

# LONGITUDINAL DIFFUSION AND PERMEABILITY OF NONPOLAR GASES IN EASTERN HEMLOCK<sup>1</sup>

F. C. Beall and J-H. Wang

Associate Professor of Wood Science and Technology, and  
Graduate Assistant in Wood Science,  
School of Forest Resources, The Pennsylvania State University,  
University Park, PA 16802

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## ABSTRACT

Longitudinal ethane diffusion and nitrogen permeability were measured in oven-dry eastern hemlock sapwood. Samples were selected from 2 trees, 3 heights, and 4 quadrants, and either air- or solvent-dried for aspirated or unspirated conditions. An IR method was used to detect ethane concentration in nitrogen at 25 C from which diffusion coefficients were calculated. The mean diffusion coefficient of the solvent-dried samples was 40% of free diffusion; the air-dried coefficient was about 16% of the free diffusion coefficient. No significant differences were found between position in the tree or oven-dry density and the diffusion coefficients. Diffusion coefficients were used to determine tortuosity differences in air- and solvent-dried wood. Effective pore openings obtained from permeability measurements, the Klinkenberg equation, and the temperature coefficient of diffusion confirmed that diffusion was occurring in the Kundsén end of the slip-flow region. A linear relationship was found between the permeability constant and diffusion coefficient. Diffusion and permeability measurements produce separate and complementary data that can be used to determine the mode of conductivity of gases in wood.

*Additional keywords:* *Tsuga canadensis*, diffusion coefficient, temperature coefficient, tortuosity, infrared detection, pore openings.

An understanding of the factors governing the movement of fluids in and through wood is of extreme importance to the wood industry. Increased knowledge in this area would undoubtedly lead to improved methods for the drying of lumber, and treatment with preservatives, fire retardants, and other chemical modifiers. In addition, such studies could help to produce a better understanding of the intricate structure of wood tissue and be useful in the development of improved pulping methods.

One of the main advantages in employing gases rather than liquids in wood treatment lies in the fact that the gas molecules can move through the pits without a surface tension problem. An externally applied pressure to force the gas into and through wood is then much more efficient than a procedure using a liquid. The passage of

water vapor through wood has been shown by Stamm (1964) to be attributable to at least two different diffusion processes: (1) bound water—water vapor may become physically absorbed and move by diffusion through the cell-wall material, and (2) water vapor—true vapor diffusion through the coarser capillary voids. The same pathways are assumed to be available for other gases that swell wood. Nonpolar gases, such as CO<sub>2</sub> and the hydrocarbons, do not swell wood and it is assumed that they diffuse through wood along the same pathways as does water vapor.

Investigations into the influence of molecular weight, size, and shape, and the mean free path of the diffusing gas molecules upon the diffusion coefficient in wood have not yet been reported in the literature. A better knowledge of the influence of temperature on the rate of diffusion would also be of fundamental importance. The influence of these parameters must be known before the behavior of a gas diffusing through wood can be predicted.

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“Diffusion” and “permeability” have specialized meanings when used by wood physicists. Generally, they reserve “diffusion” for movement of fluids under a concentration gradient, with the system under constant pressure. Most diffusion studies are conducted with binary gases or liquids at atmospheric pressure. “Permeability” (flow) refers to a net mass flux that occurs from a pressure differential. It must be emphasized that in many scientific areas, diffusion is more generally defined and often encompasses the realm of permeability. In addition, where concentration and pressure differences occur simultaneously, both diffusion and flow contribute to the net flux. This interrelationship can be expressed mathematically if the pressure dependence of the diffusion coefficient is known (Youngquist 1970). In both diffusion and flow (permeability), the size of the pore openings determines the flux mode and the applicable solutions. The pore size, as defined for porous media, is the effective opening with regard to the process, and not necessarily of anatomical significance when applied to wood.

There are four major diffusion and flow regimes of interest in the movement of fluids, and, in particular, gases (Youngquist 1970):

1. Activated diffusion. When the gas molecular diameter approaches the pore size, no gas-gas interaction takes place and the gas molecule can be thought of as vibrating through the opening. The flow of the gas is independent of pressure and binary gas interactions. For most simple gases under ambient conditions, the effective pore size would be about  $0.001 \mu\text{m}$  (10 Å). The temperature effect on activated diffusion follows an Arrhenius relationship. Movement of gases through hardwood pit membranes, which have no discernible openings using transmission electron microscope techniques, is almost certainly activated.

