Hindered Diffusion of Gases in "Leaky" Membranes Using the Dusty Gas Model

The modified Enskog theory of van Beijeren and Ernst for dense fluid mixtures of rigid spheres is applied to diffusion of inert, nonadsorbing gases in microporous "leaky" membranes. *Utilizing the concept of a dense dusty gas, the resulting expressions for the permeability and flux ratio illustrate the influence of steric hindrance on the transport process. The results obtained serve as corrections to the original dusty gas model of Mason and others.*

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SCOPE

The dusty gas model, which was originally proposed by Derjaguin and Bakanov (1957) and extended and studied in greater detail by Mason and others (1961, 1963, 1964, 1967), is now accepted as providing a suitable description for gas diffusion and flow in porous media over a wide range of conditions. With a proper choice of porous medium structure factors, and/or by introducing the concept of the pore size distribution, reasonably accurate predictive transport models may be obtained (Wakao and Smith, 1962; Johnson and Stewart, 1965; Henry et al., 1967; Brown et al., 1969; Feng et al., 1973, 1974). In certain cases, however, the dusty gas model cannot describe the transport process adequately. This has been found to be the case when the gas species adsorb, forming a mobile adsorbed phase (Bell and Brown, 1973, 1974; Spencer and Brown, 1975; Thakur et al., 1980); it is also inadequate for diffusion in pores of 50 Å radius or less (Omata and Brown, 1972) and cannot be expected to describe diffusion in the configurational regime (Weisz, 1973). The main reason for the failure of the dusty gas model in these cases lies in its use of dilute gas kinetic theory, inferring that the number density of the "dust" species is low that each of the components in the dilute gas mixture may be represented as point particles and that the existence of bound states (molecular clustering) may be neglected. When it is recognized that the structure of rigid isotropic porous media more closely resembles a "frozen" dense fluid, it is more appropriate to use dense fluid kinetic theory as a basis for a dusty gas model.

In this work the influence of membrane density and the molecular size of diffusing, nonadsorbing gases is investigated by applying the dusty gas concept to the rigid sphere model of dense fluid mixtures. Expressions are obtained for the permeability and the flux ratio of counterdiffusing gases which introduce a new parameter, the dimensionless ratio of molecular radius to membrane particle radius, into the results of the original dusty gas model.

CONCLUSIONS AND SIGNIFICANCE

It is shown that the results of dense fluid kinetic theory may be used to advantage in predicting diffusional transport of gases through partially rejecting, "leaky" membranes. For the particular case of inert gases, the modified Enskog theory for dense fluids of rigid spheres, which considers volume exclusion and shielding due to molecular size, furnishes corrections to the gas diffusion equations in current use. Comparison with the results of the original dusty gas model shows that even for the simplest gases (e.g., helium and nitrogen), considerable overestimation of the diffusion flux may be incurred. In one case it is shown that the flux estimated using the dusty gas model of Derjaguin, Mason and others (1957, 1961, 1967) may be as much as a factor of 3 too high. For polyatomic species, the errors will be proportionately greater and may lead to misinterpretation of surface diffusion parameters, tortuosity factors, and membrane porosities.

The applicability of Graham's inverse square-root law (as cited by Mason et al., 1967) to diffusion in microporous media is also questioned. This law, which relates the ratio of the fluxes of two counterdiffusing gases to the square-root of the inverse ratio of their molecular masses, is corrected for steric effects. Only in the open membrane limit (diffusion of point molecules) will counterdiffusion rates obey Graham's law.

INTRODUCTION

Recently Mason and Viehland (1978) and del Castillo et al. (1979) proposed a general theory for passive transport in open and semipermeable membranes. The starting point of this theory is the partial equation of motion of species α in a classical multicomponent fluid, as given by the Bearman-Kirkwood (1958, 1959) statistical-mechanical theory of transport; this equation may be expressed as

$$\sum_{\lambda=1}^{\nu} \frac{n_\alpha n_\lambda}{nkT} \zeta_{\alpha\lambda}(\bar{\vec{u}}_\alpha - \bar{\vec{u}}_\lambda)$$

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$$= -\frac{n_\alpha}{nkT}[\{\nabla_T\mu_\alpha - \vec{X}_\alpha\} + \gamma_{\alpha o}\nabla LnT] - \frac{\vec{B}_\alpha}{nkT} \quad (1)$$

where

$$\gamma_{\alpha o} = \gamma_{ao}^{(1)} + \frac{1}{n_\alpha}\left(\frac{\partial P_\alpha}{\partial LnT}\right)_{P,n_\lambda}$$

$$\vec{B}_\alpha = \frac{\partial \rho_\alpha \bar{\vec{u}}_\alpha}{\partial t} - \nabla \cdot (\vec{\vec{\sigma}}_\alpha^{(1)} - \rho_\alpha(\bar{\vec{u}}_\alpha \vec{u} + \vec{u}\bar{\vec{u}}_\alpha - \vec{u}\vec{u}))$$

To apply Eq. 1 to transport in porous media, the customary assumption that the membrane is one of the components of the fluid mixture is made with the constraint,

$$\bar{\vec{u}}_m = 0 \quad (2)$$

where the subscript m refers to the membrane component. In the following this will be taken as component ν of the ν component mixture.

Equation 1 may then be written as

$$n_m\zeta_{\alpha m}\vec{J}_\alpha + \sum_{\lambda=1}^{\nu-1} \zeta_{\alpha\lambda}(n_\lambda\vec{J}_\alpha - n_\alpha\vec{J}_\lambda)$$
$$= -n_\alpha[\{\nabla_T\mu_\alpha - \vec{X}_\alpha\} + \gamma_{\alpha o}\nabla LnT] - \vec{B}_\alpha \quad (3)$$

where

$$\vec{J}_\gamma = n_\gamma\bar{\vec{u}}_\gamma \quad (4)$$

Equation 3 is the most general form of the model proposed by Mason and Viehland and del Castillo et al. When the kinetic theory of dilute gases is used to evaluate the parameters, Eq. 3 reduces to the dusty gas model. Mason et al. have, however, pointed out that $\zeta_{\alpha m}$, $\zeta_{\alpha\lambda}$ and $\gamma_{\alpha o}$ must usually be determined by experiment, this being particularly true of liquids, for which no exact closed analytical formulae are available at present. Their analysis was, therefore, confined to developing expressions for $\vec{B}_\alpha$, and to comparison with earlier models.

Although dense fluid kinetic theory has not so far yielded exact tractable expressions for the parameters appearing in Eq. 3, we do have at our disposal a number of approximate kinetic theories, notably the Enskog rigid sphere kinetic theory and its extension to mixtures (Chapman and Cowling, 1970; Tham and Gubbins, 1971; van Beijeren and Ernst, 1973 a,b); the square-well kinetic theory for dense fluids and mixtures (Davis et al., 1961; McLaughlin and Davis, 1966; MacElroy, 1982), and also the Rice-Allnatt theory (Rice and Gray, 1965; Wei and Davis, 1966, 1967). Of these three kinetic theories, both the rigid sphere theory and the square-well theory are the simplest and have been employed with comparative success in correlating dense fluid transport data (Chapman and Cowling, 1970; Tham and Gubbins, 1971; Bell et al., 1977; Davis and Luks, 1965; Luks et al., 1966; Palyvos et al., 1967).

In an earlier paper (MacElroy and Kelly, 1980) we proposed using the square-well dense fluid kinetic theory. Although this theory is only a crude representation of real dense fluids, it was found to predict the correct temperature and pressure dependence of the transport parameters in Eq. 3. In this paper we consider in further detail the special case of the rigid sphere fluid and we employ the modified Enskog theory of van Beijeren and Ernst (1973 a,b), to obtain corrections to the dusty gas model arising from statistical correlations within the membrane-fluid system. Also, since the diffusion contribution to the total flux of species α is of primary interest here, we assume that the membrane-fluid system is at mechanical equilibrium. Under these conditions the inertial and viscous terms in Eq. 3 may be dropped; i.e., $\vec{B}_\alpha = 0$ (Bearman, 1959) and the fluxes $\vec{J}_\alpha$ now refer to diffusion flows alone.

In the first two sections below we consider the equations for the diffusion fluxes in the modified Enskog approximation and their application to multicomponent diffusion of ideal gases in rigid membranes. In both these sections we include the expressions for the thermal diffusion terms for completeness; however in the final sections, where two special cases are examined, the discussion is confined to isothermal conditions.

