COMMUNICATIONS TO THE EDITOR

Determination of Surface Diffusion Rates from Thermal Transpiration Measurements

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The accurate determination of surface diffusion of adsorbed molecules is a problem of engineering interest for flow through porous media and heterogeneous catalysis (Satterfield, 1970). However, gas flow through porous media also occurs by Knudsen flow through the pores, viscous flow in the pore volumes, and, in the presence of a temperature gradient, by thermal transpiration (Reynolds, 1879), and since flow due to several of these mechanisms can occur simultaneously, it has been not possible to directly measure each flow contribution separately. The common technique for measuring the surface permeability of a microporous solid is first to determine the (Knudsen) permeability of a nonadsorbed gas such as helium ($Q_{NA}{}^{K}$) and then the total permeability of an adsorbed gas (Q_A). The surface diffusion contribution to the gas permeability is then gotten from

$$Q_A{}^S = Q_A - Q_A{}^K$$

where $Q_A{}^K$, the Knudsen permeability of the adsorbed gas, is calculated from (Knudsen, 1950)

$$Q_A{}^K = \sqrt{\frac{M_{NA}}{M_A}}\, Q_{NA}{}^K$$

Hwang and Kammermeyer (1966) have raised an objection to this technique based on the fact that it is a relative rather than absolute measure of surface diffusion and depends upon the use of helium as a nonsurface diffusing standard. Furthermore, they have interpreted their experimental data as establishing that surface diffusion is present with helium on vycor glass. The purpose of this note is to establish the basis for a new method for the measurement of surface diffusion.

The dusty gas theory, originally proposed by Maxwell (1860) and greatly refined by Deriagin and Bakanov (1957) and Mason et al. (1967), is perhaps the richest theory for flow through porous media, in the sense of the experimental data that can be correlated, and the interrelationships which have been established between flow phenomena. It will be used as a starting point here. Mason et al. (1967) have shown that the gas flux due to Knudsen flow J_K and thermal transpiration J_{TT} can be written as

$$J_K + J_{TT} = -\frac{D_k}{kT}\frac{dP}{dz} + \frac{P}{k}\,\frac{\dfrac{1}{5}\dfrac{\epsilon}{q}\lambda_{tr}}{P + \dfrac{1}{5\alpha_L}\dfrac{kT}{D_k}\dfrac{\epsilon}{q}\dfrac{\lambda_{tr}}{k}}\,\frac{dT}{dz} \tag{1}$$

Here λ_{tr} is the translational component of the gas thermal conductivity (Mason and Monchick, 1962), D_k is the Knudsen permeability coefficient, and α_L is analogous to the gas-porous medium thermal diffusion factor, which, from kinetic theory, is taken to be 0.5. The viscous flux J_v is given by a generalization of Poiseuille's law to porous media, that is,

$$J_v = -\frac{B_0 P}{\eta kT}\frac{dP}{dz} \tag{2}$$

where B_0 a geometric parameter characterizing the porous media. Finally, the surface diffusion flux J_{sD} can be written as (Satterfield, 1970)

$$J_{sD} = -\frac{D_s}{q} S \frac{dC_s}{dP}\frac{dP}{dz} \tag{3}$$

The total flux in the presence of both temperature and pressure gradients J is sum of the individual contributions above. Our interest here is with a microporous solid, that is, a solid with small pores and high surface area, so that surface diffusion can be significant. For such solids

$$1 >> \frac{B_0 P}{\eta D_k}$$

and

$$\frac{1}{5D_k}\frac{\epsilon}{q}\frac{\lambda_{tr}}{k} >> P \tag{4}$$

The first of these assumptions is usually verified by experimentally establishing that the isothermal gas permeability of a nonadsorbed gas is independent of pressure, that is, showing that the second term in

$$Q_{NA} = \frac{J_v + J_K}{-\left(\dfrac{dP}{dz}\right)} = \frac{D_K}{kT}\left[1 + \frac{B_0 P}{\eta D_k}\right]$$

is negligible. Alternatively, if the porous media can be characterized by an average pore diameter d, viscous flow will be negligible if the Knudsen number is large, that is, $L/D > 100$, where L is the mean free path in the gas (Chapman and Cowling, 1970). The second assumption can be shown to be true, by direct calculation, for much of the microporous media permeability data at 1 atm or below which have appeared in the literature (for example, Gilliland et al., 1958; and Weaver and Metzner 1966). Therefore, for microporous solids, we have

$$J = -\frac{D_k}{kT}\left[1+\frac{kT}{q}\,\frac{D_s}{D_k}\,S\,\frac{dC_s}{dP}\right]\frac{dP}{dz} + \frac{PD_k}{kT}\,\alpha_L\,\frac{d\ln T}{dz} \quad (5)$$