2. Knudsen diffusion. As the pore size increases, a transition to Knudsen diffusion occurs that dominates when  $r \leq 0.1\lambda$ , where  $r$  = pore radius and  $\lambda$  = mean free path. Under STP conditions, the pore

radius would be about  $0.01 \mu\text{m}$  (100 Å). This corresponds to the smaller openings in the margo of softwood bordered pit pairs. Although these openings are still much smaller than the mean free path, the movement is no longer activated. Instead, the temperature (T) effect on the diffusion coefficient (D) can be expressed by  $D \propto T^{0.5}$ .

3. Slip (Adzumi) flow. In the region of pore size defined by the approximate limits of  $0.1\lambda \leq r \leq 10\lambda$ , a transition occurs between Knudsen and viscous flow. This unnamed transition is sometimes referred to as Adzumi (1937) flow since the author first combined the equations for Knudsen and viscous flow to explain the behavior in the slip flow region. For wood, the region of slip flow is about  $r = 0.01$  to  $1 \mu\text{m}$  (100 to 10,000 Å), which includes all but the larger pore sizes in the softwood margo ( $r = 0.01$  to  $3 \mu\text{m}$ , Sebastian et al. 1965). The temperature effect on diffusion for the pore size range in this region is not defined, but probably varies with pore size, being intermediate between  $T^{0.5}$  and  $T^{1.5}$ .

4. Molecular diffusion and viscous flow. When  $r > 10\lambda$ , free diffusion occurs, independent of the pore size. This is also the region of viscous (Poiseuille) flow when a pressure difference exists. In this region the theoretical temperature dependence of diffusion is  $D \propto T^{1.5}$ . Most of the diffusion that occurs in wood is free diffusion (in the lumens), but unless the pit openings are large ( $r > 10\lambda$ ), the controlling mode will be in the transition region between Knudsen and free diffusion.

The parallels between diffusion and permeability (flow) suggest that complementary information might be obtained for both on the same samples. In this study, independent measurements were made of nitrogen permeability and ethane/nitrogen diffusion to clarify the independent and interdependent nature of the results.

#### LITERATURE

Little research has been reported on the diffusion of nonpolar gases in wood. The ultrastructure of wood differs appreciably

TABLE 1. Diffusion and temperature coefficients for carbon dioxide in Sitka spruce (Tarkow and Stamm 1960a).

Structural direction	Sample thickness (mm)	CO <sub>2</sub> concentration in air (%)	Temperature (C)	Diffusion coefficient (cm <sup>2</sup> /sec)	Temperature coefficient <sup>a</sup>
Longitudinal	10	3.0, 4.3	30	4.7, 5.6 x 10 <sup>-2</sup>	----
Tangential	8, 2.5	3.7-28.5	25, 30, 35	6.3-8.4 x 10 <sup>-5</sup>	2.01

<sup>a</sup>Calculated from the data given on 2 samples at 25 and 35 C.

from most other porous media and does not appear to be easily resolvable in terms of mathematical models. Stamm (1964) has proposed a model based on an electrical analogy of openings in wood. However, the use of average values required by the model rather than distributional functions appears to be self-defeating in predicting diffusion coefficients. Where diffusion is controlled by the openings in pit membranes, it is necessary to assume values for effective pore diameter and thickness, each of which is nebulous in concept.

The effect of system temperature and pressure on bulk diffusion is defined (Barrer 1941) by:

$$D_i = D_o \left( \frac{T_i}{T_o} \right)^n \left( \frac{p_o}{p_i} \right) \quad (1)$$

where  $D_o$  = bulk diffusion coefficient at reference temperature  $T_o$  and pressure  $p_o$  (cm<sup>2</sup>/sec)

$D_i$  = bulk diffusion coefficient at temperature  $T_i$  and pressure  $p_i$  (cm<sup>2</sup>/sec)

$T$  = temperature (K)

$p$  = pressure

$n$  = temperature coefficient.

Values for  $n$  have been determined theoretically ( $n = 1.5$ ) and empirically ( $n = 1.75$ ) for nonpolar gases (Barrer 1941).

Tarkow and Stamm (1960a) determined the longitudinal and tangential diffusion coefficients of CO<sub>2</sub> in Sitka spruce heartwood under the conditions shown in Table 1. There was no appreciable difference attributable to either sample thickness or gas concentration, in agreement with Fick's

first law for steady-state diffusion. Using an electrical analogy for diffusion, the theoretical free diffusion coefficient obtained was twice that of the experimental value for longitudinal diffusion and 30 times greater for tangential. The very low observed value for tangential diffusion was attributed to Knudsen diffusion through the pit membranes, assuming the average pore radius of 0.03  $\mu$ m and the mean free path of CO<sub>2</sub> as 0.06  $\mu$ m. The temperature coefficient for tangential diffusion in Table 1 is a mean value for two samples at 25 and 35 C, for which the values calculated from their data were 1.65 and 2.37 (with a possible error of  $\pm 20\%$ ). The mean value is quite reasonable when compared with the normally observed temperature coefficient of 1.75.

