquad (23)$$

$$\epsilon/k_{A-O_2} = (\epsilon/k_A\ \epsilon/k_{O_2})^{1/2}$$

$$\sigma_{A-O_2} = (\sigma_A + \sigma_{O_2})/2$$

where r_n is the pore neck radius (m), σ is the distance between the oxygen atom on the neck perimeter and the diffusant, and subscript A refers to the diffusant molecule. This approach to the calculation of the activation energy can be utilized only for the fraction of gas molecules in the gas phase within the porous body. For the adsorbed molecules, the activation energy is determined as a difference between the potentials of the adsorbed phase in the pores and in the necks. An example of such an analysis was provided by Xiao and Wei (1992a,b).

Selectivity of gas separation

An ideal selectivity factor is defined as the ratio of the permeability coefficients

$$\alpha = \frac{P_A}{P_B} = \left(\frac{M_B}{M_A}\right)^{1/2} \exp\left(-\frac{\Delta E_A - \Delta E_B}{RT}\right) \qquad (24)$$

From Eq. 24 it follows that only the exponential term depends on the temperature. As the temperature increases, this term exponentially decreases and at infinitely high temperature the membrane selectivity is the Knudsen selectivity of the gas separation (Figure 5).

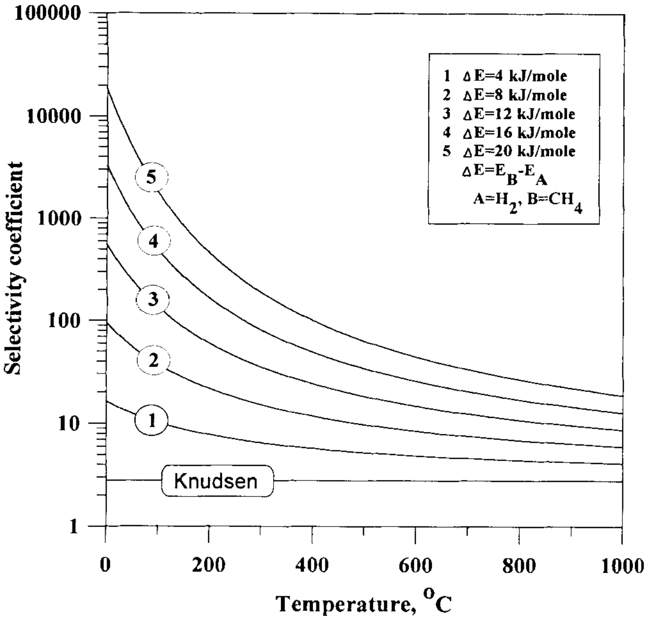

Figure 5. Selectivity coefficients vs. temperature in molecular-sieve membranes.

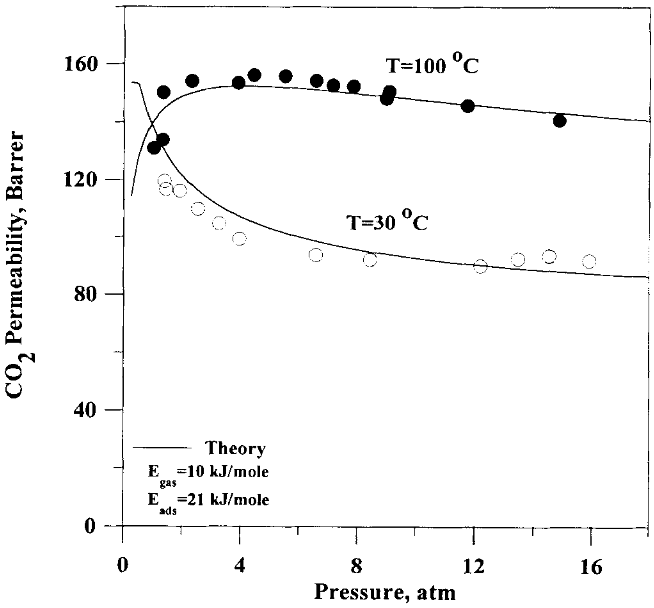

Figure 6. Pressure dependence of CO_2 permeability coefficient.

