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Tortuosity of Microporous Glass for Gas Diffusion

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Abstract

A random network model of microporous glass with uniform pores was constructed. On the basis of this model, an equation for gas diffusion through microporous glass in the Knudsen regime was derived. The tortuosity of microporous glass was expressed in terms of the ratio of half-length of pore to diameter, ψ. The model was applied to previous data of helium diffusion through microporous glass, thus a value of $\psi = 2.6 \pm 0.7$ was obtained.

INTRODUCTION

Microporous glass membranes have been used for gas separations. The effective diffusion coefficient of gas in a microporous material such as microporous glass in Knudsen's regime, $\mathscr{D}_e$, is given by

$$\mathscr{D}_e = \frac{\varepsilon}{\tau} \mathscr{D}_K \tag{1}$$

where $\mathscr{D}_K$ is Knudsen's diffusion coefficient, ε is the porosity, and τ is the tortuosity. The tortuosity τ has been treated as a correction factor which

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combines experimental values with theoretical values. The physical meaning of the tortuosity has not been given.

Wheeler (*1*) derived $\tau = 2$ from his simple pore model. However, it gives no explanation for the tortuosity of microporous glass, because microporous glass has a much greater value of tortuosity than 2, as described later. (See Table 1.) Clausing (*2*) developed the method of calculating the flow as a function of the ratio of capillary length over capillary radius. Pollard and Present (*3*) performed a similar computation. They pointed out that gaseous diffusion in a microporous medium is essentially different from that in a long capillary tube. However, the physical meaning of the tortuosity of microporous material was not elucidated in their paper. Haring and Greenkorn (*4*) developed a random network model of a porous medium for laminar flow.

In this paper, taking into account the geometric structure of microporous glass, an equation for gas diffusion in Knudsen's regime is theoretically obtained. A consideration of the tortuosity of microporous glass is made. The tortuosity of microporous glass is expressed in terms of the ratio of half-length of pore to diameter.

KNUDSEN'S FORMULA

On the basis of a long capillary tube model, Knudsen's diffusion coefficient $\mathcal{D}_K$ is given as (*5–7*)

$$\mathcal{D}_K = \frac{\bar{u}}{4\pi} \int\int_0^{2\pi}\int_{-\infty}^{\infty} \frac{x^2 dx}{(s^2 + x^2)^2} s^2 d\beta dS \Big/ \int dS \qquad (2)$$

The meanings of the variables in Eq. (2) are shown in Fig. 1. $\bar{u}$ is the mean molecular velocity, which is given by

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}} \qquad (3)$$

For a tube with a circular cross section of diameter D, Eq. (2) is readily calculated, the result being

$$\mathcal{D}_K = \frac{\bar{u} D}{3} \qquad (4)$$

TABLE 1
Tortuosity of Microporous Glass for Helium Diffusion

Reference	Pore diameter D (nm)	Porosity ε (-)	Tortuosity τ (-)	Ratio ψ (-)
Barrer and Barrie (*8*)	6.0	0.30	6.3	1.9
Gilliland et al. (*9*)	6.1	0.28	5.7	2.4
Shindo et al. (*10*)	4.0	0.28	5.4	2.7
Okazaki et al. (*11*)	7.0	0.31	5.1	3.3

Knudsen's theory was derived assuming that gas molecules flow in a straight capillary tube of infinite length at low pressures. Hence, without the tortuosity factor, Knudsen's formula is not available for gaseous diffusion through a microporous medium of complicated structure such as microporous glass.

GASEOUS DIFFUSION IN MICROPOROUS GLASS

It is considered that microporous glass contains a network of interconnecting single pores of length L and diameter D as shown in Fig. 2. It is supposed that the diffusive transport in microporous glass will differ from that in a long capillary tube mainly in two respects. One is that the pores in microporous glass have a finite length. The other is that the pores in microporous glass are random in direction. By considering these differences, a formula expressing the effective diffusion coefficient of gas in microporous glass was derived.