In a subsequent study, Tarkow and Stamm (1960b) found the diffusion coefficients for water vapor (RH = 15 to 50%) through the same samples that CO<sub>2</sub> diffusion had been measured. Using Graham's Law,  $D_A/D_B \propto (M_B/M_A)^{0.5}$ , water vapor was assumed to diffuse 1.56 times as fast as CO<sub>2</sub>. This provided a calculated value for water vapor diffusion at 0% RH, which appeared reasonably close to the anticipated value.

In neither study (Tarkow and Stamm 1960a, 1960b) was the effect or influence of surface migration or surface diffusion considered, which in the case of polar molecules, could be considerable.

Elers (1965) measured the diffusion coefficient of ethylene in nitrogen through the heartwood of oven-dry eastern hemlock in the three structural directions as a function of ethylene concentration, sample

TABLE 2. Diffusion and temperature coefficients for ethylene in eastern hemlock (Elers 1965).

Structural direction	Sample thickness (mm)	Ethylene concentration in N <sub>2</sub> (%)	Temperature (C)	Diffusion coefficient <sup>a</sup> (cm <sup>2</sup> /sec)	Temperature coefficient <sup>b</sup>
Longitudinal	18-40	10-20	5-70	1.7-2.7 × 10 <sup>-2</sup>	1.68
Tangential	1-4	10-40	5-70	9.1-24 × 10 <sup>-5</sup>	1.68
Radial	1-3.5	10-40	5-70	8.9-27 × 10 <sup>-5</sup>	1.31

<sup>a</sup>Calculated for 0 C.<sup>b</sup>Temperature range 5-50 C.

thickness, and temperature. The range of variables and resulting diffusion and temperature coefficients are given in Table 2. Ethylene concentration and sample thickness had no appreciable effect on the diffusion coefficient. The temperature coefficients for longitudinal and tangential diffusion were very close to the empirical value of 1.75 for free diffusion. Above 50 C, the temperature coefficient apparently decreased, but could not be quantitatively analyzed. The decrease was attributed to hindered diffusion.

Comstock (1967) measured flow through eastern hemlock heartwood and sapwood to relate liquid and gas permeability. Gas permeability values were obtained from Darcy's equation for compressible fluids. He found that when gas slip flow was corrected using Klinkenberg's equation, it was possible to equate liquid and gas flow. The slope of the Klinkenberg equation,  $K_b$ , can be used to determine the effective pore radius in a wood sample. The pore radius and true permeability for heartwood were 0.380 to 0.540  $\mu\text{m}$  and 0.044 to 0.176 × 10<sup>-10</sup> cm<sup>2</sup>, and for sapwood were 0.382 to 1.01  $\mu\text{m}$  and 0.207 to 4.31 × 10<sup>-10</sup> cm<sup>2</sup>. A plot of  $\ln r$  vs.  $\ln K$  had a slope equal to about 4, in agreement with the theoretical models for laminar flow in capillaries.

#### EXPERIMENTAL PROCEDURE

##### Sample selection and preparation

1. *Specimen selection:* Two eastern hemlock (*Tsuga canadensis* (L.) Carr.) trees (A & B), selected on the basis of uni-

form growth, orientation, and similar diameter (0.5 m DBH), were cut from the University Experimental Forest, Stone Valley, Pennsylvania. Increment cores were used both to survey and select the trees before cutting, and to identify the heartwood-sapwood areas within the cross-section. The heartwood-sapwood separation was indicated by the reaction of 45% perchloric acid to provide a color distinction. Each tree was identified, marked for the northern exposure, and cut into ten 2-m bolts. A 150-mm-thick disc was removed from the butt end of each bolt and quartered into the respective exposure quadrants (N, E, S, & W). Sapwood was removed from each quadrant and circumferentially divided for replications. Samples were stored in a freezer at -20 C. The density range for all samples was 0.4 to 0.5 (oven-dry volume basis).