Results and Discussion

The mathematical model of gas diffusion in the microporous membranes provides a set of corollaries that can be verified experimentally. Based on our previous gas permeability data (Shelekhin et al., 1992), these theoretical predictions are compared with the experimental observations. The microporous glass membranes used in the experiments were acquired from PPG Industries, Inc. with main characteristics in Table 1.

Pressure dependence of the permeability coefficient

A linear dependence of the transmembrane flux on the pressure gradient across the membrane was observed for He, H_2, O_2, and N_2 (Shelekhin et al., 1992). However, a closer analysis of the pressure dependence of the permeability coefficient for CO_2, which is a highly adsorbable gas, reveals that the permeability coefficient in this case is pressure-dependent (Figure 6). It is also interesting to note that at 100°C the permeability initially increases when the pressure increases. As the pressure increases further, the permeability starts to decrease. At 30°C the permeability always decreases when the pressure increases. These seemingly puzzling dependencies can be explained well within the framework of the developed theory. Two terms in Eq. 19 determine the permeability coefficient. The second term in Eq. 19 is independent of the pressure. Since for slightly adsorbable gases it would be the only term determining the permeability coefficient, the permeability is independent of the pressure. For highly adsorbable gases the first term in Eq. 19 also affects the value of the permeability coefficient. Depending on the temperature of the experiment the first term may increase, decrease, or increase, and then decrease when the pressure increases.

Table 1. Characteristics of Microporous Glass Membranes [1, 2, 4-6, 14]

Property	Value
Pore diameter	5-20 Å
Surface area	700-1,000 m^2/cm^3
Micropore volume	0.11-0.3 cm^3/g
Temperature stability	up to 300°C
Chemical stability	Except in HF
Porosity	15-40%
Membrane structure	symmetrical
Hollow-fiber OD/ID	32/22 μm
Crystallinity	100% amorphous
Chemical composition	$SiO_2 + (TiO_2)$

Solid lines in Figure 6 represent the theoretical values calculated from Eq. 19 based on the adsorption isotherms of CO_2 on the molecular-sieve glass membrane. The Dubinin-Radushkevich isotherm was used to approximate the adsorption isotherms of CO_2, and the derivatives in the first term of Eq. 19 were calculated numerically. In addition, one needs to know two activation energies of diffusion, ΔE_{ads} and ΔE_{gas}, while for slightly adsorbable gases only ΔE_{gas} is needed. The activation energies ΔE_{ads} and ΔE_{gas} were calculated from the best fit of Eq. 19 to the pressure dependencies of the permeability coefficient. The experimental data agree well with the theoretical predictions. It should be remembered that the derivatives in the first term of Eq. 19 were calculated from the experimental data on gas adsorption obtained in a separate independent adsorption study (Bhandarkar et al., 1992).

Permeability coefficients as a function of the kinetic diameter

Fitting the activation energy in terms of the kinetic diameter proved that the activation energy depends on the kinetic diameter of the diffusant to the 12th power. Therefore, even small differences in the kinetic diameters of the gas molecules result in large divergences in the values of the activation energy. Large

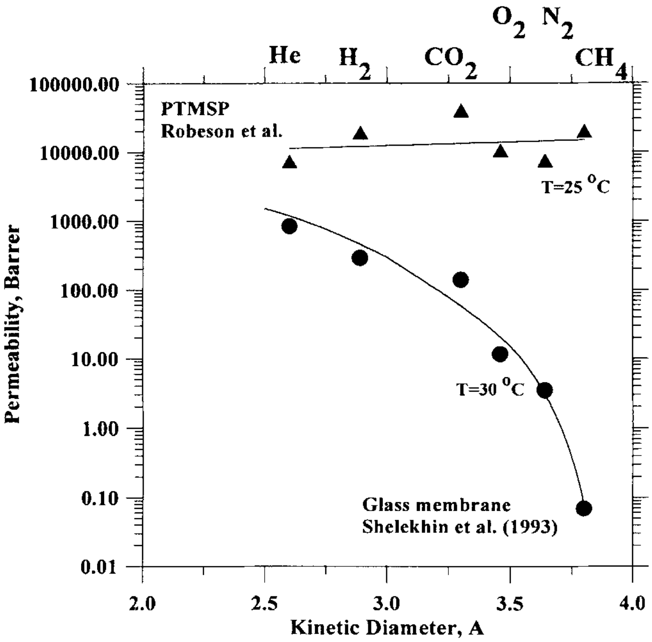

Figure 7. Dependence of permeability coefficients on the kinetic diameter in the molecular-sieve glass membrane.

