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Geometric Correction Factors for the Weisz Diffusivity Cell

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Weisz has proposed a most convenient method of measuring the effective diffusion coefficient of a porous medium in which a spherical pellet of radius a is held in an elastic tube which effectively seals off an equatorial zone between the latitudes $\pm\gamma$ and allows the spherical caps to be exposed to two different concentrations c_1 and c_2. The effective diffusion coefficient D_e is related to the observed flux F by $D_e = \alpha_w F(\pi a^2)^{-1}[(c_1 - c_2)/(2a)]^{-1}$ where α_w, a correction factor due to the spherical geometry, is a function of γ. A graph of α_w is given for $10° \leq \gamma \leq 80°$. It agrees well with experimental measurements.

1. FORMULATION OF THE PROBLEM

A porous sphere whose equatorial zone is as a sealed surface has its polar caps exposed to two different concentrations as shown in Fig. 1. The axisymmetric concentration $c(r, \theta)$ within the sphere satisfies the equation

$$\nabla^2 c = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial c}{\partial \theta}\right) \quad (1)$$

and the boundary conditions

$$c(a, \theta) = c_1 \qquad 0 \leq \theta < \gamma, \quad (2)$$

$$\partial c/\partial r = 0 \qquad \gamma < \theta < \pi - \gamma, \quad (3)$$

$$c(a, \theta) = c_2 \quad \pi - \gamma < \theta \leq \pi. \quad (4)$$

The flux is

$$F = D_e 2\pi a^2 \int_0^\gamma \left(\frac{\partial c}{\partial r}\right)_{r=a} \sin\theta d\theta, \quad (5)$$

where D_e is the effective diffusion coefficient. If the sphere were replaced by a cylinder of the same radius with length equal to its diameter the flux would be

$$F = D_e \pi a^2[(c_1 - c_2)]/2a], \quad (6)$$

and D_e could be calculated as $F/[\pi a^2(c_1 - c_2)/2a]$. Weisz suggested that a correction factor be used to give a similar formula for the spherical pellet

$$D_e = \alpha_w F(\pi a^2)^{-1}\left(\frac{c_1 - c_2}{2a}\right)^{-1}. \quad (7)$$

If this is substituted for D_e in Eq. (5) we have

$$\alpha_w = \left[\frac{4a}{c_1 - c_2}\int_0^\gamma \left(\frac{\partial c}{\partial r}\right)_{r=a} \sin\theta d\theta\right]^{-1}. \quad (8)$$

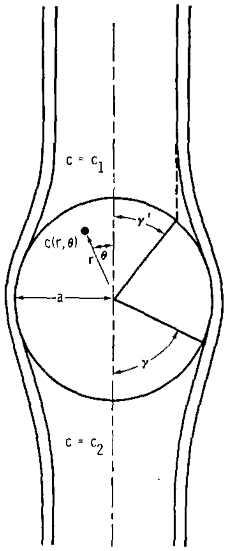

FIG. 1. The geometry of the Weisz diffusivity cell.

Weisz determined $\alpha_w = 0.79$ for $\gamma' = 49°$ experimentally as a calibrating measurement (*1*). It is proposed here to calculate α_w as a function of γ. The mathematical method will only be sketched very lightly, but the calculations raised some computational points that workers on other diffusion problems may be glad to have outlined. The method by which Fig. 2 can be employed in the practical use of the Weisz diffusion cell is described at the end of the paper.

Let

$$\begin{aligned} \rho &= r/a, \\ u(\rho, \theta) &= \{2c(a\rho, \theta) - (c_1 + c_2)\}/(c_1 - c_2); \end{aligned} \tag{9}$$

then

$$\nabla^2 u = \frac{1}{\rho^2}\frac{\partial}{\partial \rho}\left(\rho^2 \frac{\partial u}{\partial \rho}\right) + \frac{1}{\rho^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial u}{\partial \theta}\right) = 0, \tag{10}$$

and

$$u(1, \theta) = 1, \qquad 0 \le \theta < \gamma, \tag{11}$$

$$u_\rho(1, \theta) = 0, \qquad \gamma < \theta < \pi - \gamma, \tag{12}$$

$$u(1, \theta) = -1, \qquad \pi - \gamma < \theta \le \pi, \tag{13}$$

and

$$\frac{1}{\alpha_w} = 2\int_0^\gamma \left(\frac{\partial u}{\partial \rho}\right)_{\rho=1} \sin\theta d\theta. \tag{14}$$