MODIFIED ENSKOG THEORY FOR A DENSE FLUID MIXTURE OF RIGID SPHERES

When expressed in Stefan-Maxwell form, the diffusion flux for species α in a multicomponent mixture of rigid spheres is given to a first approximation as

$$\sum_{\lambda=1}^{\nu} \frac{n_\alpha n_\lambda}{n[D_{\alpha\lambda}]_1}(\bar{\vec{u}}_\alpha - \bar{\vec{u}}_\lambda) = -n[\vec{d}_\alpha^{(1)} + [k_{T\alpha}]_1\nabla LnT] \quad (5)$$

where

$$[D_{\alpha\lambda}]_1 = \frac{3}{8n\sigma_{\alpha\lambda}^2}\left(\frac{kT(m_\alpha + m_\lambda)}{2\pi m_\alpha m_\lambda}\right)^{1/2}\frac{1}{g_{\alpha\lambda}(\sigma_{\alpha\lambda})} \quad (6)$$

$$[k_{T\alpha}]_1 = \sum_{\lambda=1}^{\nu}\left[x_\alpha x_\lambda \frac{8}{15}\sqrt{\frac{2\pi}{kT}}\frac{\sigma_{\alpha\lambda}^2}{k}\left(\frac{m_\alpha m_\lambda}{m_\alpha + m_\lambda}\right)^{3/2} g_{\alpha\lambda}(\sigma_{\alpha\lambda})\right.$$
$$\left.\times\left[\frac{1}{m_\lambda}\sum_{k=1}^{\nu}\frac{x_k\beta_k|c|_{k\lambda}}{|c|} - \frac{1}{m_\alpha}\sum_{k=1}^{\nu}\frac{x_k\beta_k|c|_{k\alpha}}{|c|}\right]\right] \quad (7)$$

$$\beta_k = 1 + \frac{12}{5}\sum_{\lambda=1}^{\nu} b_{k\lambda}\rho g_{k\lambda}(\sigma_{k\lambda})M_k M_\lambda \quad (8)$$

$|c|$ is the determinant whose elements are c_{jk} and $|c|_{kj}$ is the cofactor of the element c_{kj} where

$$c_{jk}(j \neq k) = -\frac{72}{25}\frac{\sigma_{jk}^2}{k}\sqrt{\frac{2\pi}{kT}}\left(\frac{m_j m_k}{m_j + m_k}\right)^{3/2}\frac{x_j x_k}{(m_j + m_k)}g_{jk}(\sigma_{jk}) \quad (9)$$

$$c_{jj} = \frac{32}{75}\sqrt{\frac{2\pi}{kT}}\frac{x_j m_j}{nk}\left[\frac{2n_j\sigma_{jj}^2 g_{jj}(\sigma_{jj})}{\sqrt{2m_j}} + \sum_{k\neq j}^{\nu}\left(\frac{m_k}{m_j(m_j + m_k)^5}\right)^{1/2}\right.$$
$$\left.\times n_k\sigma_{jk}^2 g_{jk}(\sigma_{jk}) \times \left(\frac{15}{2}m_j^2 + \frac{13}{4}m_k^2 + 4m_j m_k\right)\right] \quad (10)$$

The difference between the modified Enskog theory of van Beijeren and Ernst (1973 a,b), the extension of Enskog's single component rigid sphere theory to a binary mixture (Thorne, as cited in Chapman and Cowling, 1970) and the extension of Enskog's theory to multicomponent mixtures (Tham and Gubbins, 1971) arises in the vector $\vec{d}_\alpha^{(1)}$. At mechanical equilibrium the Thorne-Tham-Gubbins extension of Enskog's theory gives

$$\vec{d}_\alpha^{(1)} = \frac{1}{nkT}\left[\nabla P_\alpha - n_\alpha\vec{X}_\alpha + n_\alpha kT\sum_{\lambda=1}^{\nu} b_{\alpha\lambda}\rho g_{\alpha\lambda}(\sigma_{\alpha\lambda})\right.$$
$$\times\left[\frac{1}{n_\lambda}\nabla n_\lambda - \frac{1}{n_\alpha}\nabla n_\alpha\right]$$
$$\left. + n_\alpha kT\sum_{\lambda=1}^{\nu} b_{\alpha\lambda}\rho g_{\alpha\lambda}(\sigma_{\alpha\lambda})(M_\alpha - M_\lambda)\nabla LnT\right] \quad (11)$$

where

$$P_\alpha = n_\alpha kT\left[1 + \sum_{\lambda=1}^{\nu} b_{\alpha\lambda}\rho g_{\alpha\lambda}(\sigma_{\alpha\lambda})\right] \quad (12)$$

The modified Enskog theory of van Beijeren and Ernst, however, gives

$$\vec{d}_\alpha^{(1)} = \frac{1}{nkT}\left[n_\alpha kT\sum_{\lambda=1}^{\nu}\left[\frac{\delta_{\alpha\lambda}}{n_\lambda} - \tilde{C}_{\alpha\lambda}^{(0)}\right]\nabla n_\lambda - n_\alpha\vec{X}_\alpha\right.$$
$$\left. + n_\alpha kT\left(1 + \sum_{\lambda=1}^{\nu} 2M_\alpha b_{\alpha\lambda}\rho g_{\alpha\lambda}(\sigma_{\alpha\lambda})\right)\nabla LnT\right] \quad (13)$$

Van Beijeren and Ernst have shown that of the two relationships given above, Eq. 13 is the only one which satisfies the Onsager reciprocal relations. In particular it was shown that

$$kT\left[\frac{\delta_{\alpha\lambda}}{n_\lambda} - \tilde{C}_{\alpha\lambda}^{(0)}\right] = \left(\frac{\partial\mu_\alpha}{\partial n_\lambda}\right)_{T,n_\gamma \neq n_\lambda} \quad (14)$$

i.e.

$$kT\sum_{\lambda=1}^{\nu}\left[\frac{\delta_{\alpha\lambda}}{n_\lambda} - \tilde{C}_{\alpha\lambda}^{(0)}\right]\nabla n_\lambda = \nabla_T\mu_\alpha \quad (15)$$

Comparing Eqs. 1 and 5 we further note the correspondence between the terms

$$[D_{\alpha\lambda}]_1 \equiv \frac{kT}{n\zeta_{\alpha\lambda}}$$

$$\gamma_{\alpha o} = \frac{nkT}{n_\alpha}[k_{T\alpha}]_1 + kT\left(1 + \sum_{\lambda=1}^{\nu} 2M_\alpha b_{\alpha\lambda}\rho g_{\alpha\lambda}(\sigma_{\alpha\lambda})\right)$$

$$= \gamma_{\alpha o}^{(1)} + \frac{1}{n_\alpha}\left(\frac{\partial P_\alpha}{\partial LnT}\right)_{P,n_\lambda}$$

where

$$\frac{1}{n_\alpha}\left(\frac{\partial P_\alpha}{\partial LnT}\right)_{P,n_\lambda} = kT\left(1 + \sum_{\lambda=1}^{\nu} b_{\alpha\lambda}\rho g_{\alpha\lambda}(\sigma_{\alpha\lambda})\right)$$

To complete the specification of the diffusion flux, expressions for $g_{\alpha\lambda}(\sigma_{\alpha\lambda})$ and μ_α are required. Here we chose to use the results of scaled particle theory (Lebowitz et al., 1965).

$$g_{\alpha\lambda}(\sigma_{\alpha\lambda}) = \frac{1}{1-\xi_3} + \frac{6\xi_2}{(1-\xi_3)^2}\left(\frac{R_\alpha R_\lambda}{R_\alpha + R_\lambda}\right) + \frac{12\xi_2^2}{(1-\xi_3)^3}\left(\frac{R_\alpha R_\lambda}{R_\alpha + R_\lambda}\right)^2 \quad (16)$$

$$\mu_\alpha = \mu_\alpha^0 + kTLn\gamma_\alpha n_\alpha \quad (17)$$

where

$$Ln\gamma_\alpha = -Ln(1-\xi_3) + \frac{1}{(1-\xi_3)}[6\xi_2 R_\alpha + 12\xi_1 R_\alpha^2 + 8\xi_o R_\alpha^3] + \frac{1}{(1-\xi_3)^2}[18\xi_2^2 R_\alpha^2 + 24\xi_2\xi_1 R_\alpha^3] + \frac{24\xi_2^3 R_\alpha^3}{(1-\xi_3)^3} \quad (18)$$

$$\xi_i = \frac{\pi}{6}\sum_{j=1}^{\nu} n_j(2R_j)^i \quad (19)$$

and

$$\mu_\alpha^\circ = kTLn\left(\frac{h^3}{(2\pi m_\alpha kT)^{3/2}}\right) \quad (20)$$

