Wood Sci. Technol. 15: 105–112 (1981)

Wood Science
and Technology

Thermal Diffusion of Bound Water in Wood

Ch. Skaar

Department of Forest Products, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA

J. F. Siau

Department of Wood Products Engineering, SUNY College of Environmental Science and Forestry, Syracuse, New York, USA

Summary. There are few references in the wood science literature to nonisothermal moisture movement. Some experiments by Voight, Babbitt, and Choong indicate that thermal diffusion in wood may be very significant.

Three equations are presented to represent nonisothermal moisture movement through wood in the transverse direction. The first, described in detail in a previous paper, is based upon two driving forces: Soret potential which results in thermal diffusion and chemical potential which results from a gradient of equilibrium relative humidity. All three equations include the same term for Soret potential and, in the second two equations, the thermal-diffusion term was derived by the application of activation theory. The isothermal term in these two equations utilizes moisture content gradient as the driving force and therefore a knowledge of the sorption isotherm is not necessary. The third equation contains an additional term for moisture-content activation to account for the increase in flux with an increased moisture content. All three equations give approximately the same result with the same input data at low moisture contents. The results diverge at high moisture contents and experimental data are required to determine which equation is most representative of the physical phenomenon of nonisothermal moisture movement.

Results and Discussion

There is a conspicuous absence in the wood science literature of references to thermal diffusion of water through wood. Siau (1971) has pointed out that transverse moisture diffusion through wood below the fiber-saturation point is controlled essentially by diffusion through the cell wall. This paper will be limited to consideration of the thermal diffusion of bound water through the cell wall of wood under a combined moisture and temperature gradient. A general discussion of the phenomenon of thermal diffusion in wood will be given first. This will be followed by the derivation of an equation for calculating the magnitude of thermal diffusion for the movement of bound or hygroscopic water through the cell wall of wood.

0043-7719/0015/0105/$ 1.60

Some insight into the importance of thermal diffusion in wood is provided by the nonisothermal experiments of Babbitt (1940), Voight et al. (1940), and Choong (1963). Babbitt studied fiber board rather than wood. His results, therefore, are not typical of wood due to the presence in fiber board of continuous openings in which gaseous diffusion would dominate. He found a significant flux with a temperature difference of 10 °C and with small gradients of relative humidity and moisture content. In Babbitt's experiment, bound water movement is expected to be negligible and thermal diffusion of gases should be dominant. Such diffusion is discussed by de Groot (1951), Katchalsky (1965), and Jost (1960). Generally, the activation energy has a low value in intergas diffusion.

The results of Voight, et al. and of Choong were discussed by Siau (1980). These experiments were carried out with relatively steep thermal gradients of approximately 10 °C/cm, and the specimens were encapsulated to prevent the entry or removal of moisture. Slicing of the specimens after equilibrium was achieved indicated the presence of a water vapor pressure gradient, although the net flux was zero. Bramhall (1979) modified Choong's data to account for sorption hysteresis, but even with this modification there were distinct vapor pressure gradients in all cases for transverse movement.

Siau (1980) proposed an equation based upon one given by Briggs (1967), in which Soret potential (causing thermal diffusion) and chemical potential (resulting from gradients of water vapor pressure) are assumed to be the two driving forces. The resulting equation is reproduced here in modified form:

$$J = K_b \frac{dM}{d\mu} \left[\frac{Q^*}{T} \frac{dT}{dx} + \frac{d\mu}{dx} \right] \tag{1}$$

Where: J = flux (g water/cm^2 · s)
K_b = Moisture conductivity coefficient of the cell wall (g water/cm · s %), a function of M and T, as well as of sorption history.
M = percent moisture content, based on oven-dry weight of wood.
T = temperature in Kelvin degrees
μ = chemical potential (cal/mole water)
Q^* = thermal heat of transfer (cal/mole water)
x = distance in direction of flux (cm)

Siau (1980) applied Eq. (1) to the results of Voight et al. (1940) and of Choong (1963), under conditions such that the net flux J was zero. By equating the gradients of Soret potential ($(Q^*/T)(dT/dx)$) and chemical potential ($d\mu/dx$), he calculated Q^*. The calculated values of Q^* were in reasonable agreement with the activation energy for transverse water-vapor movement through wood, as determined by Choong (1963) and Stamm (1962). It was also shown by Siau (1980) that, according to the theory of Briggs (1967), the thermal heat of transfer Q^* should equal the activation energy E_b for bound-water diffusion, assuming that the latter was the controlling factor for transverse water diffusion through the gross wood used in the experiments of Voight et al., and of Choong.

