p_3 = pressure in the fiber, N/m^2
p_{atm} = pressure at the open end of fiber, N/m^2
ΔP = $p_1 - p_{atm}$
r_i = fiber bore radius, m
r_o = outside fiber radius, m
S = surface area of fibers per unit shell volume, m^2/m^3
V = shell volume, m^3
V_w = permeation velocity, m/s
$\bar{V}_w$ = length averaged permeation velocity, m/s
z = axial coordinate measured from the closed end of a fiber, m
z_1 = axial coordinate measured from the midpoint of a fiber, m

Greek Letters

β = defined by Equation (6)
β_o = optimum value of β
ϵ = void fraction
μ = solvent viscosity, kg/m·s
ψ = defined by Equation (9)

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Knudsen Diffusion Through Noncircular Pores: Textbook Errors

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Eldridge and Brown (1976) state that: "For Knudsen flow, while the cylindrical pore formula derivation is presented in many places, the effect of a noncircular cross section on the transport rate does not appear to have been considered quantitatively." They then present the results of their numerical calculation for the Knudsen diffusion coefficient (D_K) in pores of rectangular and elliptical cross section of varying aspect ratio. In fact, the problem of the effect of geometry on the Knudsen diffusion coefficient has been treated in the past, though not always correctly (Knudsen, 1909; Smoluchowski, 1910; Loeb, 1934; Dushman, 1962); it is the purpose of this note to single out the error which appears in these references and to indicate an efficient, numerical procedure for the accurate calculation of D_K for arbitrary pore geometry. Moreover, an incorrect equation initially obtained by Knudsen has been used inadvertently in two recent investigations involving diffusion through rhomboidal pores (Quinn et al., 1972; Beck, 1969), while in other studies no correction for the noncircular cross section has been made (Ho, 1971; Petzny and Quinn, 1969). We have computed the correct results for this case and discuss the error involved in these studies wherein pore size was deduced from measured Knudsen flux.

The following formula was derived by Knudsen (1909) for the flow of a rarefied gas through a long cylindrical tube of arbitrary cross section:

$$N = \frac{4}{3} \frac{\bar{v}}{\int_0^L \frac{H}{A^2} dL} \frac{(P_2 - P_1)}{R_o T} \tag{1}$$

This result follows from equating the momentum transferred to the pore wall by colliding gas molecules to the force acting on the gas due to the pressure difference across the pore. If the Knudsen diffusion coefficient is defined as the ratio of the molar flux to concentration gradient along the pore, then the above equation gives

$$D_K = \frac{4}{3} \bar{v} \left(\frac{A}{H} \right) = \frac{4}{3} \bar{v}\, r_h \tag{2}$$

where r_h is simply the hydraulic radius. For the circular pore ($r_h = r/2$), Knudsen's expression yields the familiar result. Although Equation (1) is cited in standard references (Loeb, 1934; Dushman, 1962), it is, in fact, correct only for a circular pore.

Equation (2) has been employed in connection with measurements of Knudsen flow in 100 to 1 000Å pores created in thin ($\sim 7\,\mu$) mica sheets by an irradiation-etching technique. Briefly, the technique consists of bombarding mica sheets with massive fission fragments from a radioactive source and etching material from the resulting damage tracks with acid. Model pores with parallel walls are formed which are rhomboidal in cross section (the included angles being 60 and 120 deg). Pore size has been determined by two independent means (by measuring Knudsen flow through gas filled pores and by monitoring conduction of electrolytes through solution filled pores), and these have been compared on the basis of an equivalent pore radius defined as that of a circle having area equal to that of the rhomboidal pore (Quinn et al., 1972):

