Transport Properties of Gases in Porous Media at Reduced Pressures With Reference to Freeze-Drying

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Theory is outlined relative to the effect of pressure on permeabilities and thermal conductivities of gases in porous solids in the slip flow and free-molecule flow regions, and experimental results are reported for several freeze-dried food materials. Mean pore diameters for the porous materials calculated from permeability data were about 100 μ and were in agreement with microscopic observations. Thermal conductivities followed the predicted behavior of a constant value at high pressures, with a gradual decrease to another constant value at very low pressures. The results show that the usual operating pressure range of freeze-dryers (0.1 to 1.0 mm. Hg) corresponds to the transition region between slip flow and free-molecule flow.

Transport properties of gases in porous media are important in many industrial and agricultural processes. A number of these processes involve combined mechanisms of heat flow, hydrodynamic vapor flow, and diffusion. Examples of such combinations are to be found in drying, heterogeneous catalysis, combustion, transpiration cooling, and soil-atmosphere energy relations, to mention a few. Of special interest are applications with a pressure low enough that the ordinary laws of continuum flow are not valid, and the so-called *slip flow* or *free-molecule flow* conditions exist. An ideal example of such a condition is in freeze-drying, a vacuum drying process in which the water is sublimed from the frozen state. As freeze-drying of a water-containing solid proceeds, the ice phase recedes inward and becomes surrounded by a layer of porous, dried material. In the conventional process the heat of sublimation must then be conducted through this insulating layer, and the vapor must flow out through the same layer. These porous materials are excellent thermal insulators, and it is found in practice that the rate of drying is severely limited by heat transfer.

In recent years freeze-drying has assumed an increasing role in the production of dehydrated foods, where economic aspects are much more important than producing high-cost items such as pharmaceuticals. Engineering design of freeze-drying equipment for food processing has been hampered by a lack of fundamental information on the properties of the materials. This paper presents the results of experimental studies on permeabilities, diffusivities, and thermal conductivities in certain freeze-dried food products. It should be noted that the properties of the frozen, undried material are of secondary importance. Specific applications to the freeze-drying process are discussed elsewhere (*2*).

THEORY

Vapor Transport

In freeze-drying, vapor may move from the ice surface to the surrounding vacuum space by both hydrodynamic flow and diffusion. Hydrodynamic flow will generally be of more significance, and the following discussion is concerned primarily with this subject.

The most widely used analytical treatment of the flow of gases through porous solids is based on results obtained for the flow of gases in capillary tubes. The relationships for both slip flow and free-molecule flow are presented by Kennard (*3*). Carman (*1*) discusses the application of these relationships to flow through porous media. For the slip-flow region his equations may be put into the following form:

$$\frac{u_o P_o \mu L}{\Delta P} = \frac{\phi d_e^2 P_m}{32(L_e/L)^2} + \frac{\phi s d_e^2 \lambda_o P_o}{4(L_e/L)^2} \tag{1}$$

In Equation (1) the reflection coefficient has been taken as unity, in accordance with results presented by Carman. The shape factor s accounts for the fact that the pores are short and may be noncircular, and the ratio $(L_e/L)^2$ is a tortuosity factor that is applied because the gas does not have a straight path through the solid. The tortuosity correction can be estimated from diffusivity measurements with the assumption that the effect is the same for a flowing gas as for a diffusing gas. Accordingly the ratio of the diffusivity of the vapor in free air to its diffusivity through the solid should be equal to $(L_e/L)^2/\phi$.

The analyses and discussion of Carman and of Peterson (*7*) raise questions regarding the application of these factors in this simplified manner, and the uncertainties are such that the exact physical interpretation of the constants in Equation (1) is unclear. General agreement with the form of Equation (1) has been observed by a number of investigators, and it may be presumed that the experimentally determined values of the constants will be useful in characterizing porous solids.

Flow of Heat

The thermal conductivity of the gas-filled solid depends on the individual conductivities of the gas and solid and on the geometry of the porous system. In the present application, involving consolidated porous structures at low temperatures, the effects of both radiation and convection may be neglected. A number of investigators have presented relationships for over-all thermal conductivities of porous solids or beds. Analyses particularly relevant to the present study are given in references *5* and *10*. Inasmuch as neither the thermal conductivity nor the geometrical arrangement of the solid material can readily be evaluated for the freeze-dried materials studied, the following discussion will be limited to the effect of gas pressure on the thermal conductivity of the gas-filled porous solid. At pressures high enough that the mean free path of the gas molecules is small compared with the pore size, kinetic theory predicts that the over-all thermal conductivity should be independent of pressure. At a sufficiently high vacuum the contribution of the gas becomes insignificant, and heat is conducted only along the interconnected solid structure.