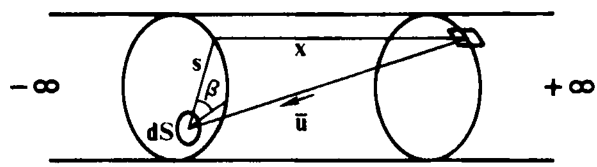

FIG. 1. Knudsen's tube model.

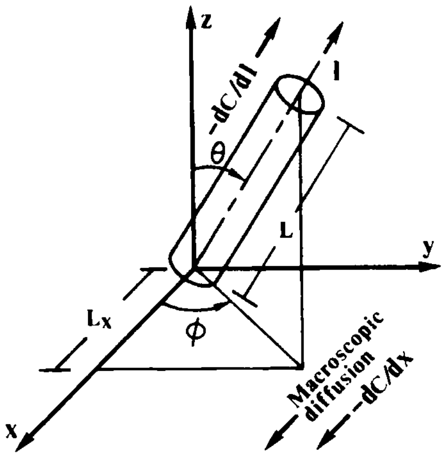

FIG. 2. Schematic illustration of a network of interconnecting single pores in microporous glass.

Finite Pore Length

In Knudsen's tube model, molecules which pass across the cross-section dS in a capillary tube are considered to come from walls of infinite length. (See Fig. 1.) In microporous glass the gas molecules are supposed to come from walls of finite length. We consider that at the middle of a single pore the gas molecules come from walls of finite length from $-\psi D$ to $+\psi D$. The parameter ψ is the ratio of the half-length of pore to the diameter, that is

$$\psi = L/2D \tag{5}$$

We obtained the following equation to express the diffusion coefficient, $\mathcal{D}_L$, in a pore of finite length L, by replacing the integral with respect to x from $-\infty$ to ∞ in Eq. (2) by the integral from $-\psi D$ to ψD:

$$\mathcal{D}_L = \frac{\bar{u}}{4\pi} \int \int_0^{2\pi} \int_{-\psi D}^{\psi D} \frac{x^2 dx}{(s^2 + x^2)^2} s^2 d\beta dS \bigg/ \int dS \tag{6}$$

The value of the diffusion coefficient at the middle of a single pore is taken as the representative value. If the direction of the pore axis and the macroscopic diffusion are the same, the flow rate in a single pore of finite length L, f_L, is given by

$$f_L = -\mathscr{D}_L \frac{dC}{dx} \tag{7}$$

where dC/dx is the molar concentration gradient.

Random Direction of Pores

In Knudsen's tube model the direction of diffusion agrees with that of the axis of the tube. In microporous glass, pores are random in direction. The direction of the axis of a pore, in general, does not agree with the direction of macroscopic diffusion. We consider a pore as shown in Fig. 3. The following relation is obtained in terms of geometrics:

$$\sin\theta \cos\phi \, dl = dx \tag{8}$$

Therefore the molar concentration gradient along the pore axis, dC/dl, is expressed with dC/dx:

$$\frac{dC}{dl} = \sin\theta\cos\phi \frac{dC}{dx} \tag{9}$$

The x-component of the length of the pore with angles of θ and ϕ, L_x, is

$$L_x = \sin\theta\cos\phi L \tag{10}$$

This means that when a gas molecule moves a distance of L in the pore, it

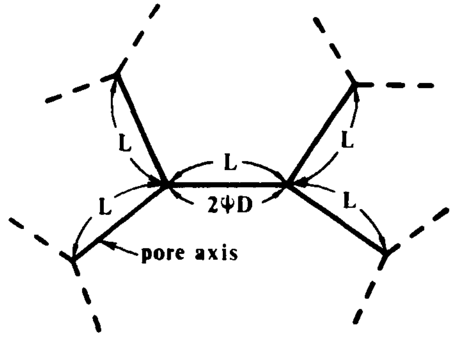

FIG. 3. Typical pore in microporous glass.