Substituting Eqs. 13 and 17 into Eq. 6 gives

$$\sum_{\lambda=1}^{\nu}\frac{1}{n[D_{\alpha\lambda}]_1}(n_\lambda \vec{J}_\alpha - n_\alpha \vec{j}_\lambda)$$

$$= -\left[\left[\sum_{\lambda=1}^{\nu}\frac{n_\alpha}{n_\lambda}\left(\delta_{\alpha\lambda} + \left(\frac{\partial Ln\gamma_\alpha}{\partial Lnn_\lambda}\right)_{T,n_\gamma\neq n_\lambda}\right)\nabla n_\lambda - \frac{n_\alpha\vec{X}_\alpha}{kT}\right] + n_\alpha\left[1 + \frac{n}{n_\alpha}[k_{T\alpha}]_1 + \sum_{\lambda=1}^{\nu}2M_\alpha b_{\alpha\lambda}\rho g_{\alpha\lambda}(\sigma_{\alpha\lambda})\right]\nabla LnT\right] \quad (21)$$

APPLICATION TO DIFFUSION IN POROUS MEDIA

Using the condition expressed in Eq. 2 and the additional conditions

$$\nabla n_m = 0 \quad (22a)$$

$$m_\alpha/m_m \rightarrow 0 \ (\alpha = \text{pore fluid component}) \quad (22b)$$

then Eq. 21 may be rearranged giving

$$\frac{\vec{J}_\alpha}{[D_{\alpha M}]_1} + \sum_{\lambda=1}^{\nu-1}\frac{1}{n[D_{\alpha\lambda}]_1}(n_\lambda\vec{J}_\alpha - n_\alpha\vec{J}_\lambda)$$

$$= -\left[\left[\sum_{\lambda=1}^{\nu-1}\frac{n_\alpha}{n_\lambda}\left(\delta_{\alpha\lambda} + \left(\frac{\partial Ln\gamma_\alpha}{\partial Lnn_\lambda}\right)_{T,n_\gamma\neq n_\lambda}\right)\nabla n_\lambda - \frac{n_\alpha\vec{X}_\alpha}{kT}\right] + n_\alpha\left[1 + \frac{n}{n_\alpha}[k_{T\alpha}]_1 + \sum_{\lambda=1}^{\nu-1}2M_\alpha b_{\alpha\lambda}\rho g_{\alpha\lambda}(\sigma_{\alpha\lambda})\right]\nabla LnT\right] \quad (23)$$

where

$$[D_{\alpha M}]_1 = \frac{n[D_{\alpha m}]_1}{n_m} \quad (24)$$

To express the parameters appearing in Eq. 23 in terms of membrane properties, we make use of the following relationships;

$$\sigma_{kj} = \frac{\sigma_{kk} + \sigma_{jj}}{2} \quad (25a)$$

$$\frac{1}{6}\pi n_m \sigma_{mm}^3 = (1-\psi) \quad (25b)$$

$$\pi n_m \sigma_{mm}^2 = \rho_p S \quad (25c)$$

$$R_{\text{EFF}} = \frac{2\psi}{\rho_p S} \quad (25d)$$

and

$$\sigma_{mm} = 2R_m = 3\left(\frac{1-\psi}{\psi}\right)R_{\text{EFF}} \quad (25e)$$

After rearranging, one finds

$$[D_{\alpha M}]_1 = \frac{3\pi}{16}R_{\text{EFF}}\bar{v}_\alpha\frac{1}{\psi g_{\alpha m}(\sigma_{\alpha m})\left[1 + \frac{R_\alpha}{R_m}\right]^2} \quad (26)$$

$$[k_{T\alpha}]_1 = \sum_{\lambda=1}^{\nu-1}\frac{n_\alpha n_\lambda}{n^2}\frac{8}{15}\sqrt{\frac{2\pi}{kT}\frac{\sigma_{\alpha\lambda}^2}{k}}\left(\frac{m_\alpha m_\lambda}{m_\alpha + m_\lambda}\right)^{3/2} g_{\alpha\lambda}(\sigma_{\alpha\lambda}) \times \left[\frac{1}{m_\lambda}\sum_{k=1}^{\nu-1}\frac{x_k\beta_k|c|'_{k\lambda}}{|c|'} - \frac{1}{m_\alpha}\sum_{k=1}^{\nu-1}\frac{x_k\beta_k|c|'_{k\alpha}}{|c|'}\right] - \frac{n_\alpha}{n}\left[\frac{1}{5kn[D_{\alpha M}]_1}\right]\sum_{k=1}^{\nu-1}\frac{x_k\beta_k|c|'_{k\alpha}}{|c|'} \quad (27)$$

where the matrix $[c]'$ is given by

$$[c]' = \begin{bmatrix} c_{11} & c_{12}\cdot\ldots\ldots c_{1,\nu-1} \\ c_{21} & c_{22}\cdot\ldots\ldots c_{2,\nu-1} \\ & \\ c_{\nu-1,1} & c_{\nu-1,2}\cdot\,\cdot\,\cdot c_{\nu-1,\nu-1} \end{bmatrix}$$

In specializing to diffusion of dilute, nonadsorbing gases, we note that the parameters ξ_i given in Eq. 19 simplify to

$$\xi_i = \frac{\pi}{6}n_m(2R_m)^i$$

$$= \frac{\pi}{6}n_m\sigma_{mm}^i$$

Substituting Eq. 25b gives

$$\xi_i = \frac{1-\psi}{\sigma_{mm}^{3-i}} \quad (28)$$

Equations 16 and 18 for the contact radial distribution function and the activity coefficient may then be rearranged, giving

$$g_{\alpha\lambda}(\sigma_{\alpha\lambda}) = \frac{1}{\psi}\left[1 + 3\left(\frac{1-\psi}{\psi}\right)\frac{\delta_m}{(1+\delta_\lambda)} + 3\left(\frac{1-\psi}{\psi}\right)^2\left(\frac{\delta_m}{1+\delta_\lambda}\right)^2\right] \quad (29)$$

$$\gamma_\alpha = \frac{1}{\psi}\exp\left[\left(\frac{1-\psi}{\psi}\right)[3\delta_m + 3\delta_m^2 + \delta_m^3] + \left(\frac{1-\psi}{\psi}\right)^2\left[\frac{9}{2}\delta_m^2 + 3\delta_m^3\right] + 3\left(\frac{1-\psi}{\psi}\right)^3\delta_m^3\right] \quad (30)$$

where

$$\delta_j = \frac{R_\alpha}{R_j}$$

For diffusion of dilute gases, Eq. 23 simplifies since γ_α is independent of n_λ ($\lambda = 1, \ldots, \nu - 1$) and $b_{\alpha\lambda} \rightarrow 0$. One finds

$$\frac{\vec{J}_\alpha}{[D_{\alpha M}]_1} + \sum_{\lambda=1}^{\nu-1}\frac{1}{n[D_{\alpha\lambda}]_1}(n_\lambda\vec{J}_\alpha - n_\alpha\vec{J}_\lambda) = -\left[\nabla n_\alpha - \frac{n_\alpha\vec{X}_\alpha}{kT}\right] - n_\alpha\left(1 + \frac{n}{n_\alpha}[k_{T\alpha}]_1\right)\nabla LnT \quad (31)$$

In the following, Eq. 31 will be examined for two specific cases: (i) steady-state isothermal diffusion of a pure gas and (ii) steady-state isothermal counterdiffusion of a binary gas mixture. We will assume that diffusion is taking place unidirectionally across a membrane with bulk gas/membrane interfaces at $z = 0$ and $z = L$. The vector notation in Eq. 31 may, therefore, be dropped and ∇ replaced by d/dz. For simplicity we will also neglect the external forces $\vec{X}_\alpha$ acting on component α of the gas.