One theoretical approach to the problem is through the use of the well-known temperature jump relationships, conveniently presented by Kennard. These may be expressed as follows:

Slip region:

$$\frac{k_g}{k_{go}} = \frac{1}{1+\left(\frac{2-a}{a}\right)\left(\frac{4\gamma}{\gamma+1}\right)(1/N_{pr})(\lambda/L)} \qquad (2)$$

Free-molecule region:

$$k_g/k_{go} = (1/10)\left(\frac{a}{2-a}\right)(\gamma+1)(L/\lambda) \qquad (3)$$

Schotte (*9*) applied a relationship equivalent to Equation (2) to obtain a correlation of thermal conductivities of beds of packed solids by evaluating the length L in terms of an average distance between particle surfaces. Agreement between experimental and predicted results was good on a relative basis, but the absolute magnitude of the term representing pore size showed poorer correlation.

The approach used by Kistler (*4*) and Verschoor and Greebler (*11*) makes use of the fact that, according to kinetic theory, thermal conductivity in a gas is proportional to the product of density and mean free path. At low pressures, where mean free path is large compared with pore size, they defined an effective mean free path based on collisions of gas molecules with solid surfaces as well as with other molecules. Their result was identical to Equation (2), except that the factors involving γ and N_{pr} did not appear in the denominator. It should be noted that their result makes no distinction between the slip and free-molecule regions.

The relationships presented by Kennard are based on conduction of heat through a gas between two parallel flat surfaces. The situation for a porous solid is different in that there is a connected passageway for movement of gas through the solid. An approach that corresponds to the postulates used in treating flow behavior is to consider the conduction of heat through a gas contained in a capillary tube. This problem can be solved by direct application of the results of Pollard and Present (*8*) for gaseous self-diffusion in capillary tubes. Pollard and Present obtained equations that they integrated numerically to give the self-diffusion coefficient in terms of mean free path and tube diameter over the entire pressure range from the free-molecule region up to normal pressures.

Kinetic theory relates thermal conductivity and self-diffusion coefficient as follows:

$$k_g/D = cPC_v/RT \qquad (4)$$

in which the value of the constant c depends on the molecular model. For the simple kinetic theory, which was used by Pollard and Present, c is equal to unity. In the free-molecule region there is no interaction between molecules, and diffusive flow must be identical with hydrodynamic flow. The self-diffusion coefficient under these conditions is given by the expression (*8*)

$$D = d\bar{v}/3 \qquad (5)$$

A combination of Equations (4) and (5) with the free-molecule flow equation for capillary tubes, with the value of the reflection coefficient taken as unity, leads to the result

$$\frac{u_o P_o L}{\Delta P} = \frac{k_g RT}{C_v P} \qquad (6)$$

Equation (6) provides a direct relationship between thermal conductivities and permeabilities in the free-molecule region. It should be noted that, according to this approach, interchange of energy between the gas molecules and the solid does not enter into the calculation of thermal conductivity. Accordingly, the reflection coefficient, rather than the accommodation coefficient, is of significance.

TABLE 1. THERMAL CONDUCTIVITY VARIATION BASED ON RESULTS OF POLLARD AND PRESENT (*8*)

d/λ	k_g/k_{go} Exact solution	k_g/k_{go} Approximate equation
0.001	0.002	0.003
0.01	0.010	0.013
0.1	0.091	0.118
1.0	0.500	0.571
10	0.926	0.930
100	0.992	0.993
1,000	0.999	0.999

The solution of Pollard and Present for long capillary tubes is presented graphically (*8*). Because of simplifications made in the numerical solution it cannot be extended to length-diameter ratios of 1:1, which might be expected for many porous solids. In the free-molecule region the solution reduces to Equation (5), and in the high-pressure region it is represented by

$$D/\bar{v}\,\lambda = 1/3 - \lambda/4d \qquad (7)$$

Noting that $k_g/k_{go} = (DP)/(DP)_o$, in which the subscript o refers to the value in the free gas, and that the mean free path is inversely proportional to pressure, one may summarize the preceding results as follows:

High-pressure region

$$k_g/k_{go} = 1 - C_2/P \qquad (8)$$

Free-molecule region

$$k_g/k_{go} = P/C_1 \qquad (9)$$

The ratio C_2/C_1 is equal to 0.75. In the limits of high and low pressure Equations (2) and (3) can be put into the same form as (8) and (9). In this case the C_2/C_1 ratio is equal to 0.4 γ/N_{pr}. Both C_1 and C_2 should be inversely proportional to an effective pore diameter and directly proportional to a standard pressure value of the mean free path. Because of the agreement in the results obtained by the three quite different approaches considerable confidence may be held that these adequately express the form of variation with pressure. In view of the lack of close correspondence of any of the model systems with an actual porous solid and the uncertainty in accommodation coefficients, not too much significance can be attached to the numerical values of the constants. In an actual situation these would have to be determined empirically. The last approach, based on the development of Pollard and Present, would seem to be the most promising for developing interrelationships among the various properties.

From the standpoint of simplicity there is considerable advantage in using an equation with a single constant to cover the entire pressure range, as follows:

$$k_g/k_{go} = \frac{1}{1+(C/P)} \qquad (10)$$

Equation (10) is of the same form as

Equation (1) and reduces to Equations (8) and (9) in the high- and low-pressure limits. In Table 1 the exact results of Pollard and Present for infinitely long tubes are compared with results obtained with a relationship equivalent to Equation (10). Although there is a substantial percentage difference between the two sets of values in the low-pressure region, the absolute magnitude is so low that the error is unimportant for engineering design purposes.

EXPERIMENTAL PROCEDURE

Material Used

Samples of freeze-dried beef, apples, and peaches, prepared in a conventional tray freeze-dryer, were used for the measurements. The beef was a commercial grade of round steak, selected to be as free as possible from fat and connective tissue. Samples for these measurements were cut so that all flows were parallel to the grain. This is the usual method of preparation for consumer cuts and has the advantage that the transport properties have much higher values parallel to the grain than across the grain. The apples were a Delicious variety, and the peaches were clingstones. These fruits are uniform in texture, and there is no preferred direction of cutting. Pretreating by blanching or sulfite dipping appeared to have no effect on the results. Freeze-dried beef is somewhat reminiscent of balsa wood in appearance, although it is coarser in texture and lacks the strength of the wood. The freeze-dried fruits, under the microscope, have an appearance similar to some of the common open-pored plastic foams.

The fruits are hygroscopic, and any sample handling must be done with rubber gloves in a dry atmosphere. Also, being quite friable, they must be cut and handled with care to avoid crumbling the edges. The meat is much more durable, requiring no special measures in handling. The oxidative browning which occurs with all these materials has no apparent effect on the transport properties. Measurements made on the same sample showed good agreement over periods as long as several months.

Permeability

A plug of sample about 2.3 cm. in diameter and 1 cm. in length was placed in the mid-section of a glass tube. The tube was held under a vacuum, and room air or cylinder nitrogen was allowed to flow through the sample to the vacuum pump. The nitrogen was used to provide a dry gas for the hygroscopic fruit samples. Flow rates were measured at atmospheric pressure with a capillary tube flow meter. Absolute pressure was measured with a vacuum gauge, and pressure drop across the sample was obtained with a butyl phthalate manometer or with a pressure transducer. As discussed above, permeabilities are correlated on the basis of average pressure. About 40 μ was the lowest average pressure that could be maintained with the flow rate large enough to give a measurable pressure drop.

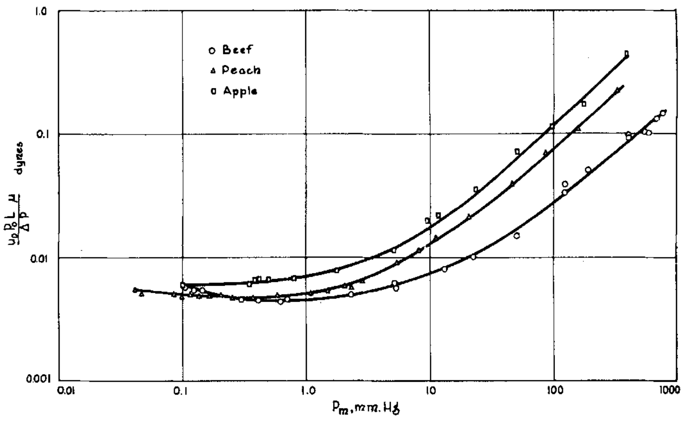

Fig. 1. Observed permeability data.