In order to derive Eq. (1), it is convenient to consider the diagram shown in Fig. 1, adapted from Skaar (1972). This shows the relative energy state of water in the cell wall of wood (bound water) as a function of wood moisture content under isothermal conditions, compared with the energy states of water vapor and of liquid water. Bound water has the lowest state, increasing with wood moisture content and reaching essentially the same state as liquid water at or above the fiber-saturation point.

The terms E_0 and E_v refer to the additional energy in calories which must be supplied to evaporate a mole of liquid water (E_0) or bound water (E_v). According to this diagram, bound water is held at sorption sites in the cell wall at energy levels lower than for liquid water. The difference $E_v - E_0$) is designated as E_L. Under isothermal conditions, bound water tends to move toward regions of lower moisture content because the chemical potential μ or free energy decreases with decreasing relative vapor pressure. In the model used in this derivation, it is assumed that the rate of bound water movement is governed by an activation process. In other words, a bound water molecule can move only if it receives sufficient kinetic energy to escape from its sorption site and become an activated molecule. In this case, it tends to move to another sorption site of lower potential energy, that is to a region of lower moisture potential where it gives up the kinetic energy.

The activation energy for bound water diffusion, designated here as E_b, is expected to be somewhere between E_L and E_v (Fig. 1). Choong (1963) and Stamm (1964) give activation energies of approximately 8,500 calories per mole at 10 percent moisture content based on application of the Arrhenius rate equation to moisture diffusion. Bramhall (1979) contends that the actual value is higher.

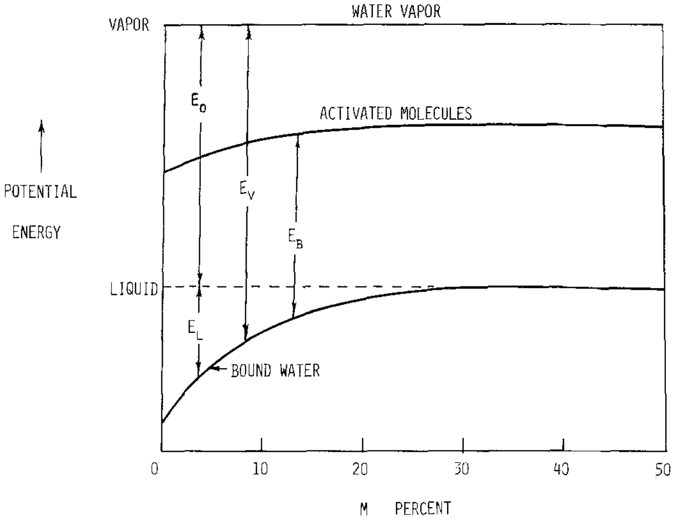

Fig. 1. Schematic diagram showing the relative energy levels of water in vapor, liquid, and bound water form as related to wood moisture content. Also shown is a hypothetical curve for activated molecules in the cell wall

Figure 1 includes a hypothetical curve showing how E_b might vary with wood moisture content. It is expected to increase with decreasing wood moisture content, as is indicated later in this paper. At the fiber-saturation point, it should approach as a lower limit the activation energy required for a molecule of liquid water to break away from a cluster of other liquid water molecules. This activation energy is approximately 4,000 calories per mole of water, as calculated from the variation of the viscosity of water as a function of temperature. However, Jost (1960, p. 295) gives a value of 5,300 cal/mole for the self-diffusion of water through water. In Stamm's (1946) early model for calculating the bound water diffusion coefficient for the cell wall of wood, he used the Einstein diffusion equation, which includes the viscosity of the water as a temperature variable. The increase with temperature of the cell wall diffusion coefficient as calculated by Stamm was caused primarily by the decrease of water viscosity with increasing temperature, an Arrhenius or activation type of process.