$$r = \left(\frac{\sqrt{3}}{2\pi} \right)^{1/2} w \tag{3}$$

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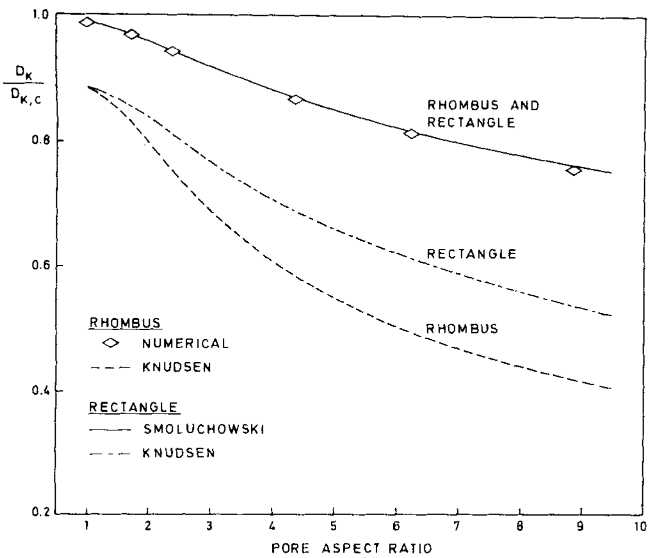

Fig. 1. Knudsen diffusion coefficient as a function of pore shape.

The article of Eldridge and Brown brought to our attention the error in using Knudsen's expression to interpret the gas diffusion results. [The technique of pore size determination by Knudsen flow measurement was also used in a similar study by Beck and Schultz (1972).]

Smoluchowski (1910) treated the problem of pore shape correctly 1 yr after Knudsen's paper appeared. Smoluchowski avoided the error Knudsen had made in not recognizing that the intensity of molecular streaming or average transport velocity varies with position in the pore cross section (Pollard and Present, 1948), and he obtained a result equivalent to

$$D_K = \frac{\bar{v}}{8A} B \tag{4}$$

where

$$B = \frac{1}{2} \int_x \int_{-\pi/2}^{\pi/2} k^2 \cos\theta \, d\theta \, dx \tag{5}$$

and k is the length of the chord extending across the pore from an element of perimeter dx drawn at an angle θ to the normal to dx. An equivalent formula used by Eldridge and Brown is (Kennard, 1938; Present, 1958)

$$D_K = \frac{\bar{v}}{8A} \int_A \int_0^{2\pi} s \, d\Phi \, dA \tag{6}$$

where s is the distance from an element of cross-sectional area dA to the pore wall taken at an angle Φ to some arbitrary reference direction. The actual effect of geometry is seen to be considerably more complicated than Knudsen's equation suggests.

Clausing (1932) states "That the formula [derived by Knudsen] is most probably correct [for the circular cylinder] is, so to speak, a coincidence." The circular geometry is unique in that Knudsen's erroneous analysis gives the correct result by a fortuitous cancellation of errors. It is this point which has led to the incorrect equations presented by Dushman and others. In fact, Knudsen himself obtained identical expressions for the diffusivity in the circular pore using both momentum transfer arguments and the rigorous procedure employed by Smoluchowski. Understandably, the agreement reinforced his belief in the validity of the arguments leading to Equation (2).

Smoluchowski derived the following analytical expression for the geometry factor for a rectangular pore of sides a and b:

$$B = 2 \left\{ a^2 b \ln\left[\frac{b}{a} + \sqrt{1 + \left(\frac{b}{a}\right)^2}\right] + a b^2 \ln\left[\frac{a}{b} + \sqrt{1 + \left(\frac{a}{b}\right)^2}\right] - \frac{(a^2 + b^2)^{3/2}}{3} + \frac{a^3 + b^3}{3} \right\} \tag{7}$$

Figure 1 shows the ratio of the Knudsen coefficient for a rectangular pore (D_{Kr}) calculated with this equation to that for a circular pore of equal area (D_{Kc}); the numerical calculations of Eldridge and Brown (not shown) are in agreement. For comparison, the ratio of diffusivities predicted on the basis of Equation (2) is also plotted. The discrepancy is substantial, even at an aspect ratio (the ratio of major to minor pore axes) of unity.*

We have carried out numerical calculations for the rhombus (D_{Ks}) based on both Equations (4) and (6); the former is to be preferred in this case over the expression used by Eldridge and Brown in that the number of variables of integration is reduced from three to two with a corresponding economy in computer time required for solution. The diffusivity ratios for the rhombus (D_{Ks}/D_{Kc}) and rectangle (D_{Kr}/D_{Kc}) plotted in Figure 1 are indistinguishable; considered along with the calculations of Eldridge and Brown for the ellipse, these results indicate that aspect ratio but not the type of pore shape is important in determining the diffusivity. The diffusivity ratio for the rhombus based on the incorrect Knudsen formula is also shown in Figure 1. Application of Equation (2) to correct for pore shape is seen to lead to a larger error than would be incurred by ignoring the noncircular nature of the pore altogether.