Measuring the pressure drop across the sample gave considerable trouble. A number of types of sensitive micromanometers are available, but these are not suitable for use under high vacuum. A transducer was built for this purpose in which the motion of a stainless steel diaphragm caused by a pressure difference was detected by a linear differential transformer. This instrument had a sensitivity of about 0.001 mm. Hg but lacked stability.

Thermal Conductivity

Heat flow transducers were used to measure thermal conductivity. The transducers consist essentially of a multijunction thermopile in a thin Bakelite sandwich 2 in. square by 3/64 in. thick. They are calibrated so that the potential difference in millivolts multiplied by a constant gives the heat flow rate in British thermal units per hour square feet. In use, a sample of dried product was placed between two of the transducers. Two transducers are used in order to provide a check on the measurements. This assembly was in turn placed between two hollow brass plates through which two water streams of different temperatures were circulated. Tap water at about 80°F. was used for one of the streams; the other was either ice water or water from a bath at about 110°F. Meat samples ¾ in. thick by 2 in. square were surrounded by flexible plastic-foam insulation which was held under compression to offset a slight tendency of the meat to shrink. A single sample 2 in. square could not be cut from the fruit, and it was necessary to insert the sample in sections. For this reason the fruit samples were cut ½ in. thick and were placed in a rigid holder of balsa wood. A rigid holder was satisfactory, since the fruit showed no shrinkage tendency. The entire sample assembly was placed inside a chamber connected to a vacuum pump. The pump operated continuously, and pressures were controlled by bleeding air into the chamber through capillary tubes. Pressures could be obtained ranging from a few microns up to atmospheric.

Diffusivity

Measurements were made with the sample used for the permeabilities. Water vapor was the diffusing component with the meat. The sample was inserted into a glass tube above a small quantity of water, and a wire gauze basket of magnesium perchlorate was placed above the meat. The tube was held at atmospheric pressure in a constant temperature chamber, and the gain in weight of the magnesium perchlorate was noted over a series of time intervals. Because of the hygroscopic nature of the fruit, toluence was used as the diffusing substance, with activated charcoal as the absorbent. The particular diffusing component is not important, since the desired result is the ratio of the diffusivity in the sample to that in free air.

Porosity

Samples from the diffusivity measurements were used in a conventional air displacement procedure. A measured air pressure was placed on a small cell containing the sample. The pressure was then released, and the volume of air discharged was noted. This procedure was repeated on the empty cell, and the porosity was obtained by a simple calculation.

RESULTS AND DISCUSSION

Permeability results for the three materials are shown in Figure 1, which is a logarithmic plot of the data with coordinates as suggested by Equation (1). It may be seen that the flow curves of the beef and peach show a minimum. This behavior was observed many times with other samples, and it is believed that the apple would show similar behavior if more points had been obtained in the low-pressure region. The permeability data plotted with linear coordinates in Figure 2 give straight lines as required by theory. Diffusivity and porosity results for the three samples are shown in Table 2. The diffusivity measurements were not easy to reproduce, and there is an uncertainty of 10 to 15%.

Table 2 also includes slopes and intercepts from Figure 2 and pore diameters calculated by Equation (1). A value of unity was used for the shape factor s in the last term of Equation (1). It is seen that the

	Beef	Apple	Peach
Diffusivity, sq. cm./sec.			
in sample	0.0451 water	0.0149 toluene	0.0191 toluene
in free air	0.310 at 38°C.	0.865 at 30°C.	0.0855 at 27°C.
Porosity	0.64	0.88	0.91
Tortuosity factor (by diffusion)	4.4	5.1	4.1
Figure 2 slope, dyne/mm. Hg	0.00024	0.0012	0.00075
Figure 2 intercept, dyne	0.0045	0.0060	0.0045
d_e (slope), μ	60	130	90
d_e (intercept), μ	190	215	125
d_e by microscope	50-150	120-300	80-300

diameters calculated by the two methods do not show close agreement, although all the diameters are within the range of sizes observed under the microscope. It should be pointed out that these calculations are based on an extremely simplified model of the porous solid, and the agreement between calculated and observed diameters is of limited significance. Discrepancies between the two sets of calculated diameters cannot be attributed to the shape factor, since theory shows that this correction should have the opposite effect. The Poiseuille-term diameter is a much more reliable measure of pore size than the slip term diameter, since it is substantially determined by higher-pressure characteristics where slip effects are less important. Indeed, Klinkenberg (*6*) and others have found that the Poiseuille-term permeability for various core samples is equal to the permeability obtained with liquids and thus does not depend on slip-flow effects. The slip-term diameters, as calculated from the intercepts on Figure 2, are strongly dependent on the low-pressure results, particularly on results in the region of the minima observed in Figure 1. As the following discussion shows, the validity of the slip-flow formulation in this region is questionable.