differences in the activation energy of diffusion provide even larger differences in the permeability coefficients as the permeability coefficient is an exponential function of the activation energy. These differences in permeability of gases with different kinetic diameters far exceed the differences in polymeric membranes, thus yielding much greater selectivity factors unseen in polymeric membranes such as the poly(trimethylsilylpropyne) (PTMSP) membrane (Figure 7) (Robeson et al., 1995). For example, for the pair of gases He/CH_4 the selectivity coefficient in the molecular-sieve glass membrane is 11,000.

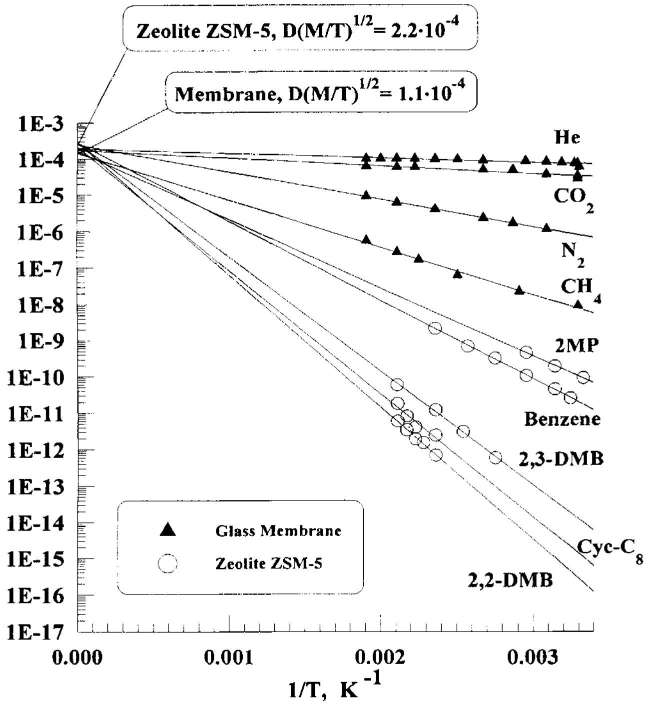

Figure 8. Dependencies of $D(M/T)^{1/2}$ on the reciprocal temperature in the molecular-sieve glass membrane and zeolite ZSM-5.

Diffusion Coefficients

The conventional time-lag technique was used to measure the diffusion coefficients in the hollow-fiber silica membranes. For all the gases under study, the time lag t_L was less than 2–3 s and was too small to be measured. Even though the diffusion coefficients cannot be measured directly, they can be calculated from the permeability coefficients in accordance with Eq. 22 for He, N_2, O_2 and CH_4 or Eq. 19 for CO_2. The diffusion coefficients calculated in accordance with this technique were obtained from the steady-state permeability data. Therefore, the values of the diffusion coefficients were not affected by the heat of adsorption.

Figure 8 presents the dependence of the diffusion coefficients on the reciprocal temperature for the microporous silica glass membranes and zeolite ZSM-5 (Xiao and Wei, 1992a,b). Straight lines on the graph represent best fits to the experimental data. The diffusion coefficients calculated in accordance with Eq. 22 for the microporous silica glass membrane agree well with a variety of data on gas diffusion in zeolites. For comparison, the diffusion coefficients in zeolite ZSM-5 are also depicted in the same figure. A remarkable agreement is observed between the two sets of the experimental data. The experimental data on the diffusion coefficients in ZSM-5 were obtained from dynamic unsteady-state measurements (uptake curves), while the data on the gas diffusion in glass membrane were calculated from steady-state permeability measurements based on the proposed model. Therefore, the microporous silica membrane exhibits essentially the same gas transport properties as zeolites.