For the 60 deg rhomboidal pores (aspect ratio of $\sqrt{3}$) created in mica membranes by track etching, the true diffusivity ratio D_{Ks}/D_{Kc} is 0.969. Thus, we determine that the Knudsen flow equivalent pore radii reported previously (Quinn et al., 1972) are too large by 5.5% by virtue of the overcorrection for pore shape made by Equation (2). These model pores in mica membranes represent one of few instances in which the pore geometry is sufficiently well characterized to warrant consideration of the effect of pore shape on the Knudsen diffusion coefficient.

ACKNOWLEDGMENT

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NOTATION

- A = cross-sectional area of pore
- a = length of side of rectangular pore
- B = integral expressing geometry factor in Smoluchowski equation
- b = length of side of rectangular pore
- D_K = Knudsen diffusion coefficient

* The diffusion coefficient predicted by Knudsen for the circular pore is lower by a factor of $8/3\pi$ (0.849) than predicted by the simplified momentum balance treatment presented by Jeans (1940), Pollard and Present (1948), and Lyubitov (1967); this factor is comparable to the ratio (0.897) between the relative diffusivities of the rectangle or rhombus of aspect ratio one (that is, the square) as determined by the Knudsen (0.866) and Smoluchowski (0.988) equations. We emphasize that the $8/3\pi$ factor does not enter into the interpretation of the difference between the Knudsen and Smoluchowski curves, since the respective equations are derived on the same basis; that is, both the Knudsen and Smoluchowski expressions reduce to $D_{Kc} = 2/3\ \bar{v}r$ (rather than $\pi/4\ \bar{v}r$) for the circle. The curves thus differ by a factor dependent on the geometry rather than by a constant.

H = circumference of pore
k = length of cross-sectional chord extending from an element of perimeter dx
L = pore length
N = molar flow rate through pore
P = gas pressure
r = radius of circular pore
r_h = hydraulic radius, ratio of area of conduit to wetted perimeter
R_o = universal gas constant
s = distance from cross-section area element dA to perimeter of pore
T = absolute temperature
$\overline{v}$ = mean molecular velocity
x = coordinate representing position on perimeter of pore
w = length of side of rhomboidal pore
θ = angle between cross-sectional chord k and the normal to pore wall
Φ = angle representing direction in which distance between area element dA and pore wall is measured

Subscripts

c = circular cross section
r = rectangular cross section
s = rhomboidal cross section
1 = entrance of pore
2 = exit of pore

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Predicted Comparisons of the Efficiency of Large Valve Trays and Large Sieve Trays

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Valve trays are proprietary devices, and as such the designs are usually provided by the supplier. However, there are times when a knowledge of the performance of such trays is desirable for preliminary studies. Recently, Bolles (1976) has considered the relationship between valve trays and sieve trays with a view to using the vast amount of data available for sieve trays. For tray efficiency, he recommends, in the absence of more detailed figures, that an efficiency similar to that of a sieve tray be assumed.

This approach appears to be reasonable based on the studies which have been reported by various authors comparing trays. However, these studies have been made in small to medium sized columns, and the question arises whether these similarities would still exist for very large trays. Recently, Garrett et al. (1977) have attempted to compare the scale-up of sieve tray and valve tray efficiencies. They have assumed similar mixing characteristics on the two types of trays.

During the course of a computer simulation of a 2.43 m diameter valve tray column separating benzene from a benzene/toluene/xylene mixture (Biddulph and Ashton, 1977), the mixing characteristics of a Koch valve tray have been established. This was achieved using a 0.69 m diameter air/water simulator which has been described