One of the postulates on which the slip-flow equation is based is that capillary diameters are substantially greater than the mean free path. The mean free path of air at normal atmospheric conditions is about 0.065 μ. At pressures in the region of 0.5 to 1.0 mm. Hg, which correspond to the minima in Figure 1, the mean free path is of the same order of magnitude as the calculated and observed pore diameters. In this connection it may be noted that Knudsen's data on flow by Carman (*1*) and Pollard and Present (*8*) in plots equivalent to Figure 1, show a minimum at a pressure corresponding to a λ/d ratio of about 2.0. The minimum points on the beef and peach curves occur at approximately the same ratio of λ/d. These results contradict the conclusion of Pollard and Present, who reasoned that such minima should be observed with flow through long capillary tubes but not with flow through porous media. Since the pressure range of 0.5 to 1.0 mm. Hg apparently corresponds to a transition region between slip and free-molecule flow, it is not to be expected that the slip-flow equation would apply quantitatively. The data reported here were not obtained with sufficient precision to permit accurate calculation of slip-flow effects at high pressures, where absolute deviation from Poiseuille flow is small.

Thermal conductivities of the meat and fruit samples are shown in Figure 3 and summarized in Table 3. The data exhibit the expected behavior of constant value at high pressure with a smooth transition to a lower constant value as the pressure is reduced. Within the limits of experimental error the difference between the high- and low-pressure conductivities is about 0.016 B.t.u./(hr.)(ft.)(°F.) for all three samples, compared with a value of 0.015 for free air at the same average

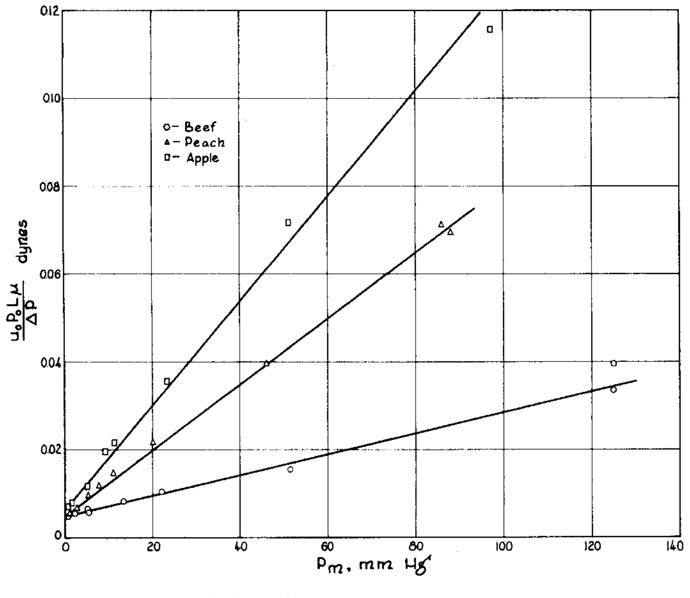

Fig. 2. Straight-line permeability plot.

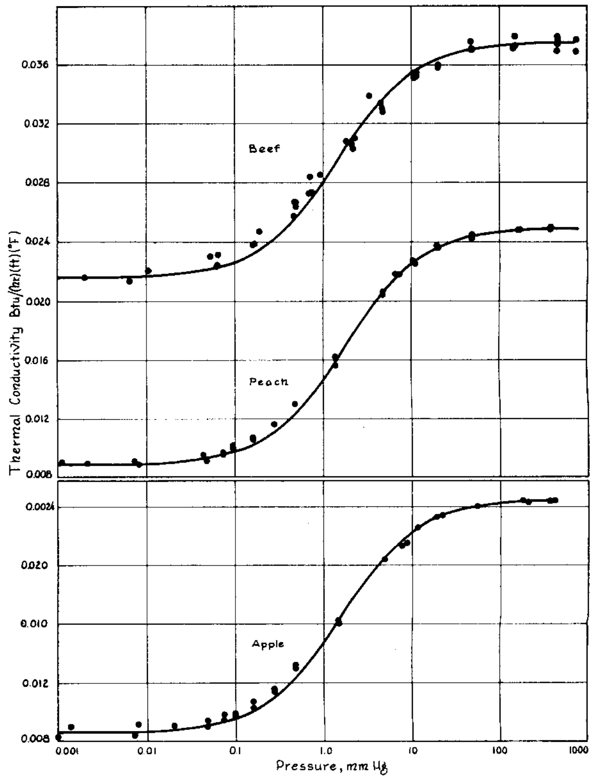

Fig. 3. Observed and calculated thermal conductivities, points: observed data, lines: Equation (10).