2. *Sample preparation:* Each portion of sapwood was split into 28- by 28-mm cross-sections, 150 mm long. Splitting, rather than sawing, was used to provide the best possible grain orientation in samples.

a. *Drying:* The 150-mm sapwood pieces were randomly divided into two different drying method groups: air and solvent. The air-dried samples were sequentially conditioned at 90, 65, and 30% RH (ambient temperature) before vacuum drying at 70 C. Solvent exchange consisted of three changes of acetone in one-week intervals, followed by a similar exchange of acetone with benzene. The benzene was removed by vaporizing it from the samples

over an increasing range of temperatures to above the boiling point of benzene. Moisture was excluded from the samples during vaporization. Later tests showed no effects on IR (infrared) readings from residual traces of acetone or benzene. The final vacuum-drying step for all samples was identical. The samples were stored over  $\text{CaSO}_4$  (Drierite) until needed.

b. *Machining*: The oven-dry samples were oriented on a lathe for the best longitudinal grain alignment and cut to a 20-mm diameter. Each sample was coated with epoxy to seal the surface, and then end-trimmed to 50 mm after curing was completed. They were then redried under vacuum at 70 C and returned to storage over the desiccant.

### Experimental design

1. *Diffusion*: A nominal 6 samples were selected from (a) 3 height levels (butt, middle, top) in the north quadrant of each tree (A, B) and (b) 4 quadrants of the intermediate level in each tree. The above design was used for both air-dried and solvent-dried samples.

2. *Permeability*: Twenty air-dried samples were randomly selected from those of which the diffusion coefficient had been measured. In addition, 20 samples were also randomly selected from solvent-dried diffusion samples.

### Diffusion measurements

1. *Equipment*: Figure 1 shows the equipment flow patterns for the diffusion system. In normal operation, symmetrical flow ( $3 \text{ cm}^3/\text{sec}$ ) occurs in the mixture ( $\text{N}_2 + \text{E}$ ) and sweeping ( $\text{N}_2$ ) channels. The pressure in one channel is adjusted to maintain a differential pressure of less than  $10^{-3}$  torr across the sample. Bubblers exposed to the bath temperature are located on each side of the diffusion cell halves to minimize back diffusion. A manometer attached to one side of the diffusion cell is used to determine the absolute system pressure. The aluminum diffusion cell is contained in a water bath capable

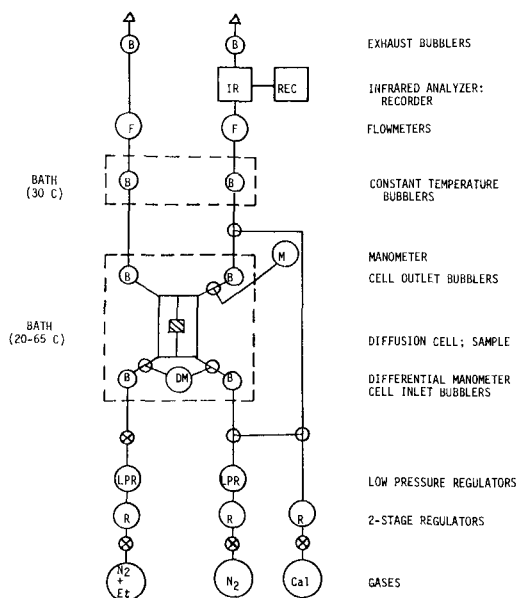


FIG. 1. Infrared detection system for longitudinal diffusion of ethane through eastern hemlock.

of temperature control from 20 to 65 C ( $\pm 0.05$  C). Each gas exits from the bath into another set of bubblers held at a constant 30 C ( $\pm 0.05$  C) in a water bath, and through flowmeters. The sweeping gas proceeds to the IR unit (Beckman IR 215, 2–4.5  $\mu\text{m}$ ) and through an exhaust bubbler, while the mixture goes directly to an exhaust bubbler. In the “zero” or “calibration” mode of operation, the appropriate gas bypasses the diffusion cell in being fed to the IR unit. All gas flow rates are determined at 30 C.

2. *Procedure*: The conditioned sample was placed in a sample holder and sealed in place by O-ring compression. The holder was inserted into the diffusion cell and locked. Then, with the diffusion cell access-port closed, the gases passed through each side of the cell. All runs were started at a bath temperature of 25 C. After a steady-state reading was obtained from the IR unit recorder, the next temperature steps, where required, (45 and 65 C) were sequentially established. Following the 65 C reading, the IR unit zero reading was rechecked

using prepurified nitrogen in the bypass. The sample was removed, weighed, and stored for later tests. About 18 hr were required for three steady-state readings plus calibration.