moves a distance of $\sin\theta\cos\phi L$ along the x-direction. Therefore, we obtain the flow rate in the pore along the x-direction as

$$f_x = -\mathscr{D}_L \sin^2\theta \cos^2\phi \frac{dC}{dx} \tag{11}$$

Here, we introduce the factor η, which is a measure of the contribution of diffusion in the pore to diffusion along the x-direction. On comparing Eq. (7) with Eq. (11), the factor η of a pore with angles of θ and ϕ is given by

$$\eta = \sin^2\theta \cos^2\phi \tag{12}$$

The mean value of η is calculated as

$$\bar{\eta} = \int_0^{\pi}\int_{-\pi/2}^{\pi/2} \sin^2\theta\cos^2\phi \, d\phi d\theta \Big/ \int_0^{\pi}\int_{\pi/2}^{\pi/2} d\phi d\theta \tag{13}$$

$$= \frac{1}{4} \tag{14}$$

Effective Diffusion Coefficient

It is considered that the porosity ε represents the ratio of diffusion space to the apparent volume of microporous glass. Therefore, the overall effective diffusion coefficient $\mathscr{D}_e$ is derived from Eq. (6) by multiplying by the two factors ε and $\bar{\eta}$ (= 1/4). The result is

$$\mathscr{D}_e = \frac{\varepsilon}{4}\frac{\bar{u}}{4\pi}\int\int_0^{2\pi}\int_{-\psi D}^{\psi D} \frac{x^2 dx}{(s^2 + x^2)^2} s^2 d\beta dS \Big/ \int dS \tag{15}$$

For a circular cross section of diameter D, the calculation is easily made.

$$\int_0^{2\pi} d\beta = 2\pi \quad \text{and} \quad \int dS = \frac{\pi D^2}{4}$$

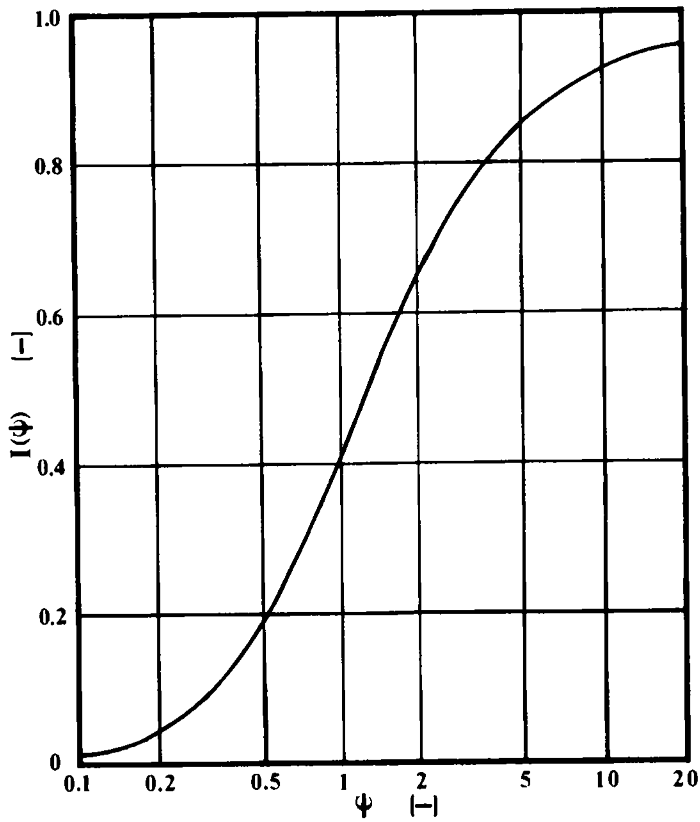

FIG. 4. Relation between $I(\psi)$ and ψ.

Therefore

$$\mathcal{D}_e = \frac{\varepsilon}{4}\frac{\bar{u}}{2}\int\int_{-\psi D}^{\psi D} \frac{x^2dx}{(s^2+x^2)^2}s^2dS \Big/ \frac{\pi D^2}{4} \tag{16}$$

Here, function $I(\psi)$ is defined as

$$I(\psi) = \frac{6}{\pi D^3}\int\int_{-\psi D}^{\psi D} \frac{x^2dx}{(s^2+x^2)^2}s^2dS \tag{17}$$