Xiao and Wei (1992a,b) noted that the value of $D(M/T)^{1/2}$ is almost the same for all gases at $1/T=0$ (Figure 8). At infinitely high temperature, the diffusivity in the molecular sieves is determined solely by the geometry of the porous medium including such parameters as the mean free jump and the geometrical probability which are independent of the temperature. Remarkably, for both zeolite ZSM-5 (Xiao and Wei, 1992a,b) and the molecular-sieve glass membrane all of the fitted lines extrapolate very close to single points at $1/T=0$, even though the extrapolation was taken over a wide range of diffusion coefficients for different gases that differ by several orders of magnitude. A mathematical proof for the above statement can be derived from the following expression

$$\lim_{1/T\to 0}\left[D\left(\frac{M}{T}\right)^{1/2}\right]=\lim_{1/T\to 0}\left[\rho_g d_p\left(\frac{8RT}{\pi M}\right)^{1/2}e^{-\frac{\Delta E}{RT}}\left(\frac{M}{T}\right)^{1/2}\right]=\rho_g d_p\left(\frac{8R}{\pi}\right)^{1/2} \qquad (25)$$

All of the terms on the righthand side are constants and can be estimated independently. The theoretical values of $D(M/T)^{1/2}$ were 1.1×10^{-4} $(M/T)^{1/2}$ and 2.2×10^{-4} $(M/T)^{1/2}$ for the molecular-sieve glass membrane and zeolite ZSM-5, respec-

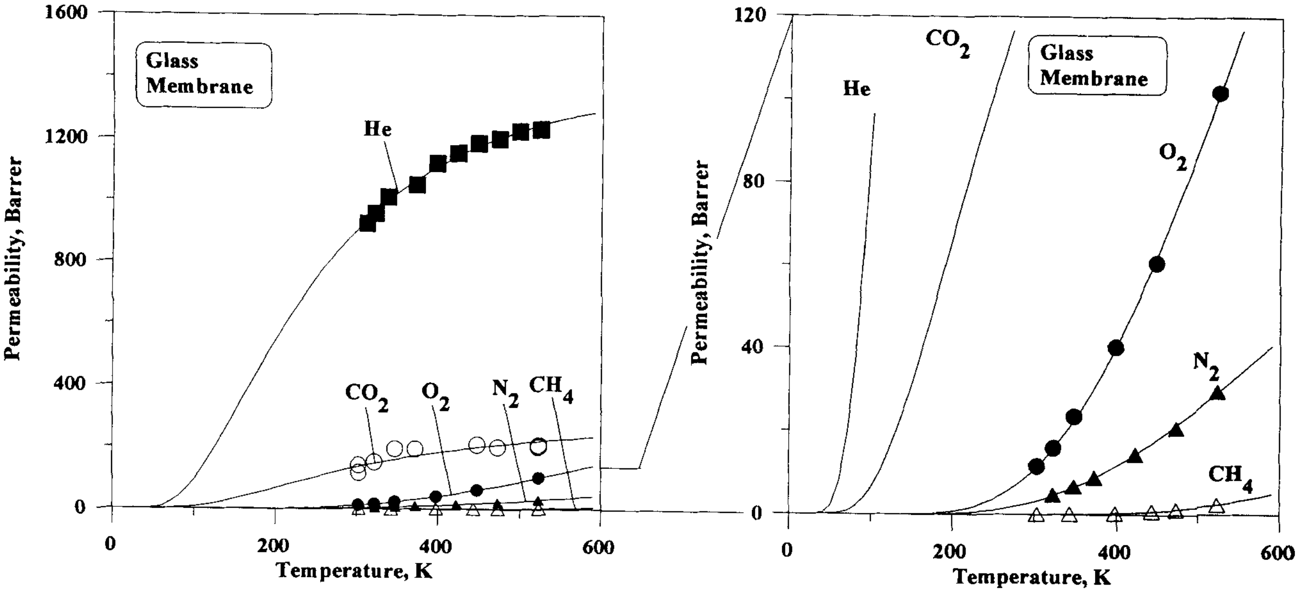

Figure 9. Dependencies of permeability coefficients in the molecular-sieve membrane on temperature.