The solution of Eq. (10) which is regular in the sphere is

$$u(\rho, \theta) = \sum_{n=0}^{\infty} a_n \rho^n P_n(\cos\theta), \tag{15}$$

and the boundary conditions will be satisfied if the a_n can be chosen so that

$$\begin{aligned} &\Sigma a_n P_n(\cos\theta) = 1, && 0 \le \theta < \gamma, \\ &\Sigma n a_n P_n(\cos\theta) = 0, && \gamma < \theta < \pi - \gamma, \\ &\Sigma a_n P_n(\cos\theta) = -1, && \pi - \gamma < \theta \le \pi. \end{aligned} \tag{16}$$

This is known as a triple series problem and it is one of the types discussed by Collins (*2*) and Sneddon (*3*).

Suppressing the details of the manipulations, which are indeed painful, Collins' solution may be expressed as follows. Let

$$\begin{aligned} j(\psi) &= \int_{|\psi|}^{\gamma} u_\rho(1, \theta)(2\cos\psi - 2\cos\theta)^{-\frac{1}{2}} \sin\theta d\theta, && |\psi| < \gamma, \\ &= 0, && \gamma < |\psi| < \pi \end{aligned} \tag{17}$$

then $j(\psi)$ must satisfy the Fredholm integral equation

$$j(\psi) = \cos\tfrac{1}{2}\psi + \frac{1}{\pi}\int_{-\gamma}^{\gamma} K(\psi - \chi) j(\chi) d\chi, \tag{18}$$

where the kernel is

$$K(\omega) = \tfrac{1}{2}[\sec\tfrac{1}{2}\omega + \cos\tfrac{1}{2}\omega \times \ln|\tan\tfrac{1}{2}\omega| + (\pi/2)|\sin\tfrac{1}{2}\omega|]. \tag{19}$$

The correction factor is given in terms of

$j(\psi)$ by

$$\frac{1}{\alpha_w} = \int_0^\gamma j(\psi) \cos \tfrac{1}{2}\psi d\psi. \tag{20}$$

2. METHOD OF SOLUTION

Before outlining the method of solution (due to W.W.M.) it is worth mentioning that some other suggestions proved unfruitful. Thus, a Galerkin method using a finite number of terms of the series (15) and making the weighted residuals of the boundary conditions equal to zero was not easily convergent. Similarly, although we would expect $u(1, \theta)$ for $\gamma < \theta < \pi - \gamma$ to be a smooth interpolating function between 1 and -1, attempts to approximate this by a finite series and so solve a Dirichlet problem were unsuccessful.

The solution to Eqs. (18) and (19) is best accomplished by setting

$$c = \tan \tfrac{1}{2}\gamma, \quad cx = \tan \tfrac{1}{2}\psi, \quad cy = \tan \tfrac{1}{2}\chi$$
$$j(\psi) = (1 + c^2x^2)h(x) \tag{21}$$

so that $h(x)$ satisfies

$$h(x) = (1 + c^2x^2)^{-\frac{1}{2}} + \frac{c}{\pi}(1 + c^2x^2)^{-1}\int_{-1}^{1} G(x, y)h(y)dy, \tag{22}$$

where

$$G(x, y) = \{H(x, y)\}^{-1} + \{H(x, y)\} \ln J(x, y) + (\pi/2)H(x, y)J(x, y), \tag{23}$$

$$H(x, y) = \frac{1 + c^2xy}{(1 + c^2x^2)^{\frac{1}{2}}(1 + c^2y^2)^{\frac{1}{2}}},$$
$$J(x, y) = \frac{c|x - y|}{1 + c^2xy}. \tag{24}$$

The kernel $G(x, y)$ is further written as

$$G(x, y) = G_0(x, y) + G_1(x, y),$$
$$G_0(x, y) = \ln |x - y| + \frac{\pi}{2} c \frac{|\gamma - y|}{1 + c^2x^2}, \tag{25}$$