Equation (1) can be derived in terms of moisture content M or moisture concentration C (g water/cm^3 wood). Since Eq. (1) is given in terms of M, this notation will be used here. The moisture conductivity coefficient K_b in bound water movement may be written in terms of the Arrhenius equation in the form:

$$K_b = B \exp(-E_b/RT) \tag{2}$$

where K_b is the bound-water conductivity coefficient, B is a constant, and R is the gas constant (cal/mole-deg).

The flux J of bound-water may be considered to be proportional to the gradient of activated molecules. That is

$$J = -A_0\,(dM^*/dx) \tag{3}$$

where A_0 is a constant, assumed to be independent of M and T, and M^* is the content of activated water molecules (% of dry weight) in the cell wall. This can be calculated from the Boltzmann distribution equation in the form,

$$M^* = M \exp(-E_b/RT) \tag{4}$$

In general, the gradient dM^*/dx is a function of both M and T. Thus,

$$dM^*/dx = [(\partial M^*/\partial T)(dT/dx) + (\partial M^*/\partial M)(dM/dx)] \tag{5}$$

Eq. (3) then becomes,

$$J = -A_0[(\partial M^*/\partial T)(dT/dx) + (\partial M^*/\partial M)(dM/dx)] \tag{6}$$

Taking $\partial M^*/\partial T$ and $\partial M^*/\partial M$ in Eq. (4) gives

$$\partial M^*/\partial T = (ME_b/RT^2)\exp(-E_b/RT) \tag{7}$$

$$\partial M^*/\partial M = [1 - (E/RT)(\partial E_b/\partial M]\exp(-E_b/RT) \tag{8}$$

assuming that E_b is a function of M, but constant with T. Substituting (7) and (8) into (6) and simplifying gives,

$$J = -\frac{A_0 M^*}{RT}\left[\frac{E_b}{T}\frac{dT}{dx} + \left(\frac{RT}{M} - \frac{\partial E_b}{\partial M}\right)\frac{dM}{dx}\right] \tag{9}$$

The conductivity coefficient K_b may be defined for the isothermal case by

$$J = -K_b\,(dM/dx) \tag{10}$$

Comparing (9) and (10) for the isothermal case ($dT/dx = 0$), it is evident that,

$$K_b = \frac{A_0 M^*}{RT}\left(\frac{RT}{M} - \frac{\partial E_b}{\partial M}\right) \tag{11}$$

Equation (9) may then be rewritten as

$$J = -\frac{K_b M}{(RT - M\partial E_b/\partial M)}\left[\frac{E_b}{T}\frac{dT}{dx} + \left(\frac{RT - M(\partial E_b/\partial M)}{M}\right)\frac{dM}{dx}\right] \tag{12}$$

Equation (1) can be obtained from (12) if two simplifying assumptions are made. The first of these is that E_b is independent of moisture content M, that is, $\partial E_b/\partial M = 0$. In this case, Eq. (12) becomes,

$$J = -\frac{K_b M}{RT}\left[\frac{E_b}{T}\frac{dT}{dx} + \frac{RT}{M}\frac{dM}{dx}\right] \tag{13}$$

The second assumption is that the sorption isotherm is linear, that is that $M = kh$, where h is the relative vapor pressure and k is a constant. With this assumption, the term RT/M in Eq. (13) can be shown to be equivalent to $\partial\mu/\partial M$, where μ is the chemical potential. This can be shown by recalling that, for the isothermal case,

$$\partial\mu/\partial M = RT\,\partial \ln h/\partial M = (RT/h)\,(\partial h/\partial M) \tag{14}$$

since $h = M/k$, and $\partial h/\partial M = 1/k$ for a linear sorption isotherm,

$$\partial\mu/\partial M = RT/M \tag{15}$$

and Eq. (13) reduces to Eq. (1) when E_b is taken to be equivalent to Q^*.