tively. The limiting value of $D(M/T)^{1/2}$ for zeolite ZSM-5 differs from the value calculated by Xiao and Wei (1992a), because the geometrical probability was used in the calculations instead of the coordination number. Figure 8 shows that the predicted values for $D(M/T)^{1/2}$ are in excellent agreement with the experimental observations for both zeolite ZSM-5 and the molecular-sieve membrane. It is a very important corollary deduced from the theory, which is proved here to be valid for two different materials studied by different techniques for different sets of gases and under different conditions.

Activation energy and pore size determination

The preexponential term in Eq. 19 for the permeability coefficient in microporous membranes is temperature-dependent. Therefore, determination of the activation energy of permeation in the microporous membranes by plotting a dependence of the effective permeability coefficient vs. the reciprocal temperature will be erroneous. Instead, a nonlinear least-squares method (LSM) should be used to calculate the activation energy of diffusion in this case. In Figures 9a and 9b dependencies of the permeability vs. the temperature are presented for simple gases. The data were fitted in accordance with Eq. 19 by using the nonlinear LSM. The activation energies of diffusion thus obtained are listed in Table 2. In the case of CO_2, the activation energy ΔE_{gas} is listed in Table 2 (ΔE_{ads} was fitted at the same time).

Table 2. Experimental vs. Theoretical Values of Activation Energy of Diffusion in Molecular-Sieve Membrane

Gas	d Å	ϵ_o/k K	E_D (exp.) kJ/mol	E_D (Theory) kJ/mol Eq. 23
He	2.6	10.22	0.52	0.05
CO_2	3.3	195.2	9.9	10.3
O_2	3.46	118.0	10.6	11.9
N_2	3.64	95.05	18.2	16.2
CH_4	3.8	148.2	28.7	28.3

The porous structure of the silica glass membrane is random and disordered. However, based on some general physical and topological considerations, the porous structure can be evaluated as consisting of relatively large pores, approximately 15 Å in diameter (Hammel, 1989; Hammel et al., 1989; Bhandarkar et al., 1992). These pores are formed during the nucleation process of the boron-oxide-phase formation. This phase is then leached out, and the pores become interconnected with even smaller pore openings (Figure 1). One of the possible approaches to determine the diameter of the pore openings is to measure the activation energy of diffusion for several gases with different kinetic diameters. Then, the activation energies of gas diffusion can be compared to the activation energies of gas diffusion in zeolites. For many zeolites, the pore apertures were determined from the crystalline structure which can be relatively well defined based on the X-ray diffraction analysis. Thus, dependencies of the activation energy vs. the kinetic diameter in various zeolites can be used as a set of "rulers" to measure the size of the pore opening for the unknown membrane material. There is no limitation on the applicability of the technique even in the case of structurally disordered materials. Figure 10 represents dependencies of the activation energy on the kinetic diameter for the molecular-sieve membrane and zeolites ZSM-5 and KA. The correlation curve of the activation energy on the kinetic diameter for the molecular-sieve membrane lies in-between the curves for zeolites ZSM-5 and KA. The pore diameter for zeolite KA is ~3 Å, while for zeolite ZSM-5 is ~6 Å. Therefore, as a first approximation, the pore size of the molecular-sieve glass membrane can be estimated as $d = 3\text{-}6$ Å.