Bearing in mind that the number densities in the above equations refer to a unit volume of the fluid mixture including the membrane, it is necessary to specify boundary conditions at $z = 0$ and $z = L$ relating the membrane fluid number densities to the bulk fluid number densities on both sides of the membrane. To do so we neglect boundary film resistances and mass transfer resistances which may arise at the bulk fluid/membrane interface. Under these conditions we have for both sides of the membrane

$$\begin{aligned}\mu_{\alpha m} &= \mu_\alpha^0 + kTLn\gamma_\alpha n_\alpha \\ &= \mu_\alpha^0 + kTLnn_{\alpha f} \\ &= \mu_{\alpha f}\end{aligned} \tag{32}$$

i.e.

$$\begin{aligned}n_\alpha &= \frac{1}{\gamma_\alpha} n_{\alpha f} \\ &= K_\alpha n_{\alpha f}\end{aligned} \tag{33}$$

where K_α is frequently referred to as the partition coefficient and is given by the inverse of Eq. 30 for the rigid sphere model.

ISOTHERMAL DIFFUSION OF A PURE GAS IN A POROUS MEDIUM

In this case, Eq. 31 simplifies to

$$J_\alpha = -[D_{\alpha M}]_1 \frac{dn_\alpha}{dz} \tag{34}$$

Since $[D_{\alpha M}]_1$ is independent of n_α (with reference to Eqs. 26 and 29), Eq. 34 may be immediately integrated over the region $z = 0$ to $z = L$, giving

$$J_\alpha = [D_{\alpha M}]_1 \frac{n_\alpha|_0 - n_\alpha|_L}{L}$$

Substituting Eqs. 33 and noting that γ_α is also independent of n_α gives

$$J_\alpha = K_\alpha [D_{\alpha M}]_1 \frac{\Delta n_{\alpha f}}{L} \tag{35}$$

Equation 35 is a modified Knudsen diffusion flux, incorporating the influence of steric exclusion on the free molecule transport of the gas. Using Eqs. 26, 29 and 30 one finds

$$K_\alpha [D_{\alpha M}]_1 = \frac{3\pi}{16} \psi R_{\mathrm{EFF}} \bar{v}_\alpha f(\delta_m) \tag{36}$$

where

$$f(\delta_m) = \frac{\exp\left[-\left(\frac{1-\psi}{\psi}\right)[3\delta_m + 3\delta_m^2 + \delta_m^3] - \left(\frac{1-\psi}{\psi}\right)^2\left[\frac{9}{2}\delta_m^2 + 3\delta_m^3\right] - 3\left(\frac{1-\psi}{\psi}\right)^3\delta_m^3\right]}{\left[(1+\delta_m)^2 + 3\left(\frac{1-\psi}{\psi}\right)\delta_m(1+\delta_m) + 3\left(\frac{1-\psi}{\psi}\right)^2\delta_m^2\right]} \tag{37}$$

The usual definition of the Knudsen permeability is

$$P_{\alpha M}^{(o)} = \frac{\psi}{\tau}\left(\frac{2}{3} R_{\mathrm{EFF}} \bar{v}_\alpha\right) \tag{38}$$

where the superscript o refers to transport of point particles.

In the limit $\delta_m \rightarrow 0$, Eq. 36 reduces to

$$K_\alpha [D_{\alpha M}]_1 = \frac{3\pi}{16} \psi R_{\mathrm{EFF}} \bar{v}_\alpha \tag{39}$$

Comparing Eqs. 38 and 39 we note (i) that there is a numerical discrepancy, and (ii) that no tortuosity term appears in Eq. 39. The numerical difference occurs because $[D_{\alpha M}]_1$ is simply the first approximation to the binary diffusion coefficient in the Chapman-Enskog theory. The true Knudsen limit ($Kn \rightarrow \infty$) is obtained by multiplying Eq. 36 by 1.132 (Chapman and Cowling, 1970, p. 260), i.e.,

$$K_\alpha [D_{\alpha M}]_{Kn \rightarrow \infty} = \frac{2}{3} \psi R_{\mathrm{EFF}} \bar{v}_\alpha f(\delta_m) \tag{40}$$

The absence of a tortuosity term in Eqs. 36 and 39 arises for the following reasons. The Enskog rigid sphere theory correctly leads to the porosity terms since the influence of statistical correlations (volume exclusion and shielding) is included within its framework. However, it is because of the assumed dynamical nature of the particle collisions that no tortuosity term appears in the present results. Although the exact kinetic theory of dense fluids of rigid spheres has, so far, eluded solution, theoretical results have been obtained for moderately dense gases (Sengers, 1966; van Leeuwen and Weijland, 1967, 1968; Sengers et al., 1972). These results clearly show that dynamical correlations, such as a sequence of correlated binary collisions, can significantly reduce the values of the transport coefficients below those of the Enskog theory. Of particular relevance to the subject of this paper are the results obtained by van Leeuwen and Weijland (1967, 1968). They found that for a moderately dense Lorentz gas, the diffusion coefficient of the light gas molecules is given by

$$D_{\alpha M} = \frac{D_{\alpha M}|n_m \rightarrow 0}{F} \tag{41}$$

where

$$D_{\alpha M}|n_m \rightarrow 0 = \frac{\bar{v}_\alpha}{3\pi n_m \sigma_{\alpha m}^2}$$

The factor F is given by van Leeuwen and Weijland as a density expansion in n_m which they have evaluated to terms of order n_m^2. For the case $\sigma_{\alpha\alpha} \ll \sigma_{mm}$, F is given by

$$\begin{aligned}F = 1 + \frac{4}{3}\pi n_m R_m^3 &+ 0.775\pi n_m R_m^3 \\ &+ 0.0684(n_m R_m^3)^2 Ln(n_m R_m^3)\end{aligned} \tag{42}$$

The term $4/3\pi n_m R_m^3$ in Eq. 42 is the contribution predicted by the Enskog theory to lowest order in density n_m. The remaining terms in the above equation arise due to dynamical effects and small statistical correlations not taken into account in the Enskog theory. Since the last term in Eq. 42 is negligible in comparison with the first few terms it is clearly seen, to this order of density at least, that the contribution of the dynamical correlations is as large as 50% of the Enskog statistical correlation.

Van Leeuwen and Weijland also found that for the case $\sigma_{\alpha\alpha} \gtrsim \sigma_{mm}$ the dynamical effects become increasingly more important relative to the Enskog statistical contribution. Although their results apply only to a moderately dense Lorentz gas, it is reasonable to expect the above to be true of high density systems also, since cageing and backscattering of the gas molecules diffusing through extremely small pores will severely hinder, if not arrest, the diffusion process. Under these conditions, excluded volume effects will take on a secondary role.

Both the Enskog theory and the analysis of van Leeuwen and Weijland are based on specular collision dynamics. This is not, however, the primary mode of scattering in porous media. It has long been recognized that of the two scattering modes, specular and diffuse reflection, it is diffuse reflection which most frequently governs molecular scattering from solid surfaces. For diffusion in porous systems modelled as randomly distributed spherical particles, Mason and Chapman (1962) have shown that the mutual diffusion coefficient $D_{\alpha M}$, determined from the Chapman-Enskog theory, should be multiplied by the factor

$$\frac{1}{1+\frac{4}{9}f} \tag{43}$$

i.e., the permeability given in Eq. 40 should be written as

$$K_\alpha[D_{\alpha M}]_{Kn\to\infty} = \frac{1}{1+\frac{4}{9}f}\,\frac{2}{3}\,\psi R_{\mathrm{EFF}}\bar{v}_\alpha f(\delta_m) \tag{44}$$

From this equation we see that for totally diffuse reflection (f = 1) the tortuosity is given by

$$\tau = \frac{13}{9} = 1.44 \tag{45}$$

This value of τ agrees well with experimental results obtained for a number of simple porous media, e.g., compacted powders (Ash et al., 1970; Omata and Brown, 1972; Bell and Brown, 1974). In fact, the result given in Eq. 43 above for the special case $f = 1$ was originally derived by Derjaguin (1946) for the purpose of determining the specific surface areas of powders and uniform particle packings by gas permeametry. This technique has been found to be comparatively successful (Stanley-Wood and Chatterjee, 1974; Derjaguin et al., 1976).