$I(\psi)$ is a dimensionless function of ψ independent of the value of D. (See Appendix.) Figure 4 shows the relation between $I(\psi)$ and ψ, which was numerically calculated by a computer: $I(0) = 0$ and $I(\infty) = 1$. Equation (16) is rewritten by the use of $I(\psi)$ and Eq. (4):

$$\mathscr{D}_e = \frac{I(\Psi)}{4}\frac{\varepsilon \bar{u} D}{3} \tag{18}$$

$$= \frac{I(\psi)}{4}\varepsilon \mathscr{D}_K \tag{19}$$

TORTUOSITY OF MICROPOROUS GLASS

On comparing Eq. (1) with Eq. (19), the tortuosity of microporous glass is obtained as

$$\tau = 4/I(\psi) \tag{20}$$

Figure 5 shows the relation between τ and ψ by Eq. (20). Rates of diffusion of helium through microporous glass have been reported in previous work (*8–11*). Microporous glass contains no macropores, and the mean pore diameter is so small that diffusion is almost entirely by collisions with the wall. The values of the mean pore diameter and the porosity of microporous glass used by each investigator are summarized in Table 1. The tortuosity calculated in terms of Eq. (1) is also shown in Table 1. The disparity of the tortuosity values among the investigations, which cause the different values of ψ, may be due to the difference in the methods of determination of the mean pore diameter. There are several methods for determining the pore size: gas adsorption, mercury penetration, and calculating from pore volume and surface area. Each tortuosity factor is plotted in Fig. 5; thus the value of $\psi = 2.6 \pm 0.7$ corresponds to the derived values of the tortuosity. The derived value of ψ is supposed to be reasonable within geometrical consideration of the pore structure of microporous glass. Although a simplified treatment is used in the present theory, Eq. (20) is a good expression of the tortuosity of microporous glass.

CONCLUSION

The diffusive transport in microporous glass differs from that in a long capillary tube primarily in two respects. One is that pores in microporous

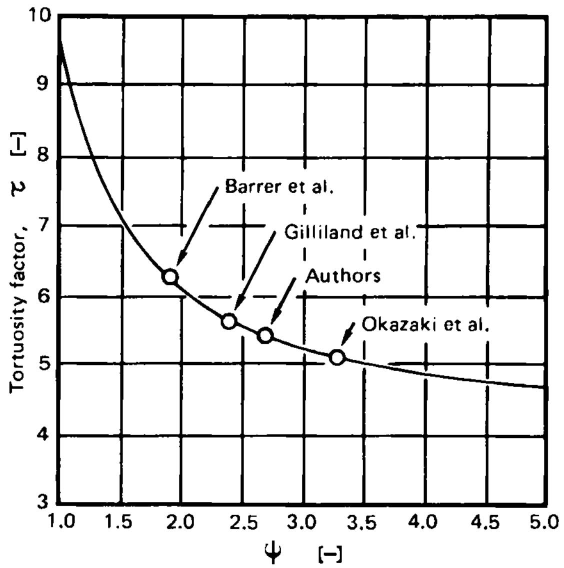

FIG. 5. Tortuosity τ as a function of ψ by Eq. (20).

glass have a finite length. The other is that pores in microporous glass are random in direction. An equation for gas diffusion through microporous glass in Knudsen's regime was derived by considering the pore structures. The tortuosity of microporous glass was expressed in terms of the ratio of half-length of pore to diameter.

APPENDIX

From Eq. (17) we obtain

$$I(\psi) = \frac{6}{\pi D^3}\int\left\{\frac{-\psi D}{(s^2+\psi^2 D^2)} + \frac{1}{s}\arctan\frac{\psi D}{s}\right\}s^2 dS \qquad \text{(A-1)}$$

Let us draw Cartesian axes as in Fig. A-1 with the origin at the center of the circle and the w-axis parallel to the line of length s. Then we can write $dS = dv dw$, and let v and w denote coordinates of a point in dS. Equation (A-1) can be rewritten as

$$I(\psi) = \frac{6}{\pi D^3}\int_{-D/2}^{D/2}\int_{-(D^2/4-v^2)^{1/2}}^{(D^2/4-v^2)^{1/2}} f(s(v,w))\,dv\,dw \qquad \text{(A-2)}$$