An analytical approach can also be used to estimate the size of the pore opening in the molecular-sieve membranes. The activation energy of diffusion is essentially the height of the Lennard-Jones potential. This potential can be calculated from Eq. 23 and compared to the experimental observations (Table

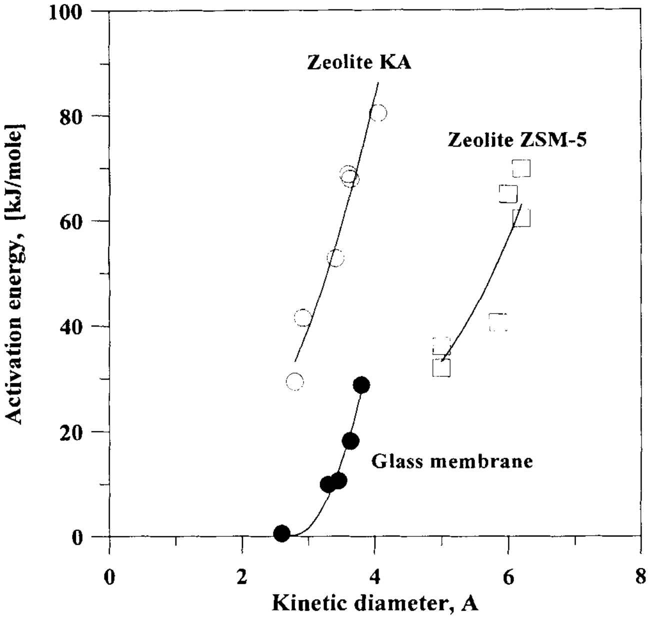

Figure 10. Dependencies of the activation energy of diffusion in the molecular-sieve membrane, zeolite ZSM-5, and zeolite KA on the kinetic diameter.

2). The only unknown variable in this equation is the pore radius. It can be derived by minimization of the differences between the experimental data on the activation energy and the theoretical predictions for a set of different gases. This approach proved that the dependence of the activation energy vs. the kinetic diameter calculated from the experimental data can be well fitted with Eq. 23, if the size of the pore openings lies within the range from 5.5 Å to 6.1 Å, for $6<n<10$ where n is the number of oxygen atoms on the pore perimeter.

The proposed methods for estimation of the pore opening in the microporous glass membranes agree well with each other. However, care should be taken while comparing the experimental results with predictions made on the basis of Eq. 23. In the microporous membrane, two types of pores can be specified. Large pores approximately 15 Å in diameter are connected by necks approximately 6 Å in diameter. The pore size of 15 Å is large enough to consider a certain fraction of the gas molecules inside the porous structure as the mobile phase, because the molecules are almost unaffected by the potential of the pore wall. In zeolites with very small apertures, the gas phase may be nonexistent due to the overlapping of the pore walls potential. In this case, the model developed by Xiao and Wei (1992a,b) may be more appropriate to use for the calculations of the activation energy.

Conclusion

A theoretical model of gas permeation in microporous molecular-sieve membranes was proposed. Good agreement between the experimental data on gas permeability and the theoretical predictions was observed. The selectivity coefficients were considerably higher in the molecular-sieve inorganic membranes than in polymer membranes. Improved selectivity was attributed to a much stronger dependence of permeability coefficients on the kinetic diameter of gas molecules. Analytical expressions for the diffusion and permeability coefficients were derived. Based on the proposed model, the upper bound for the permeability coefficient in the molecular-sieve membrane was estimated as 30,000 Barrer. Methods for pore size estimation were proposed, and the porous structure of the molecular-sieve membrane was assessed as consisting of large pores approximately 15 Å in diameter interconnected with pore necks approximately 6 Å in diameter. Based on the obtained experimental data on the permeability and selectivity of the molecular-sieve glass membrane, as well as the theoretical predictions, it is concluded that molecular-sieve inorganic membranes exhibit excellent gas separation properties far exceeding polymeric membranes. With further development of commercially viable technology for production of molecular-sieve membranes, they may capture a significant share of the gas separation market including H_2, CO_2 and possibly even O_2 separations. Superior chemical resistance of the molecular-sieve inorganic membranes also favors their application in the areas where polymeric membranes are not suitable due to their instability in organic solvents and hydrocarbons.