A conclusion which could be drawn from the above results is that the tortuosity factor for Knudsen diffusion through spherical particle assemblies is a constant, i.e., independent of both the properties of the diffusing gas and the porosity and mean pore radius of the porous medium. This is acceptable for comparatively large pore materials, i.e., for systems of small δ_m, where the relative roughness scale of the solid surface to pore radius is small. However for systems with pore radii of the same order of magnitude as the size of the diffusing gas molecule ($\delta_m \sim 1$), it is more reasonable to assume that the gas/solid collisions are specular rather than diffuse. For the present we will confine the discussion given below to the hindrance effects predicted by the rigid sphere theory from the point of view of statistical correlations alone. It will be implicitly assumed that the tortuosity τ is independent of δ_m.

A reduced partition coefficient and diffusivity may be defined as

$$\frac{K_\alpha}{K_\alpha^{(0)}} = \exp\left[-\left(\frac{1-\psi}{\psi}\right)[3\delta_m + 3\delta_m^2 + \delta_m^3] - \left(\frac{1-\psi}{\psi}\right)^2\left[\frac{9}{2}\delta_m^2 + 3\delta_m^3\right] - 3\left(\frac{1-\psi}{\psi}\right)^3\delta_m^3\right] \tag{46}$$

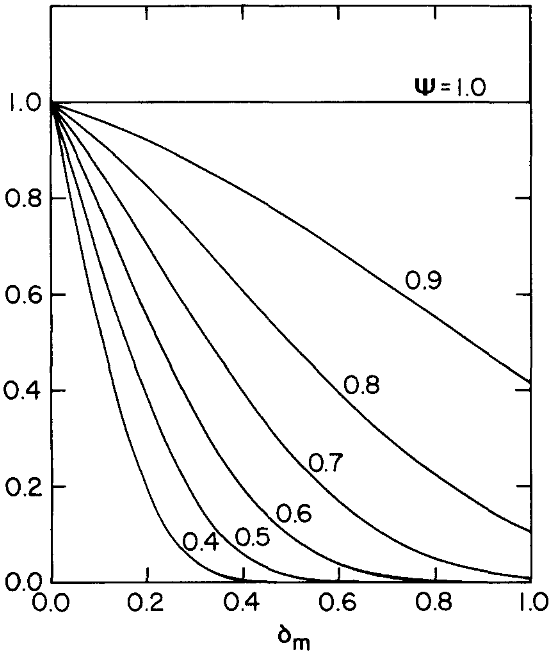

Figure 1. Effect of particle radius ratio on the partition coefficient.

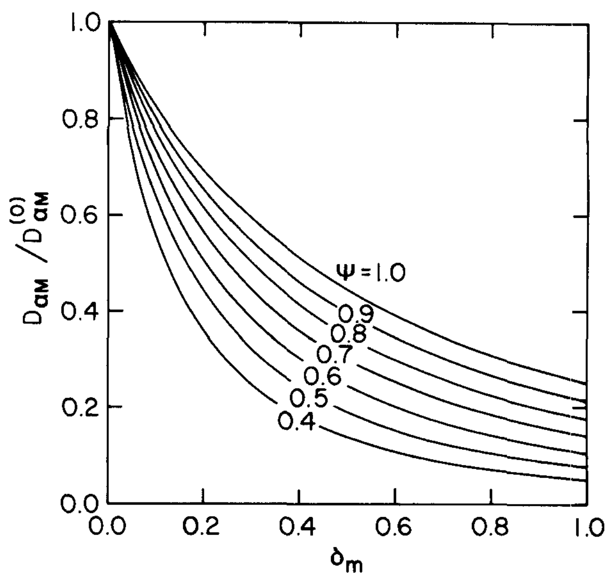

Figure 2. Effect of particle radius ratio on the Knudsen diffusion coefficient.

and

$$\frac{D_{\alpha M}}{D_{\alpha M}^{(0)}} = \left[(1+\delta_m)^2 + 3\left(\frac{1-\psi}{\psi}\right)\delta_m(1+\delta_m) + 3\left(\frac{1-\psi}{\psi}\right)^2\delta_m^2\right]^{-1} \tag{47}$$

where

$$K_\alpha^{(0)} = \psi \tag{48a}$$

$$D_{\alpha M}^{(0)} = \frac{1}{\tau}\left(\frac{2}{3}R_{\mathrm{EFF}}\bar{v}_\alpha\right) \tag{48b}$$

Plots of Eqs. 46 and 47 are given in Figures 1 and 2 respectively for the porosity range $0.4 < \psi < 1$. These results clearly show the effects of molecular sieving, particularly in the case of the partition coefficient which is very sensitive to the dimensionless ratio δ_m and to the bulk porosity of the medium. The diffusion coefficient is not as sensitive to porosity but does decrease markedly with increasing δ_m. For reasons given earlier the values of $D_{\alpha M}/D_{\alpha M}^{(0)}$ in the region $\delta_m \to 1$ are probably significant underestimates of the hindrance effect, and the values shown in Figure 2 should be considered as upper bounds on the true values.

The relationships between the partition coefficient, the diffusivity and the radius of the diffusing molecule are more frequently expressed in terms of λ (Brenner and Gaydos, 1977; Malone and Anderson, 1978) where

$$\lambda = \frac{R_\alpha}{R_{\mathrm{EFF}}}$$

i.e., from Eq. 25e one finds

$$\lambda = \frac{3}{2}\left(\frac{1-\psi}{\psi}\right)\delta_m \tag{49}$$

Equation 49 may be used to determine the reduced partition coefficient and the reduced diffusivity for a given value of λ by using Figures 1 and 2 or by direct calculation using Eqs. 46 and 47.

To further illustrate the extent to which steric hindrance can influence both K_α and $D_{\alpha M}$, Eq. 49 was used to determine $K_\alpha/K_\alpha^{(0)}$ and $D_{\alpha M}/D_{\alpha M}^{(0)}$ for diffusion of two simple gases, Helium and Nitrogen, in three different microporous media having mean pore radii typical of many industrial catalysts. The porosity ψ was taken as 0.5 in each case and the hard sphere radii of Helium (R_α = 1.096 Å) and Nitrogen (R_α = 1.892 Å) given by Chapman and Cowling (1970, p. 228) were used. The results obtained are given in Tables 1 and 2. Also included are the values for the dimensionless permeability defined as

TABLE 1. THEORETICAL ESTIMATES OF EXCLUSION EFFECTS IN POROUS MEDIA (HELIUM)

R_{EFF} (Å)	$K_\alpha/K_\alpha^{(0)}$	$D_{\alpha M}/D_{\alpha M}^{(0)}$	$P_{\alpha M}/P_{\alpha M}^{(0)}$
100	0.978	0.964	0.943
30	0.925	0.888	0.821
10	0.770	0.713	0.549

$$\frac{P_{\alpha M}}{P_{\alpha M}^{(0)}} = \frac{K_\alpha D_{\alpha M}}{K_\alpha^{(0)} D_{\alpha M}^{(0)}}$$

With respect to the entries for the reduced partition coefficient, it is observed that as the mean pore radius decreases, the pore volume available to the Nitrogen molecules becomes increasingly smaller relative to that available to the Helium atoms. Even in the case of Helium, the accessible pore volume is only 77% of the total void space for the porous solid with a mean pore radius $R_{\text{EFF}} = 10$ Å. Since Helium expansion pycnometry is frequently used to determine the density and porosity of porous catalysts, the results given in Table 1 must bring into question the values of ψ and ρ_s so obtained if steric effects are neglected.

Similar comments may be expressed with respect to $D_{\alpha M}/D_{\alpha M}^{(0)}$ and $P_{\alpha M}/P_{\alpha M}^{(0)}$. For example if a steady-state experiment is carried out to determine the "tortuosity" factor for a porous solid with $R_{\text{EFF}} = 10$ Å using Helium as the permeating gas, subsequent use of this value of "τ" to estimate the Nitrogen flux will result in an error of 60% unless steric hindrance is taken into consideration.