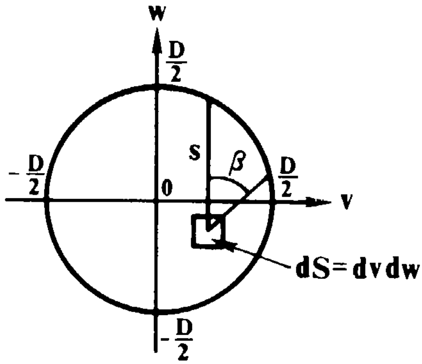

FIG. A-1. Cartesian coordinates in a pore.

where

$$f(s) = \left\{ \frac{-\psi D}{(s^2 + \psi^2 D^2)} + \frac{1}{s} \arctan \frac{\psi D}{s} \right\} s^2 \qquad \text{(A-3)}$$

$$s(v, w) = \left(\frac{D^2}{4} - v^2 \right)^{1/2} - w \qquad \text{(A-4)}$$

With $\bar{v}$ and $\bar{w}$ defined as

$$v = \bar{v} D/2 \qquad \text{(A-5)}$$

$$w = \bar{w} D/2 \qquad \text{(A-6)}$$

we obtain

$$I(\psi) = \frac{3}{4\pi} \int_{-1}^{1} \int_{-(1-\bar{v}^2)^{1/2}}^{(1-\bar{v}^2)^{1/2}} \bar{f}\,(\bar{s}(\bar{v}, \bar{w}) d\bar{v}\, d\bar{w} \qquad \text{(A-7)}$$

where

$$\bar{f}\,(\bar{s}) = \left\{ \frac{2\psi}{(\bar{s}^2 + 4\psi^2)} + \frac{1}{\bar{s}} \arctan \frac{2\psi}{\bar{s}} \right\} \bar{s}^2 \qquad \text{(A-8)}$$

$$\bar{s}\,(\bar{v}, \bar{w}) = (1 - \bar{v}^2)^{1/2} - \bar{w} \qquad \text{(A-9)}$$

Therefore, the function $I(\psi)$ is independent of D.

SYMBOLS

C	concentration (mol/m^3)
D	pore diameter (m)
$\mathscr{D}_e$	effective diffusion coefficient (m^2/s)
$\mathscr{D}_K$	Knudsen diffusion coefficient (m^2/s)
$\mathscr{D}_L$	diffusion coefficient in a single pore of length L (m^2/s)
f_L	flow rate in a single pore of length L along the pore axis (mol/m$^2 \cdot$ s)
f_x	flow rate along the x-axis (mol $\cdot$ m^2/s)
$f(s)$	function defined by Eq. (A-3) (m)
$\bar{f}(\bar{s})$	function defined by Eq. (A-8)
$I(\psi)$	function defined by Eq. (17)
L	pore length (m)
L_x	x-component of pore length (m)
l	distance along the pore axis (m)
M	molecular weight (kg/mol)
R	gas constant (J/K $\cdot$ mol)
S	cross-sectional area (m^2)
s	distance defined in Fig. 1 (m)
$s(v, w)$	function defined by Eq. (A-4), $= s$ (m)
$\bar{s}(\bar{v}, \bar{w})$	function defined by Eq. (A-9)
T	absolute temperature (K)
$\bar{u}$	mean molecular velocity (m/s)
v	Cartesian coordinate (m)
$\bar{v}$	dimensionless parameter defined by Eq. (A-5)
w	cartesian coordinate (m)
$\bar{w}$	dimensionless parameter defined by Eq. (A-6)
x	distance along diffusion (m)
y	rectanglar coordinate (m)
z	rectanglar coordinate (m)

Greek Letters

β	angle defined in Fig. 1
ε	porosity
η	parameter defined by Eq. (12)
$\bar{\eta}$	mean value of η
θ	angle in spherical coordinates
τ	tortuosity
ϕ	angle in spherical coordinates
ψ	ratio of the half-length of pore to diameter, defined by Eq. (5)

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