#### Permeability measurements

1. *Equipment*: The equipment used to determine gas permeability of both air- and solvent-dried samples included a cylinder of compressed nitrogen, adjustable pressure regulator, sample holder, flowmeters, and pressure gages for atmospheric and differential pressure. The sample holder was similar to the one used for diffusion measurements. Appropriate high and low flow-rate rotameters were used for solvent- and air-dried samples. Atmospheric and regulator pressure and flow rate were recorded.

2. *Procedure*: The sample was sealed in the holder and super-atmospheric pressure was applied to one end, with the other at atmospheric pressure. The steady-state flow rate was found from the rotameter, which was at atmospheric pressure. In each test, the pressure difference ( $\Delta p$ ) was about 1 atm for a mean pressure ( $\bar{p}$ ) of 1.5 atm along the sample. Additional tests were also run at several  $\Delta p$  for air-dried samples to correct for slip flow.

### DATA ANALYSIS AND RESULTS

#### Diffusion

1. *Diffusion coefficient*: The steady-state solution to Fick's First Law was used to determine the diffusion coefficient at a particular temperature:

$$D = \frac{\dot{m}l}{A\Delta c} \quad (2)$$

where  $D$  = diffusion coefficient ( $\text{cm}^2/\text{sec}$ )  
 $\dot{m}$  = rate of ethane mass flow ( $\text{g}/\text{sec}$ )  
 $l$  = sample length ( $\text{cm}$ )  
 $A$  = sample area ( $\text{cm}^2$ )  
 $\Delta c$  = concentration difference of ethane ( $\text{g}/\text{cm}^3$ ).

The output side of the diffusion cell was at 0% concentration of ethane, giving

$\Delta c = c$ , the mixture concentration on the input side.

The samples were directly measured for  $A$  and  $l$ . The mass flow rate was determined from the volumetric flow, gas density, and gas concentration. The input mixture was certified to  $\pm 2\%$  component accuracy by the gas supplier. Output mixture concentration reading by the IR unit was considered to be as accurate as the calibration gas, also of  $\pm 2\%$  component accuracy. The absolute concentration accuracy was under  $\pm 0.5\%$  for all conditions. Probable system error, based on RMS error analysis, was  $\pm 3\%$ , excluding sample dimension errors.

The diffusion coefficient values obtained at 25 C are given in Table 3. Mean values for air-dried and solvent-dried samples were significantly different at the 0.01 level.

2. *Temperature coefficient*: The temperature coefficient,  $n$ , may be determined from the bulk diffusion equation (Eq. 1) by plotting  $\ln(D_i/D_o)$  vs.  $\ln(T_i/T_o)$  and obtaining the slope ( $n$ ). Any convenient reference temperature may be used as  $T_o$ . The mean temperature coefficient,  $n$ , of the air-dried samples was obtained by covariance analysis using the following model:

$$y_{ij} = u + \delta_i + ax_{ij} + \epsilon_{ij} \quad (3)$$

where  $i$  = sample number  
 $j$  = temperature level  
 $\delta_i$  = effect of sample  $i$  for all temperature levels  
 $\epsilon_{ij}$  = error term for  $x_{ij}$   
 $x_{ij} = \ln(T_j/273)$   
 $y_{ij} = \ln D_{ij} - \ln(P_j/760)$   
 $a = n$ .

In the model,  $a$  represents the temperature effect on diffusion after adjustment for sample variation. A unique least-squares solution exists for  $\hat{a}$ , whereas the value of  $\delta_i$  is not unique. The effect of the temperature range on diffusion was measured without interruption to minimize the variation that could occur in system, especially from pressure differences. A statistical analysis of the data collected on four samples over the range of 20 to 65 C showed that a com-

TABLE 3. Permeability and diffusion values for air-dried and solvent-dried eastern hemlock.

Sample condition	No. samples	Permeability constant ( $10^{-10}$ cm <sup>2</sup> )	Diffusion coefficient ( $10^{-2}$ cm <sup>2</sup> /sec)	Effective radius ( $\mu$ m)
Air-dried	17	1.24 <sup>a</sup> (0.31) <sup>b</sup>	2.24 (0.31)	0.140 (0.037)
Solvent-dried	20	353 (130)	6.26 (1.02)	----

<sup>a</sup>Mean.<sup>b</sup>Standard deviation.

binned data analysis was much more meaningful than individual regression analyses. Using this method of analysis, the estimated value of  $n$  was 0.607 (standard deviation = 0.0518,  $r^2 = 0.993$ ).