STEADY-STATE ISOTHERMAL COUNTERDIFFUSION OF BINARY GAS MIXTURES

For unidirectional diffusion in the absence of external forces and temperature gradients, the flux equations for both components α and β are given by Eq. 31 as

$$\frac{J_\alpha}{D_{\alpha M}} + \frac{1}{n_f D_{\alpha\beta}}(n_\beta J_\alpha - n_\alpha J_\beta) = -\frac{dn_\alpha}{dz} \tag{50}$$

$$\frac{J_\beta}{D_{\beta M}} + \frac{1}{n_f D_{\alpha\beta}}(n_\alpha J_\beta - n_\beta J_\alpha) = -\frac{dn_\beta}{dz} \tag{51}$$

The diffusivities $D_{\alpha M}$ and $D_{\beta M}$ are to be considered as Enskog diffusivities corrected for tortuosity effects, e.g., Eq. 44. Similarly the mutual diffusion coefficient $D_{\alpha\beta}$ is also a tortuosity corrected Enskog diffusivity, i.e.,

$$n_f D_{\alpha\beta} = \frac{n}{\tau}[D_{\alpha\beta}]_1 = \frac{3}{8\tau\sigma^2_{\alpha,\beta}}\left[\frac{kT(m_\alpha + m_\beta)}{2\pi m_\alpha m_\beta}\right]^{1/2}\frac{1}{g_{\alpha\beta}(\sigma_{\alpha\beta})} \tag{52}$$

or

$$D_{\alpha\beta} = \frac{1}{\tau g_{\alpha\beta}(\sigma_{\alpha\beta})}\mathcal{D}_{\alpha\beta}$$

The group $\tau g_{\alpha\beta}(\sigma_{\alpha\beta})$ represents the total correction required to account for the influence of membrane structure. The contact radial distribution function $g_{\alpha\beta}(\sigma_{\alpha\beta})$ is given by Eq. 29 and contains not only the porosity correction but also includes the influence of molecular size and pore dimensions. The tortuosity τ is introduced in Eq. 52 for reasons similar to those given previously. Although there are no theoretical grounds for assuming that τ in Eq. 52 is equal to the tortuosity factor in Eq. 48b experimental data for simple porous media (e.g., compacted powders) do suggest that this is a good approximation (Omata and Brown, 1972; Bell and Brown, 1974). For simplicity we will make use of this assumption in the following discussion.

To avoid viscous flow contributions to the flux of both components, counterdiffusion experiments are generally carried out under gas phase isobaric conditions, i.e.,

$$P_f|_{z=0} = P_f|_{z=L} \tag{53}$$

or

TABLE 2. THEORETICAL ESTIMATES OF EXCLUSION EFFECTS IN POROUS MEDIA (NITROGEN)

R_{EFF} (Å)	$K_\alpha/K_\alpha^{(0)}$	$D_{\alpha M}/D_{\alpha M}^{(0)}$	$P_{\alpha M}/P_{\alpha M}^{(0)}$
100	0.962	0.940	0.904
30	0.869	0.818	0.711
10	0.599	0.574	0.344

$$\Delta P_f = 0,\ n_f = \text{constant}$$

We note here that this does not imply

$$\frac{dn_\alpha}{dz} = -\frac{dn_\beta}{dz} \tag{54}$$

Equation 54 is in fact only true for open membranes. For "leaky" membranes both Eqs. 50 and 51 must be solved simultaneously giving for example, for component α

$$J_\alpha = \frac{n_f D_{\alpha\beta}}{L\left(1 + \frac{J_\beta}{J_\alpha}\right)} \times Ln\left[\frac{1 + \frac{D_{\alpha M}}{n_f D_{\alpha\beta}}\left[n_\beta|_L - n_\alpha|_L\frac{J_\beta}{J_\alpha}\right] - \left[\frac{1 + \frac{J_\beta}{J_\alpha}\frac{D_{\alpha M}}{D_{\beta M}}}{1 + \frac{J_\beta}{J_\alpha}}\right]}{1 + \frac{D_{\alpha M}}{n_f D_{\alpha\beta}}\left[n_\beta|_0 - n_\alpha|_0\frac{J_\beta}{J_\alpha}\right] - \left[\frac{1 + \frac{J_\beta}{J_\alpha}\frac{D_{\alpha M}}{D_{\beta M}}}{1 + \frac{J_\beta}{J_\alpha}}\right]}\right] \tag{55}$$

Substituting Eq. 33 into Eq. 55 then gives

$$J_\alpha = \frac{n_f D_{\alpha\beta}}{L\left(1 + \frac{J_\beta}{J_\alpha}\right)} \times Ln\left[\frac{1 + \frac{D_{\alpha M}}{\gamma_\beta D_{\alpha\beta}}\left[1 - x_{\alpha f}|_L\left(1 + \frac{\gamma_\beta}{\gamma_\alpha}\frac{J_\beta}{J_\alpha}\right)\right] - \left[\frac{1 + \frac{J_\beta}{J_\alpha}\frac{D_{\alpha M}}{D_{\beta M}}}{1 + \frac{J_\beta}{J_\alpha}}\right]}{1 + \frac{D_{\alpha M}}{\gamma_\beta D_{\alpha\beta}}\left[1 - x_{\alpha f}|_0\left(1 + \frac{\gamma_\beta}{\gamma_\alpha}\frac{J_\beta}{J_\alpha}\right)\right] - \left[\frac{1 + \frac{J_\beta}{J_\alpha}\frac{D_{\alpha M}}{D_{\beta M}}}{1 + \frac{J_\beta}{J_\alpha}}\right]}\right] \tag{56}$$

The second equation required to complete the solution for the unknown fluxes is found by adding both Eqs. 50 and 51, i.e.,

$$\frac{J_\alpha}{D_{\alpha M}} + \frac{J_\beta}{D_{\beta M}} = -\frac{d(n_\alpha + n_\beta)}{dz}$$

Integrating and substituting Eqs. 33 and 53 gives

$$\frac{J_\alpha}{D_{\alpha M}} + \frac{J_\beta}{D_{\beta M}} = \frac{1}{\gamma_\alpha}\left(1 - \frac{\gamma_\alpha}{\gamma_\beta}\right)\frac{\Delta n_{\alpha f}}{L} \tag{57}$$

Equations 56 and 57 reduce to the well known open membrane results when the limit $\delta_m \to 0$ is taken. From Eq. 57 one obtains the inverse square-root relation

$$\frac{J_\alpha}{J_\beta} = -\frac{D_{\alpha M}^{(0)}}{D_{\beta M}^{(0)}} = -\sqrt{\frac{m_\beta}{m_\alpha}} \tag{58}$$

Equation 56 reduces to

$$J_\alpha = \frac{n_f D^{(0)}_{\alpha\beta}}{L\left(1 + \frac{J_\beta}{J_\alpha}\right)} \times Ln \left[\frac{1 + \frac{\psi D^{(0)}_{\alpha M}}{D^{(0)}_{\alpha\beta}}\left[1 - x_{\alpha f}|_L\left(1 + \frac{J_\beta}{J_\alpha}\right)\right]}{1 + \frac{\psi D^{(0)}_{\alpha M}}{D^{(0)}_{\alpha\beta}}\left[1 - x_{\alpha f}|_0\left(1 + \frac{J_\beta}{J_\alpha}\right)\right]}\right] \tag{59}$$

where

$$D^{(0)}_{\alpha\beta} = \frac{\psi}{\tau}\mathcal{D}_{\alpha\beta}$$

and J_β/J_α is given by Eq. 58.

For "leaky" membranes both Eqs. 56 and 57 must be solved iteratively to determine J_α and J_β. For the special case $\Delta n_{\alpha f} \rightarrow 0$ simple expressions for the fluxes and the flux ratio are obtained:

$$J_\alpha = D_{\alpha \mathrm{EFF}}\frac{\Delta n_{\alpha f}}{L} \tag{60}$$

where

$$D_{\alpha \mathrm{EFF}} = \frac{\left[1 + \frac{x_{\alpha f}}{\gamma_\alpha}\frac{D_{\beta M}}{D_{\alpha\beta}}\left(1 - \frac{\gamma_\alpha}{\gamma_\beta}\right)\right]}{\left[\frac{\gamma_\alpha}{D_{\alpha M}} + \frac{\gamma_\alpha}{\gamma_\beta D_{\alpha\beta}}\left[1 - x_{\alpha f}\left(1 - \frac{\gamma_\beta}{\gamma_\alpha}\frac{D_{\beta M}}{D_{\alpha M}}\right)\right]\right]} \tag{61}$$

$$\frac{J_\beta}{J_\alpha} = -\frac{\gamma_\alpha}{\gamma_\beta}\frac{D_{\beta M}}{D_{\alpha M}}\left[\frac{1 + \frac{x_{\beta f}}{\gamma_\beta}\frac{D_{\alpha M}}{D_{\alpha\beta}}\left(1 - \frac{\gamma_\beta}{\gamma_\alpha}\right)}{1 + \frac{x_{\alpha f}}{\gamma_\alpha}\frac{D_{\beta M}}{D_{\alpha\beta}}\left(1 - \frac{\gamma_\alpha}{\gamma_\beta}\right)}\right] \tag{62}$$