Consider now the experiment in which a porous pellet connecting two closed volumes of gas is subjected to a temperature gradient. At steady state a pressure gradient arises in response to the temperature gradient so that there is no net mass flux, that is, $J = 0$. From Equation (5) the steady state temperature and pressure gradients are related by

$$\left[1+\frac{kT}{q}\,\frac{D_s}{D_k}\,S\,\frac{dC_s}{dP}\right]\frac{d\ln P}{dz} \equiv \left[1+\frac{J_{sD}}{J_k}\right]\frac{d\ln P}{dz} = \alpha_L\,\frac{d\ln T}{dz}$$

Finally, integrating over the porous pellet, we have

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{T_2}{T_1}\right)^R$$

where $R = \alpha_L/(1 + J_{sD}/J_k)$. This equation establishes a quantitative relation between the thermal transpiration pressure difference and the ratio of the surface-to-Knudsen fluxes. For the case in which $J_{sD} = 0$, R is equal to 0.5; the result given in all elementary discussions of kinetic theory. It should be noted that for many microporous media (such as, Vycor glass), Equation (4) is satisfied at pressures up to several hundred Torr. Therefore, it is possible for T_1 and T_2 to differ by only 1°C. and still obtain a pressure difference of several tenths of a Torr, which is easily measured. This is fortunate for it allows one to neglect the temperature dependence of both J_{sD} and J_k in interpreting the experimental data.

It would now be appropriate to analyze existing data for thermal transpiration in porous media to both establish the validity of the experimental technique suggested above and to determine the extent of surface diffusion for various gas-porous media pairs. Unfortunately, while numerous thermal transpiration measurements have been made for capillary tubes and small orifices, the only steady state data for porous plugs is that of Reynolds (1879) for air and hydrogen through stucco and meerschaum, and that of Knudsen (1910) for hydrogen through asbestos and magnesia. Furthermore, it is not clear that either of these sets of data are satisfactory, since Knudsen has pointed out a possible temperature measurement error in Reynolds' work, and it is questionable whether the Knudsen number requirement was met in Knudsen's work. With this disclaimer, we note that Edmonds and Hobson (1967) have reanalyzed the data of both Reynolds and Knudsen and concluded that $R = 0.487$ for Knudsen's work, and $R = 0.397$ for Reynolds data of air through stucco. One would not expect hydrogen to be appreciably adsorbed on a nonmetal (DeBoer, 1968), so that the effect of surface diffusion should be small. This is evident from Knudsen's data in which R is, within experimental error, equal to 0.5, establishing that surface diffusion is negligible. However, the surface diffusive flux may have been as large as 26% of the Knudsen flux for the air-stucco system studied by Reynolds.

There is one possible weakness with the experimental method suggested here: the assumption that $\alpha_L = 0.5$. Ray tracing arguments (see, for example, Miller and Buice, 1966) have shown that α_L may be different than 0.5 for thermal transpiration in capillary tubes; a result which has also been found by Edmonds and Hobson (1965) and others in measurements of the capillary thermomolecular pressure difference. However, the ray tracing arguments *do not apply to the internal geometry of porous media*, and the only experimental data for a nonadsorbed gas (Knudsen's data for hydrogen) indicate that $\alpha_L \sim 0.5$. There is also the possibility that α_L may be dependent upon the gas-surface intermolecular potential function. Due to these uncertainties, the first part of an experimental program to measure surface diffusion by thermal transpiration methods should be a set of measurements with the noble gases He, Ne, and Ar. These gases, which presumably do not adsorb, have sufficient diversity in the intermolecular potential functions to test of the $\alpha_L = 0.5$ hypothesis.

ACKNOWLEDGMENT

This work was supported, in part, by a Project Themis Grant to the University of Delaware.