Stamm (1962) and Choong (1963) found an activation energy of 8500 cal/mole at a moisture content of approximately 10 percent. Choong (1962) presents evidence that the activation energy increases as the moisture content is reduced. This would be expected because Skaar (1972) shows that both the heat of vaporization of bound water (E_v) and the differential heat of sorption (E_L) increase as the moisture content is reduced.

Stamm (1959) measured the moisture diffusion coefficient of cell-wall substance at 26.7 °C at moisture contents up to 28 percent. His results are reproduced in Fig. 2. There is a rapid increase with moisture content which can be explained by a decreased

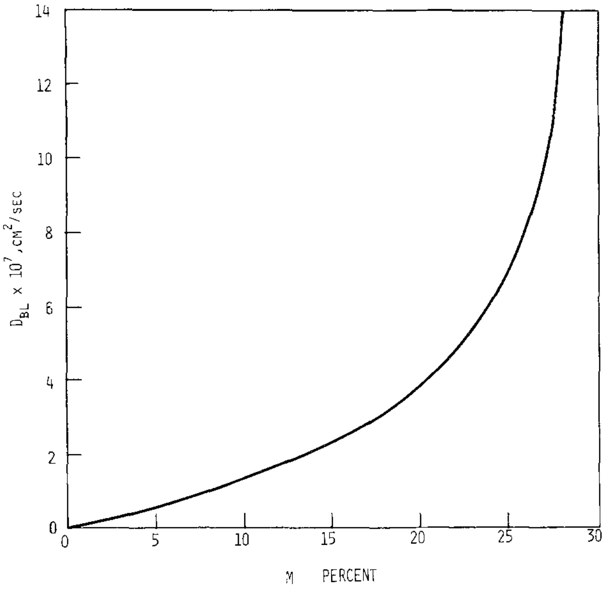

Fig. 2. Longitudinal bound-water diffusion coefficient (D_{BL}) of the cell-wall substance of Sitka spruce at 26.7 °C as a function of average moisture content according to Stamm (1959). Adapted from Siau (1971)

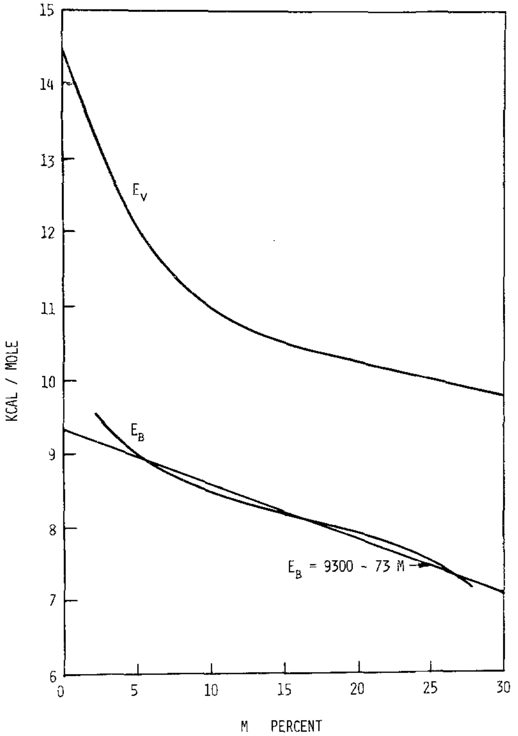

Fig. 3. The heat of vaporization of bound water in wood (E_v) and the activation energy for bound-water diffusion (E_b) as calculated from the data of Stamm (1959) using the Arrhenius equation and assuming a value of 8500 cal/mole at a moisture content of 10 percent. Also shown is a linear approximation as stated in Eq. (16)

bonding energy with moisture content which, in turn, can be attributed to a decreased activation energy. When Stamm's values of diffusion coefficient are fitted to Eq. (2), assuming a value of 8500 cal/mole at M = 10%, the calculated values of activation energy (E_b) extend from 9500 cal/mole at M = 2% to 7100 cal/mole at M = 28%. The relationship is slightly curvilinear as revealed in Fig. 3. This curvilinear function may be approximated by a linear equation as follows:

$$E_b = 9300 - 73\,M \tag{16}$$

where E_b is expressed in cal/mole.