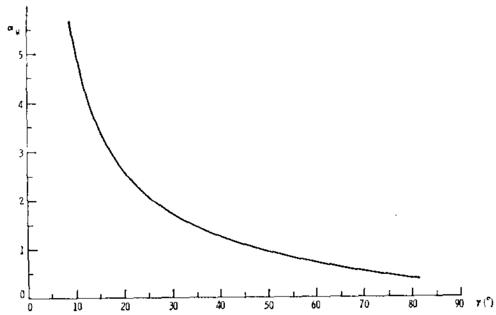

FIG. 2. The correction factor as a function of γ.

and it can be shown that G_1 has continuous first derivatives. Since G_1 is smooth, the integral $\int G_1(x, y)h(y)dy$ should be amenable to Gaussian quadrature and be well approximated by

$$\sum_{j=0}^{m} w_j G_1(x, x_j)h(x_j), \tag{26}$$

where $x_0, x_1, \ldots, x_m$ are the roots of $P_{m+1}(x) = 0$ and $w_0, \ldots, w_m$ the corresponding Gaussian weights. These weights can also be used in the representation

$$h(y) = \sum_{j=0}^{m} \sum_{k=0}^{m} (k + \tfrac{1}{2}) \times P_k(y)P_k(x_j)w_j h(x_j). \tag{27}$$

Then the integral, Eq. (22) can be expressed in terms of the collocation values $h(x_j)$ at the zeros of P_{m+1} and so also can α. The details of this reduction are not suitable for this journal but may be obtained on request from W.W.M. (*4*); suffice it to say that this method worked where the others had not.

3. RESULTS

Figure 2 shows α_w as a function of γ, between 10° and 80°. Twelve-point quadratures were used to calculate the values of α_w which are accurate to at least three significant figures.

Experiments have shown that the true angle of enclosure γ (in Fig. 1) is somewhat larger than γ' which assumes an ideal cell geometry. Figure 3 shows measured values

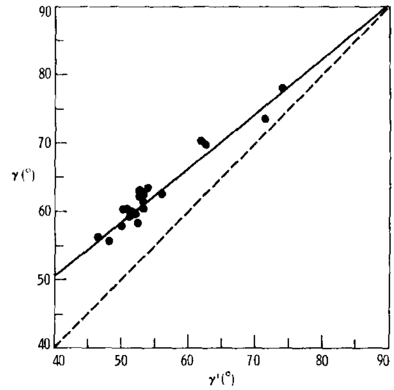

FIG. 3. γ as a function of γ' for a Tygon tube (see Fig. 1 for explanation).

of γ as a function of γ', for a range of catalyst pellet sizes fitted into a Tygon tube similar to the one used by Weisz (*1*). From Fig. 3 it was possible to estimate γ for Weisz' experiments.

Figure 4 shows the comparison of calculated and measured values of α_w for the practical range of $55° \leq \gamma \leq 70°$.

The theory agrees well with Weisz' observed value at $\gamma = 58.5°$. To check the theory at other values of γ, He–N_2 counter-diffusion measurements were carried out on porous alumina pellets of varying diameter. The data were forced to agree with theory at $\gamma = 58.5°$ and follow well the calculated curve.

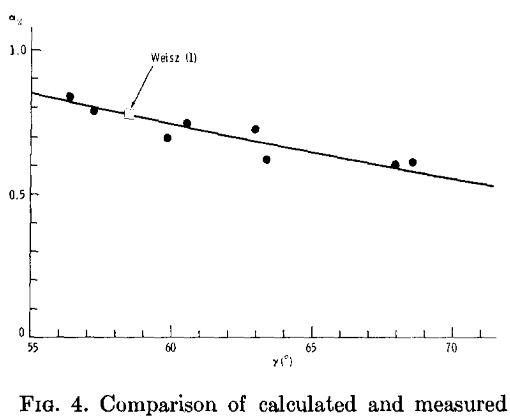

FIG. 4. Comparison of calculated and measured values of α_w.

4. APPLICATION

The graphs given here can be used as follows. If the angle γ is measured directly, then Fig. 2 gives α_w immediately and this is employed in Eq. (7) to calculate the effective diffusion coefficient. If Tygon tubing of the kind used by Weisz (i.d. = 0.125 in., o.d. = 0.25 in.) is employed, Fig. 3 can be used to find γ from γ', the angle whose sine is the ratio of tube to pellet diameter. The two figures have not been combined since Fig. 2 is universally applicable, whereas Fig. 3 is strictly speaking particular to Tygon tubing of this diameter. However, for a material of similar modulus of elasticity and for similar geometry it should provide a good approximation.

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