NOTATION

B_0 = geometric parameter characterizing porous media
C_s = surface concentration
d = average pore diameter
D_k = Knudsen permeability coefficient
D_s = surface diffusion coefficient
J = total gas flow through porous media
J_K, J_{sD}, J_{TT}, J_v = gas flow due to Knudsen diffusion, surface diffusion thermal transpiration, and laminar flow in the pores, respectively
k = Boltzmann's constant
L = mean free path of the gas
M_A, M_{NA} = molecular weight of adsorbed and nonadsorbed gases, respectively
P = pressure
q = tortuosity of porous media
Q_A, $Q_A{}^K$, $Q_A{}^s$ = total, Knudsen and surface permeability of an adsorbed gas, respectively
Q_{NA}, $Q_{NA}{}^K$ = total and Knudsen permeability of a nonadsorbed gas
R = $\alpha_L/(1 + J_{sD}/J_k)$
S = surface area per unit volume of porous pellet
T = temperature
z = flow direction
α_L = thermal diffusion factor for the gas-porous system
ϵ = porosity
λ_{tr} = translational component of the gas thermal conductivity
η = gas viscosity

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Manuscript received February 3, 1972; revision received March 30, 1972; communication accepted March 30, 1972.

Meniscus Vortexing in Free Coating

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The authors are interested in predicting meniscus flow effects. Although the need for describing curved menisci by two-dimensional flow fields has been recognized by Groenveld and Van Dortmund (1970) and others, a solution for a complete flow field in menisci has not been presented. Other aspects of this problem are referred to in the discussion.

Consider the case of free coating as shown in Figure 1A. Here a continuous flat sheet or belt is withdrawn upward at a constant velocity U_w from a liquid bath having a depth d and a width w. The thickness h of the adhering film will decrease from liquid level to a constant thickness h_0. Near the moving sheet, the streamlines are nearly parallel to the sheet and flow is upward because of the pumping action of the solid surface. Because a portion of liquid usually flows back down to the liquid bath, there is a stagnation point B at which the reverse flow occurs: a second stagnation point occurs at some point C. On the upper meniscus AB all the liquid flow is upward, and on the lower meniscus surface BC the liquid flow is downward. The case considered here is steady flow, where the same mass flux Q of liquid withdrawn by coating is added to the right corner of bath. This feed flow maintains the liquid level. Since flow is downward near the liquid inlet, an eddy is created in the lower right corner of Figure 1A and a vortex is usually created in the bath below BC.

The main purposes of this paper are to predict the vortex and stagnation points in free coating and to confirm the theory with data.

THEORY

Neglecting edge effects, the coating process can be described by a steady state, two-dimensional model in rectangular coordinates. The relevant differential equations are those of continuity and motion for the well-known Navier-Stokes fluid, which has constant density and constant viscosity. For the x direction vertically upward, these equations reduce to the following expression for velocity components $u(x, y)$ and $v(x, y)$.

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \tag{1}$$

$$\rho\left[u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y}\right] = \mu\left[\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right] - \frac{\partial P}{\partial x} - \rho g \tag{2}$$

$$\rho\left[u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y}\right] = \mu\left[\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2}\right] - \frac{\partial P}{\partial y} \tag{3}$$

Eleven boundary conditions are applicable. Six of the BC's are no slip of u or v at each of three solid boundaries (continuity of velocity). BC 7 and 8 are known velocities for the constant thickness region at a distant "a" far above the liquid level; these velocity profiles are

$$v = 0,\ u = \frac{h_0{}^2\rho g}{2\mu}\left[\left(\frac{y}{h_0}\right)^2 - 2\left(\frac{y}{h_0}\right)\right]U_w \tag{4, 5}$$

The remaining three BC's involve the gas-liquid interface $h(x)$. Here they are taken as BC 9 continuity of net flow across any horizontal cross section of the film, BC 10 negligible tangential stress, and BC 11 meniscus profiles $h(x)$ obtained experimentally.

For convenience in solution, the stream function ψ^0 and the vorticity ω^0 are introduced in the standard way, $u = \partial\psi^0/dy$, $v = -\partial\psi^0/\partial x$, and Equation (6) for ω^0. Thus Equations (1) to (3) may be replaced by

$$-\omega^0 \equiv \frac{\partial u}{\partial y} - \frac{\partial v}{\partial x} = \frac{\partial^2\psi^0}{\partial y^2} + \frac{\partial^2\psi^0}{\partial x^2} \tag{6}$$

$$\left[\frac{\partial\psi^0}{\partial y}\frac{\partial\omega^0}{\partial x} - \frac{\partial\psi^0}{\partial x}\frac{\partial\omega^0}{\partial y}\right] = \frac{\mu}{\rho}\left[\frac{\partial^2\omega^0}{\partial y^2} + \frac{\partial^2\omega^0}{\partial x^2}\right] \tag{7}$$

Equation (6) follows from the definitions of ψ^0 and ω^0. The continuity Equation (1) is automatically satisfied by the stream function ψ^0. The motion Equations (2) and (3) combine to form Equation (7) by elimination of the pressure terms.

It is convenient to make Equations (6) and (7) non-

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