TABLE 3. THERMAL CONDUCTIVITIES IN BRITISH THERMAL UNITS PER HOUR FEET DEGREES FAHRENHEIT

	Beef	Apple	Peach
High pressure	0.0375	0.0244	0.0249
Low pressure	0.0216	0.0086	0.0089
Difference	0.0159	0.0158	0.0160
C [Equation (10)], mm. Hg	1.5	1.6	1.8

temperature. The higher value of the zero-pressure conductivity for the meat is readily explained by its fiber orientation parallel to the direction of heat flow. The intrinsic conductivity of the solid must be at least as great as the zero-pressure conductivity divided by the volume fraction of solids. The respective values for the beef, apple, and peach are 0.06, 0.07, and 0.10. Since the latter two values are quite sensitive to small errors in measured porosities, these three conductivities may be considered to be roughly equal. These values are comparable to those of many organic materials reported in the literature, and it is not expected that they would be substantially greater than this. There is no ready explanation for the fact that the difference between the high- and low-pressure values is the same for all three samples despite the variation in porosity. If the gas and solid formed parallel heat flow paths, this difference would be equal to the conductivity of the free gas multiplied by the porosity. The result may reflect a fortuitous combination of circumstances or may arise from some more fundamental relationship. Similar results have been reported for glass fiber insulations (*10, 11*) and for silica aerogels (*4*). Accordingly, it appears reasonable for solids having high porosity and relatively low conductivity of the solid material to represent the total thermal conductivity as the sum of a solid and an apparent gas conductivity, where the apparent gas conductivity is equal to a constant times the true gas conductivity.

On the above basis conductivities of the three materials, calculated with Equation (10), are plotted as the lines in Figure 3. For each material k_{go} was taken as the difference between the high- and zero-pressure values. Data are not accurate enough to permit the use of Equations (8) or (9) for determining the constant C, and this constant was selected so as to give agreement with experimental data when the conductivity is equal to the average of the high- and low-pressure values. The experimental data follow the theoretical curves very closely. In view of this excellent agreement, and because of the differences between the actual porous solids and the models described by the theoretical equations, use of a more elaborate equation cannot be justified at this time. In accordance with the theory outlined above values of the constant C should be inversely proportional to the mean pore diameters. The pore diameters listed in Table 2 do not show this result. It is of interest to compare permeability and thermal conductivity data on the basis of Equation (6). If this equation is multiplied through by viscosity, the right-hand side, for the beef sample, has the limiting value 0.03. Reference to Figure 1 shows that this is appreciably higher than the limiting value indicated by the permeability data. The two limits are of the same order of magnitude however, and close correspondence could be considered only a coincidence in view of the many postulates involved in the development.

On the basis of these results it is suggested that for materials of high porosity with moderate solid conductivity (as contrasted to metals for example) the thermal conductivity of the gas-filled solid may be treated as a parallel combination of a gas and a solid; the dependency of the gas conductivity on pressure is adequately represented by Equation (10). At the present stage of development the values of k_{go} and C in Equation (10) and the zero-pressure conductivity of the porous solid must be determined by experiment. The development of a general method for predicting these constants in the absence of specific experimental measurements would require additional data both on conductivities in the presence of gases other than air and on intrinsic solid conductivities. The present results however provide information useful for direct application to freeze-drying problems.

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NOTATION

a = accommodation coefficient
c = proportionality constant relating diffusivity and thermal conductivity
C = constant in thermal conductivity equation
d = capillary diameter
d_e = equivalent pore diameter
D = self-diffusion coefficient
k_g = thermal conductivity of gas in porous solid
k_{go} = thermal conductivity of free gas
L = length of capillary tube or length of heat flow path
L_e = equivalent length for flow through porous solid
N_{pr} = Prandtl number
P_m = arithmetic average pressure across capillary tube or porous solid
P_o = reference pressure (1 atm.)
s = shape correction factor in slip flow term
u_o = velocity through capillary tube or superficial velocity through porous solid, measured at 1 atm.
$\bar{v}$ = mean molecular velocity

Greek Letters

γ = heat capacity ratio
λ = mean free path at P_m
λ_o = mean free path at P_o
μ = viscosity
ϕ = porosity (fraction of voids)

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