When E_b from (16) and $\partial E_b/\partial M = -73$ are substituted into Eq. (12) it becomes,

$$J = -\frac{K_b M}{(RT + 73\,M)}\left[\frac{(9300 - 73\,M)}{T}\frac{dT}{dx} + \left(\frac{RT + 73\,M}{M}\right)\frac{dM}{dx}\right] \tag{17}$$

Conclusions

In summary, Eq. (1), (13) and (17) are presented for calculating non-isothermal moisture movement in wood. All three contain identical terms for the Soret potential, $(E_b/T)\,(dT/dx)$, where the activation energy E_b for bound-water diffusion is assumed to be identical with Q^*, the thermal heat of transfer of Eq. (1). The most general equation in terms of moisture content gradients is Eq. (17). This reduces to Eq. (13) if activation energy E_b is constant with moisture content. It reduces further to Eq. (1) if a linear sorption isotherm is also assumed. All three equations will give approximately equal results at low moisture contents (up to 5 percent). Beyond that value, the results diverge with the coefficients decreasing in value when changing from Eq. (1) to (13) to (17). These decreasing coefficients have the effect of diminishing the relative significance of the thermal diffusion term. The question as to which equation is most representative of the actual phenomenon must be determined experimentally. If E_b is equal to E_v, the contention of Bramhall (1979) that the fundamental driving force is the water vapor pressure gradient, is a reasonable approximation.

References

Babbitt, J. D. 1940: Observations on the permeability of hygroscopic materials to water vapour. Can. J. Res. 18-A (6): 105–121

Bramhall, G. 1979: Sorption diffusion in wood. Wood Sci. Technol. 12 (1): 3–13

Briggs, G. E. 1967: Movements of water in plants. Botanical Monographs. Vol. 7. Davis. Philadelphia. Ch. 1, 2

Choong, E. T. 1962: Movement of moisture through softwood in the hygroscopic range. Ph. D. Thesis. SUNY College of Environmental Science and Forestry, Syracuse, N. Y.

Choong, E. T. 1963: Movement of moisture through a softwood in the hygroscopic range. For. Prod. J. 13 (11): 489–498

de Groot, S. R. 1951: Thermodynamics of Irreversible Gases. North-Holland Publishing Company. Amsterdam. Interscience Publications Inc., New York.

Jost, W. 1960: Diffusion of Solids, Liquids, and Gases. Academic Press. New York

Katchalsky, A.; Curran, P. F. 1965: Nonequilibrium Thermodynamics in Biophysics. Harvard University Press, Cambridge, Mass.

Siau, J. F. 1980: Nonisothermal moisture movement in wood. Wood Sci. 13: 11–13

Skaar, C. 1972: Water in wood. Syracuse University Press; Syracuse, Ch. 4

Stamm, A. J. 1946: Passage of liquids, vapors, and dissolved materials through softwoods. Tech. Bull. No. 929. U.S. Dept. Agr. Washington, D.C.

Stamm, A. J. 1959: Bound-water diffusion into wood in the fiber direction. For. Prod. J. 9 (1): 27–31

Voight, H.; Krischer, O.; Schaus, H. 1940: Die Feuchtigkeitsbewegung bei der Verdunstungstrocknung von Holz. Holz Roh Werkstoff 3 (10): 305–321

(Received May 21, 1980)

Dr. Ch. Skaar
Department of Forest Products
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061, USA
Dr. J. F. Siau
Department of Wood Products Engineering
SUNY College of Environmental Science and Forestry
Syracuse, New York 13210, USA