In contrast with Eq. 61 for "leaky" membranes, Eq. 59 for open membranes gives in the limit $\Delta n_{\alpha f} \rightarrow 0$

$$J_\alpha = D^{(0)}_{\alpha \mathrm{EFF}}\frac{\Delta n_{\alpha f}}{L} \tag{63}$$

where

$$D^{(0)}_{\alpha \mathrm{EFF}} = \frac{1}{\left[\frac{1}{\psi D^{(0)}_{\alpha M}} + \frac{1}{D^{(0)}_{\alpha\beta}}\left[1 - x_{\alpha f}\left(1 - \sqrt{\frac{m_\alpha}{m_\beta}}\right)\right]\right]} \tag{64}$$

In Figure 3, we illustrate the relative error involved if hindrance is neglected, and Eq. 63 is used to predict, a priori, the Nitrogen flux for Helium-Nitrogen counterdiffusion in porous media with mean pore radii of 100 Å, 30 Å, and 10 Å respectively. The relative error is defined as

$$E = \frac{J_\alpha\,(\mathrm{Eq.}\ 60) - J_\alpha\,(\mathrm{Eq.}\ 63)}{J_\alpha\,(\mathrm{Eq.}\ 60)} = 1 - \frac{D^{(0)}_{\alpha \mathrm{EFF}}}{D_{\alpha \mathrm{EFF}}} \tag{65}$$

The porosity of each of the three media was taken as 0.5 and the pressure dependence of the contact radial distribution functions and the activity coefficients was neglected. (The error involved in the latter assumption is negligible for the pressure range considered.) The hard sphere radii for Helium and Nitrogen were taken as those given earlier, and the temperature and mean mole fraction of both components were taken as 273 K and 0.5, respectively. The value of $P_f\mathcal{D}_{\alpha\beta}$ used was $P_f \times 0.607$ where 0.607 cm^2/s is the binary diffusion coefficient for the helium-nitrogen system at S.T.P. (Chapman and Cowling, 1970).

The tortuosity τ was assumed to be the same in both Eqs. 60 and 63. It is for this reason that E represents the relative error in predicting the flux *a priori*, i.e., a value of τ is initially assumed without reference to independent permeability measurements using another gas. If a value of tortuosity obtained from such measurements is used (subject to the assumption that the membrane is open), clearly the error in the predicted nitrogen flux will be different; the magnitude of the error in this case will depend on the difference between the molecular radii of the test gas and Nitrogen. By assuming τ to be the same in both Eqs. 60 and 63, a cancellation results in Eq. 65 and the value of τ itself does not enter into the calculations.

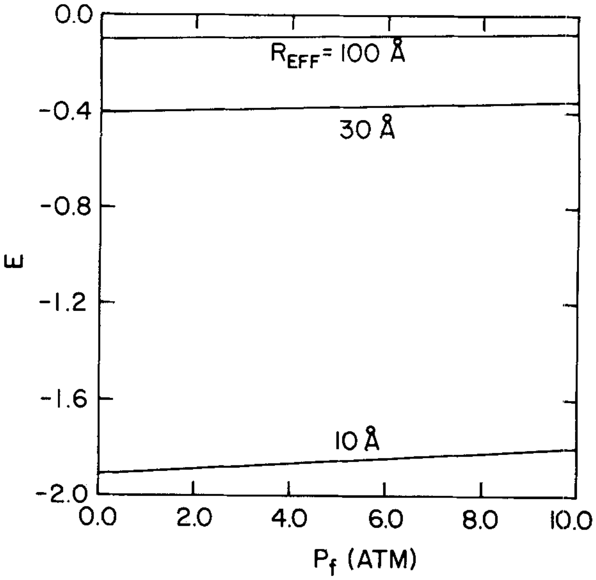

Figure 3. Relative error between the hindrance model and the dusty gas model for counterdiffusion of N$_2$ against helium at different total pressures.

It is clear from the results shown in Figure 3 that the open membrane dusty gas model cannot be used with confidence to predict diffusion fluxes in microporous media, particularly when pore radii of the order of 30 Å or less are involved. The relative error E exhibits a slight pressure dependence decreasing with increase in pressure. The principal source of this pressure dependence arises due to the difference between the denominators of Eqs. 61 and 64. The term

$$\frac{x_{\alpha f}}{\gamma_\alpha}\frac{D_{\beta M}}{D_{\alpha\beta}}\left(1 - \frac{\gamma_\alpha}{\gamma_\beta}\right)$$

in the numerator of Eq. 61 is negligible in comparison with 1.0.

From this last observation we find to a good approximation that the flux ratio (Eq. 62) is given by

$$\frac{J_\beta}{J_\alpha} \simeq -\frac{\gamma_\alpha}{\gamma_\beta}\frac{D_{\beta M}}{D_{\alpha M}}$$

The numerical results given in Tables 1 and 2 were used to estimate the flux ratio for nitrogen (α)-helium (β) counterdiffusion in the three model membranes with mean pore radii of 100 Å, 30 Å, and 10 Å. The results obtained are given in Table 3. Comparing these values with the inverse square-root relation

$$\frac{J_\beta}{J_\alpha} = -2.646$$

it is seen that the latter gives a poor estimate of the flux ratio.

DISCUSSION

Considering that the rigid sphere model applies only to nonadsorbing gases, a literature survey shows that there are few data which could directly support the present results for the most important case of microporous solids with pore sizes less than 50 Å, owing to the tendency for adsorption and surface flow, even for

TABLE 3. FLUX RATIO FOR NITROGEN AND HELIUM

R_{EFF} (Å)	J_β/J_α
100	−2.760
30	−3.055
10	−4.223

the permanent gases He, Ne, H_2 and N_2 (Barrer and Strachan, 1955; Omata and Brown, 1972). Furthermore, much of the data available has been obtained for steady-state diffusion in bimodal porous media. In the latter case, the flux measured corresponds to transport through the largest pores ($\sim 10^3 \rightarrow 10^4$ Å in radius). However, we offer below some evidence which we believe verifies qualitatively a number of the results presented here.

Those diffusion data which exist for nonadsorbing or very weakly adsorbing gases in microporous media would tend to suggest that the tortuosity of the pores in a given class of materials increases with decrease in mean pore radius (Henry et al., 1967; Gangwal et al., 1979). This trend may well be due to differences in the pore structure, however another possibility is the increasing influence of steric hindrance in smaller pores. For example, with methane as the probe molecule, the tortuosities for different samples of microporous silica-alumina catalyst with mean pore radii 43 Å → 15 Å were found to be 2.1 → 5.7 [results calculated by Gangwal et al. (1979) on the basis of data given by Gorring and de Rosset (1964)]. In estimating the above tortuosity values it was assumed that the porous media were "open" with respect to the size of the probe molecule, i.e., the simple kinetic theory expression, Eq. 38, was used. However, if Eq. 44 is used with $R_{CH_4} \sim 2.0$ Å, as obtained from dilute gas viscosity correlations for the temperature (22°C) of the experiments, then the sterically corrected tortuosities are 1.5 → 2.7. The porosities recorded by Gorring and de Rosset were used without correction, since the pycnometric method used was not described. The hindered diffusion model thus significantly reduces the apparent trend of tortuosity with mean pore radius. We believe this is physically plausible.

More direct evidence qualitatively verifying the present model is provided by comparing the "open" tortuosity, $\tau = 3.35$, obtained by Schneider and Smith (1968), for diffusion of ethane in a microporous silica gel, and the value $\tau = 2.4$ obtained by Gangwal et al. (1979) for diffusion of methane in a silica gel with essentially the same pore characteristics ($\psi = 0.49$, $R_{EFF} = 11$ Å). The tortuosities estimated using the hindrance model, when corrections are applied to both density (helium pycnometer) and diffusion measurements, are 1.2 and 1.3 for methane and ethane respectively. Although these values are lower than expected, it is observed that the discrepancy in the tortuosities is more or less eliminated. The low tortuosities may arise due to: (a) experimental error in the diffusivities ($\sim \pm 10\%$); (b) the existence of a small degree of surface diffusion, even at the high temperatures of the experiments, which may not have been eliminated completely (particularly in the case of methane where τ represents an extrapolated value); (c) the hard sphere radii for methane and ethane which were estimated to be 1.9 Å and 2.4 Å at the temperatures of the experiments (the hindrance model is sensitive to the molecular radii used); or (d) the rigid sphere model itself which we do not suggest is an exact description of the structure of silica gel.