3. *Sample variables*: Simple linear regression techniques were used to determine if significant differences existed between diffusion coefficients from tree (2), height level (3), quadrant (4), drying method (2), and oven-dry density (0.42 to 0.50). Only the drying method produced a significant difference at the 0.05 level.

### Permeability

1. *Permeability constant*: The solution of Darcy's law for compressible fluids was used to obtain the "superficial gas permeability constant,"  $K_g$ :

$$K_g = \frac{\dot{V}l\eta p}{A\Delta p\bar{p}} \quad (4)$$

where  $\dot{V}$  = flow rate (cm<sup>3</sup>/sec)  
 $l$  = sample length (cm)  
 $A$  = sample area (cm<sup>2</sup>)  
 $\eta$  = viscosity of gas (poise)  
 $p$  = pressure at  $\dot{V}$  (dyne/cm<sup>2</sup>)  
 $\Delta p$  = pressure drop over  $l$  (dyne/cm<sup>2</sup>)  
 $\bar{p}$  = mean pressure over  $l$  (dyne/cm<sup>2</sup>).

The units of  $K_g$  are cm<sup>2</sup> when cgs units are used. In SI units,  $K_g$  is in m<sup>2</sup>. Such consistent units are preferable to "darcys," which are derived from mixed units. Some authors have used "darcys" because of the convenience of using integer or unity values for some of the variables under certain ex-

perimental conditions. However, there are at least three different unit combinations in the literature either designated or interpretable as "darcys." It is also possible to find research reports with undefined "darcys." The most commonly used "darcy" for wood (cm<sup>2</sup>-cp/atm-sec) is related to consistent cgs units by:

$$1 \text{ darcy} = 9.87 \times 10^{-9} \text{ cm}^2 \approx 10^{-8} \text{ cm}^2$$

The permeability constant in Eq. 4 has, in some earlier literature, been referred to as "specific permeability," but this term is rarely used in current literature.

The true gas permeability may be determined from the Klinkenberg equation:

$$K_g = K \left(1 + \frac{b}{\bar{p}}\right) \quad (5)$$

by plotting  $K_g$  vs  $1/\bar{p}$  and obtaining the intercept,  $K$ .

The mean values of permeability constant for each group of samples are given in Table 3. For the solvent-dried samples,  $K = K_g$  (constant slope); however, it was necessary to determine  $K$  of the air-dried samples by the extrapolated intercept of the linear regression equation that related  $K_g$  to  $1/\bar{p}$ . A mean pressure range of 1.7 to 3.0 atm was obtained by maintaining the outlet pressure at 1 atm and increasing the inlet pressure by adjusting the nitrogen gas regulator.

2. *Effective pore size*. After the true gas permeability,  $K$ , is found, the slope of the Klinkenberg equation,  $Kb$ , may be defined for a:

$$b = \frac{4c\lambda\bar{p}}{r} \quad (6)$$

where  $c$  = dimensionless constant normally set to unity  
 $= \gamma$  mean free path of gas (m)  
 $\bar{p}$  = mean pressure (dyne/cm<sup>2</sup>)  
 $r$  = effective pore radius (m).

Since the measurements were made at 25 C (T = 298) and with N<sub>2</sub> (M = 28),

$$r = \frac{0.268}{b} \quad (7)$$

the units of  $a$  are dynes/cm<sup>2</sup> to obtain the effective pore radius,  $r$ , in m.

The calculated pore radii for air-dried samples (Table 3) had a range of about 0.1 to 0.2  $\mu$ m. There was no significant relationship between diffusion or permeability and the pore size. This was probably a consequence of the very limited permeability range of the air-dried samples. Effective radii could not be calculated for solvent-dried samples using the Klinkenberg equation because the flow was viscous and not within the slip flow region.

3. *Sample variables*: The sample variables for which the true permeability constant was regressed were oven-dry density (0.4 to 0.5) tree (2), height level (3), quadrant (4), and drying method (2). Density was tested to determine if the area term in the Darcy equation was related to porosity as defined by density. There was no significant relationship between the permeability constant and oven-dry density for either air-dried or solvent-dried samples. No significant relationship was found with respect to tree, height, or quadrant. Drying method produced a highly significant difference (0.01 level).