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Notation

A = empirical factor
E = activation energy, J/mol
J = transmembrane flux, $m^3/m^2 \cdot s$
L = membrane thickness, m
M = molecular weight, g/mol
n = number of oxygen atoms on the pore neck perimeter
Δp = pressure drop across the membrane, Pa
P = permeability coefficient, $m^3 \cdot m/m^2 \cdot s \cdot Pa$, or in Barrer $= 10^{-10}$ $cm^3 \cdot cm/cm^2 \cdot s \cdot cm \cdot Hg$
Q = transmembrane flow, mol/s
R = gas constant, J/mol·K
t_L = time lag, s
T_{iso} = isoconcentration temperature (point), K
$\bar{u}$ = molecular mean velocity, m/s

Greek letters

α = selectivity coefficient
ϵ/k = Lennard-Jones potential, J/mol
λ = molecular mean free path, m
τ = tortuosity of the porous membrane

Literature Cited

Bhandarkar, M., A. B. Shelekhin, A. G. Dixon, and Y. H. Ma, "Adsorption, Permeation, and Diffusion of Gases in Microporous Membranes: I. Adsorption of Gases on Microporous Glass Membranes," *J. Mem. Sci.*, **75**, 221 (1992).

Dubinin, M. M., "Adsorption Properties and Microporous Structures of Carbonaceous Adsorbents," *Carbon*, **25**, 593 (1987).

Hammel, J. J., "Porous Inorganic Siliceous-Containing Gas Enriching Material and Process of Manufacture and Use," U.S. Patent 4,853,001 (1989).

Hammel, J. J., W. J. Robertson, W. P. Marshall, H. W. Barch, B. Das, M. A. Smoot, and P. Beaver, "Process of Gas Enrichment with Porous Siliceous-Containing Material," U.S. Patent 4,842,620 (1989).

June, R. L., A. T. Bell, and D. N. Theodorou, "Transition-State Studies of Xenon and SF_6 Diffusion in Silicalite," *J. Phys. Chem.*, **95**, 8866 (1991).

June, R. L., A. T. Bell, and D. N. Theodorou, "Molecular Dynamics Study of Methane and Xenon in Silicalite," *J. Phys. Chem.*, **94**, 8232 (1990).

Koresh, J. E., and A. Soffer, "The Carbon Molecular Sieve Membranes: General Properties and the Permeability of CH_4/N_2 Mixture," *Sep. Sci. Technol.*, **22**, 973 (1987).

Roberts, D. L., I. C. Abraham, Y. Blum, and J. D. Way, "Gas Separation with Glass Membranes," Final Report, DOE Contract No. DE-AC21-88MC25204 (May 8, 1992).

Robeson, L. M., W. F. Burgoyne, M. Langsam, A. C. Savoca, and C. F. Tien, "High Performance Polymers for Membrane Separation," *Polymer*, in press (1995).

Ruthven, D. M., *Principles of Adsorption and Adsorption Processes*, Wiley, New York (1984).

Satterfield, C. N., and T. K. Sherwood, *The Role of Diffusion in Catalysis* (1963).

Shelekhin, A. B., A. G. Dixon, and Y. H. Ma, "Adsorption, Diffusion, and Permeation of Gases in Microporous Membranes: II. Permeation of Gases in Microporous Glass Membranes," *J. Mem. Sci.*, **75**, 233 (1992).

Shelekhin, A. B., A. G. Dixon, and Y. H. Ma, "Adsorption, Permeation, and Diffusion of Gases in Microporous Membranes: III. Application of Percolation Theory to Interpretation of Porosity, Tortuosity, and Surface Area in Microporous Glass Membranes," *J. Mem. Sci.*, **83**, 181 (1993).

Way, J. D., and D. L. Roberts, "Hollow Fiber Inorganic Membranes for Gas Separations," *Sep. Sci. Technol.*, **27**, 29 (1992).

Xiao, J., and J. Wei, "Diffusion Mechanism of Hydrocarbons in Zeolites: I. Theory," *Chem. Eng. Sci.*, **47**, 1123 (1992).

Xiao, J., and J. Wei, "Diffusion Mechanism of Hydrocarbons in Zeolites: II. Analysis of Experimental Observations," *Chem. Eng. Sci.*, **47**, 1143 (1992).

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