Finally, from data we obtained during a comparative study of packed bed and single pellet chromatography (MacElroy, 1982), the results of which will be presented for publication in the near future, the ratio of helium to nitrogen permeabilities in a microporous glass ($R_{EFF} \sim 40$ Å) was found to be

$$\frac{P_{He,M}\sqrt{m_{He}/T}}{P_{N_2,M}\sqrt{m_{N_2}/T}} = 1.07 \pm 1\%$$

The present model predicts this ratio to be 1.1 which is in reasonable agreement with experiment.

Although it is known that surface flow may contribute significantly to transport in micropores, a suggestion we would like to make here, based on the present results, is that the contribution of surface flow may be much larger than previously assumed. In the analysis of flow data, the total flux is usually considered to be the sum of a gas phase flux J_G and a surface flux J_A. [This itself is untrue for mobile adsorbed phases (Bell and Brown, 1974; MacElroy and Kelly, 1980) but it is a reasonably good assumption for localized adsorption (Thakur et al., 1980)]. The surface flux and in particular the surface diffusivity is then determined by subtracting theoretical estimates of J_G from the total flux. The equation usually assumed for J_G is, however, the result predicted by the open membrane dusty gas model. In view of the fact that this model is inadequate for values of $\delta_m > 0$ then overestimation of the gas phase flux will result, leading to underestimated surface flow contributions. The error will be largest for diffusion of polyatomic species in very small pores, where both adsorption force fields and steric hindrance play a major role in the transport process. One should keep this in mind when interpreting the values for surface diffusion coefficients recorded in the literature.

CONCLUSIONS

By adapting the modified Enskog Theory of Van Beijeren and Ernst (1973 a,b) to membrane transport using the simple concept of a (dense) dusty gas, we have obtained corrections to the original dusty gas model which involve the influence of steric hindrance on the diffusion process. The theoretical results should be applicable to diffusion of rigid spherical or near spherical particles in homoporous membranes, and, for this reason, they should serve in part to bridge the gap between the Knudsen and configurational diffusion regimes. Our results will not, however, apply to diffusion of nonspherical molecules in pores of atomic dimensions, since internal rotation and configurational motion of the molecules are not taken into account.

ACKNOWLEDGMENTS

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NOTATION

$\vec{B}_\alpha$ = inertial and viscous flow contribution to the partial equation of motion of component α (dyne/cm^3)
$b_{\alpha\lambda}$ = $2/3\ \pi n_\lambda \sigma^3_{\lambda\alpha}/\rho$
$\tilde{C}_{\alpha\lambda}(0)$ = long-wavelength limit of the Fourier transform of the direct correlation function $C_{\alpha\lambda}(r_{\alpha\lambda})$ (cm^3)
c_{ij} = matrix elements (Eqs. 9 and 10)
$D_{\alpha\lambda}$ = mutual diffusion coefficient of component α with respect to component λ in the membrane (cm^2/s)
$\mathcal{D}_{\alpha\lambda}$ = mutual diffusivity of α with respect to λ in free space, referred to bulk fluid number density n_f (cm^2/s)
$D_{\alpha EFF}$ = effective diffusivity of component α(cm^2/s)
$D_{\alpha M}$ = diffusivity of $\alpha$with respect to the membrane (Eq. 24) (cm^2/s)
f = reflection coefficient
$f(\delta_m)$ = parameter defined in Eq. 37
$g_{\alpha\lambda}(\sigma_{\alpha\lambda})$ = rigid sphere contact radial distribution function
h = Planck's constant (6.6256×10^{-27} erg·s)
J_α = molecular flux of component α (molecule/cm^2·s)
K_α = partition coefficient of component α
Kn = Knudsen number
k = Boltzmann constant (1.38054×10^{-16} erg/K)
$k_{T\alpha}$ = thermal diffusion ratio
L = membrane thickness (cm)
M_α = $m_\alpha/(m_\alpha + m_\lambda)$
m = molecular mass (g)
n = number density (molecules/cm^3)
P = hydrostatic pressure (dyne/cm^2)
$P_{\alpha M}$ = permeability of component α in the membrane (cm^2/s)
R_{EFF} = effective mean pore radius (Å, cm)
R_α = molecular radius of component α (Å)
S = specific surface area of the solid (cm^2/g)
T = absolute temperature (K)
t = time (s)
$\vec{u}_\alpha$ = local velocity of component α (cm/s)
$\bar{v}_\alpha$ = molecular mean speed of component α (cm/s)

$\bar{X}$ = external force (dyne)
x = mole fraction

Greek Letters

β_k = parameter defined in Eq. 8
$\gamma_{\alpha o}^{(1)}$ = thermal diffusion coupling coefficient (erg)
γ_α = activity coefficient
δ_j = ratio of molecular radii
$\delta_{\alpha\lambda}$ = Kronecker delta
ζ = molecular friction coefficient (erg·cm·s)
μ_α = chemical potential (erg/molecule of component α)
μ_α^o = standard chemical potential (erg/molecule of component α)
ξ_i = parameter defined in Eq. 19
ρ = density (g/cm^3)
ρ_P = apparent density of the membrane (g/cm^3)
ρ_s = true solid density (g/cm^3)
$\vec{\vec{\sigma}}_\alpha$ = contribution to the stress tensor arising from perturbations in the distribution functions (dyne/cm^2)
$\sigma_{\alpha\lambda}$ = hard sphere collision diameter of components α–λ (Å, cm)
τ = tortuosity
ψ = porosity

Other Symbols

∇_T = gradient under isothermal conditions
$[\ \ ]_1$ = first approximation in the Chapman-Enskog theory

Subscripts

f = exterior bulk fluid conditions
m = membrane
$j,k,\alpha,\beta,\gamma,\lambda$ = components

Superscripts

(0) = open membrane quantity

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Intermediate Storage in Noncontinuous Processes Involving Stages of Parallel Units

A model is developed to study holdup in intermediate storage as a function of system parameters such as processing unit delay times. General results concerning the periodicity of the required storage volume, the allowable unit delay times, and the calculation of the volume are presented. Analytical expressions for the limiting volume are obtained for several special network configurations. A simple upper bound is derived for purposes of quick estimates of the limiting volume for the general case, and a gradient based algorithm is reported for obtaining the minimum volume schedule for general networks.

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SCOPE

Intermediate storage is widely used in batch and semicontinuously operated plants to increase plant availability, dampen the effects of process fluctuations, reduce process cycle times, and provide flexibility in sequencing and scheduling. These roles have only recently begun to be subjected to systematic study. Oi et al. (1977) considered the optimal scheduling and sizing of intermediate storage in a waste treatment plant. Takamatsu et al. (1979) treated a case of storage intermediate to one continuous and *M* parallel batch units. Oi (1982) examined the problem of schedule revision to accommodate nonperiodic flow fluctuations, while Takamatsu et al. (1982) presented an analysis of the minimum storage for several cases of the serial batch-batch configuration. Finally, Karimi and Reklaitis (1983) developed analytical result for the limiting storage volume in serial systems composed of arbitrary configurations of batch, semicontinuous, or continuous operations.

This paper extends the analysis of the predecessor paper to periodically operated networks composed of a set of parallel units followed by intermediate storage followed by another set of parallel units. We begin with a Fourier series formulation of the network model, continue with the development of the periodicity properties of the storage volume, and then develop formulas for calculating the required storage volume, given the unit delay times, capacities, and flow rates. Next, simplified results are obtained for several special cases involving identical units including some previously considered in the literature. The paper concludes with the development of an efficient algorithm for determining the unit delay time schedule which minimizes the required storage volume.

CONCLUSIONS AND SIGNIFICANCE

A comprehensive analysis of the deterministic periodically operated parallel unit case was presented. The analytical expressions derived for the limiting storage volume required to decouple the upstream and downstream processing stages are quite simple and obviate the need for simulation. The special, but common, case involving identical parallel units and periodic operation with symmetrically spaced delay times was shown to be equivalent to the one-one serial case for which analytical results were reported earlier. A simple bound on the required volume is also derived for the general *L-M* case. The important result, giving the characteristic period of the storage volume with respect to the delay time of a given unit, generalizes results previously reported for special cases and significantly reduces the search interval for finding the optimum periodic operating