#### DISCUSSION

##### *Diffusion*

1. *Diffusion coefficient*: The concepts applied to porous media (Carman 1956) appear to be useful in analyzing diffusion in wood. In porous media, the conductivity ratio,  $J$ , is defined as:

$$J = \frac{\epsilon}{\tau} \quad (8)$$

where  $\epsilon$  is the porosity of the wood which is related to oven-dry density,  $d_o$ , by:

$$\epsilon = 1 - \frac{d_o}{d_{ws}} \quad (9)$$

where  $d_{ws}$  is the wood substance density ( $d_{ws} = 1.46$ ). Tortuosity,  $\tau$ , is an indicator of the effective diffusion path length.

It is interesting to analyze the longitudinal CO<sub>2</sub> diffusion data of Tarkow and Stamm (1960a) in this context. The porosity,  $\epsilon$ , of Sitka spruce can be calculated as 0.71. If we assume the tortuosity to be unity (no lateral diffusion), then the relative conductivity ratio,  $J$ , is 0.71. The predicted diffusion coefficient would then be 0.71 times the bulk diffusion coefficient of 0.17, or 0.12. Since the observed value was 0.11, this porous media approach appears justifiable.

We can also calculate the effective tortuosity from porosity and the observed ( $D'_{CO_2}$ ) and free ( $D_{CO_2}$ ) diffusion coefficients using the equation:

$$\frac{\epsilon}{\tau} = \frac{D'_{CO_2}}{D_{CO_2}} \quad (10)$$

In this case  $\tau = 1.1$ , indicating that the effective diffusion path was only about 10% greater than the physical length of the sample. It would appear that the uniform anatomy of such a species lends itself well to porous media analyses.

From Elers' (1965) data for longitudinal diffusion in eastern hemlock, the tortuosity is 4.37. The same species in this study in the air-dried condition had a calculated tortuosity of 4.16, within about 5% of the value determined from Elers' data.

Solvent-dried samples in this study had an average tortuosity of 1.75, indicating substantial deviation from ideal behavior, or unity tortuosity. Hindered paths could have possibly been caused by partial aspiration in the solvent exchange process. Calculations of tortuosity of different species could provide useful information relating to the type of wood cells involved in diffusion and the presence of blind cavities.

2. *Temperature coefficient*: The average value of the temperature coefficient for air-dried eastern hemlock was about 0.6.



Slip flow is bounded by temperature coefficients of 0.5 for Knudsen diffusion and 1.5 for molecular diffusion, also corresponding to effective openings with radii of 0.01 to 1  $\mu\text{m}$ . The effective radii calculated from permeability data for the four samples used in determination of the temperature coefficient ranged from 0.14 to 0.18  $\mu\text{m}$ . Assuming that the temperature coefficient in the slip flow region varies linearly with the size of openings, a calculated coefficient for these samples would be about 0.66, only 10% greater than the observed value in this study. In freshly aspirated eastern hemlock, Knudsen flow predominates.

The temperature coefficient in Elers' (1965) data for tangential diffusion decreased between 50 and 70 C. A point-to-point calculation from Elers' data gave an average value of about 0.9 for  $n$  in comparison with the given value of 1.68 over 5 to 50 C. However, the longitudinal and radial temperature coefficients increased in the range of 50 to 70 C. Calculated longitudinal values ranged from 1.8 to 4.2, and radial values from 1.1 to 2.0. It could be anticipated that an increase in temperature would cause a decrease in diffusion flux since the mean free path of the gas increases. However, a decrease in diffusion coefficient, if caused by a shift toward Knudsen flow, should also show a decrease in temperature coefficient toward the limiting value of 0.5. The temperature coefficient of 1.68 for longitudinal and tangential diffusion indicates that the smaller diffusion coefficient value (0.01 of longitudinal value) is a result of the number rather than nature of pit membranes crossed. The lower temperature coefficient of radial diffusion indicated that the diffusion was more hindered even though the radial and tangential diffusion coefficients were similar. Perhaps the series earlywood-latewood arrangement is responsible for more hindered diffusion in the radial direction.

If we consider the tangential temperature coefficient ( $\bar{n} \approx 2$ ) calculated from the published data (Tarkow and Stamm 1960a) to indicate essentially bulk diffusion, then the proposition that Knudsen diffusion ( $n =$

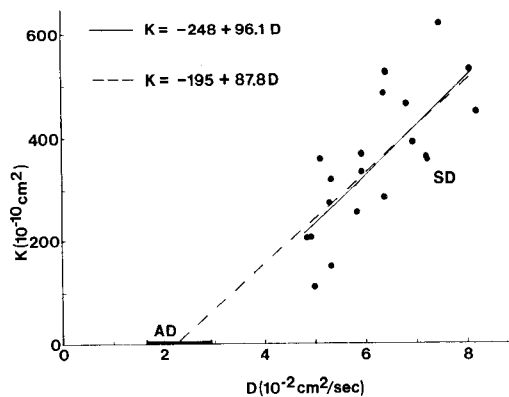


FIG. 2. Relationship between longitudinal permeability constant ( $K$ ) and diffusion coefficient ( $D$ ) for 20 solvent-dried (SD) and 17 air-dried (AD) eastern hemlock samples. Permeability range of AD samples ( $y$ -axis) is 0.9 to 1.9.

0.5) was occurring through pit membranes and reducing the diffusion coefficient appears unreasonable. Also, the assumed effective pore radius of the Sitka spruce margo of 0.03  $\mu\text{m}$  (compared with the 0.06  $\mu\text{m}$  mean free path of  $\text{CO}_2$ ) seems about an order of magnitude too small.

#### *Relationships of permeability and diffusion*

The agreement between effective pore radii from permeability data and the temperature coefficient from diffusion data implies that other possible interrelationships may exist. Prediction of diffusion behavior from permeability information would be a distinct advantage, since diffusion equipment and data acquisition are much more complex. Plots of permeability vs. diffusion were made for air-dried, solvent-dried, and combined samples types. No significant relationship existed between  $K$  and  $D$  for the air-dried samples, probably because of the very limited variation of each (Fig. 2). However, solvent-dried samples had a linear relationship:

$$K = -248 + 96.1 D \quad (11)$$

$$(r^2 = 0.55, s = 89.4)$$

where the units of  $D$  are  $10^{-2} \text{ cm}^2/\text{sec}$  and for  $K$ ,  $10^{-10} \text{ cm}^2$ . When the air-dried and

solvent-dried data were combined in a plot of  $K$  vs.  $D$ , the following linear regression line was obtained (Fig. 2):

$$K = -195 + 87.8 D \quad (12)$$

$$(r^2 = 0.893, s = 67.1)$$

The relatively small difference (about 10%) in slope between Eqs. 11 and 12 supports at least a heuristic linear relationship between diffusion and permeability over a wide experimental range. A plot of residuals for this equation, however, shows a poor relationship between predicted and observed air-dried values since the permeability values are essentially constant.

#### CONCLUSIONS AND RECOMMENDATIONS

The IR technique used for detection of diffused ethane worked satisfactorily for air-dried samples in all respects. However, it was not possible to obtain temperature coefficients for solvent-dried samples because of large variations caused by a very small differential pressure across the diffusion cell. Any detection method that is integrative rather than instantaneous could give even more erroneous results unless the differential cell pressure is continually nulled.

The temperature coefficient of diffusion between 20 and 65 C was 0.6, indicating Knudsen diffusion as the controlling mechanism. Effective pore openings obtained from permeability measurements and the Klinkenberg equation confirmed that diffusion was occurring in the Knudsen end of the slip-flow region. Since the bordered pits were assumed to be aspirated, openings of about 0.1 to 0.2  $\mu\text{m}$  existed between the torus and pit border. The particular temperature coefficient of diffusion can be used to separate effects of size and number of pore openings, which cannot be resolved from diffusion measurements at a single temperature.

Diffusion through solvent-exchanged samples was about 40% of the free diffusion coefficient; the air-dried diffusion coefficient was reduced to 16% of the free value. On the basis of hindered diffusion, the tortuosity of solvent-dried eastern hem-

lock was 1.75, indicating substantial transverse diffusion. Air-dried tortuosity, 4.4, was within 5% of the calculated value from a previous study using eastern hemlock. Determinations of tortuosity for different wood species could help clarify the ineffective pore volume and/or transverse diffusion. Tortuosity values may indicate the degree of aspiration from solvent-exchanged samples. In this regard, the 1.75 value obtained from the acetone-benzene sequence may not be the tortuosity limit for eastern hemlock.

The linear relationship found between diffusion and permeability needs confirmation for other species and conditions. Permeability data are much simpler to acquire, permitting better estimates of the diffusion of vapors through wood. It appears that the IR detection principle for diffusion could be extended to longitudinal or transverse permeability measurements by using a simple permeability cell. It would be especially advantageous for species having very low transverse permeability. In the case of hardwoods, it should be possible to confirm that activated diffusion occurs through pit membrane pores that have not been detected microscopically.

*Author's note:* After acceptance of this paper, a closely related paper was published: Petty, J. A. 1973. Diffusion of non-swelling gases through dry conifer wood. *Wood Sci. Technol.* 7:297-307.

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