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**Nonisothermal Moisture Transport in Wood**

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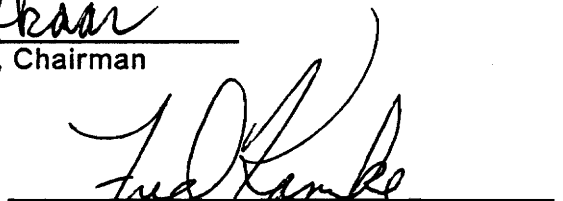
Perry N. Peralta

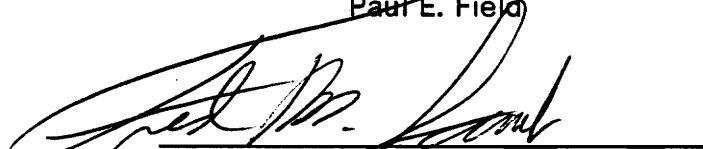
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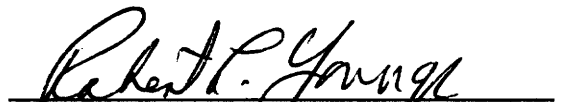
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## Nonisothermal Moisture Transport in Wood

by

Perry N. Peralta

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Wood Science and Forest Products

(ABSTRACT)

The primary purpose of this study was to measure experimentally the uniaxial (tangential direction) equilibrium moisture profiles in moisture-sealed wood samples subjected to constant but different temperatures  $T$  on opposite faces, and to compare these profiles with those predicted by each of several theoretical models. Each test assembly consisted of eight end-matched wood laminae, each 0.2 cm thick, for a total thickness of 1.6 cm in the tangential direction. Opposite faces of each moisture-sealed assembly were exposed continuously for approximately five weeks to different but constant temperatures until the original uniform moisture content  $M$  redistributed itself to a new constant but non-uniform moisture profile. At moisture equilibrium, the individual wood laminae were removed from the assembly and their moisture contents measured gravimetrically. Both temperature,  $T$  vs  $x$ , and moisture profiles,  $M$  vs  $x$ , where  $x$  is the distance from the cold face were plotted for each test. The experimental variables considered were wood species (yellow poplar and hard maple), initial moisture content (9%, 12%, and 15%), and temperature range (15°C to 35°C, and 25°C to 45°C). Each condition was replicated 3 or 4 times, giving a total number of 44 different tests.

At the steady state, a moisture content profile opposite to the temperature gradient was established. The temperature gradient  $\frac{dT}{dx}$  was constant in all cases, with the moisture content profile increasing almost exponentially with decreasing temperature. The absolute magnitude of the calculated ratio  $\frac{dM}{dT}$  was found to vary with initial moisture content, temperature range, and species. The Soret coefficient, defined as  $-\left(\frac{1}{M}\right)\left(\frac{dM}{dT}\right)$ , was also calculated and was found to vary with the above variables as the  $\frac{dM}{dT}$  ratio. These two quantities always increased with wood moisture content. They were also slightly higher at the higher temperature

range. There was only a small difference between species, with yellow poplar giving somewhat higher mean values. The Soret coefficient was generally in the range of 0.03 to 0.05 per degree Kelvin, except for the extremely high moisture contents near and above fiber saturation, where the calculated values approached 0.5 per degree Kelvin.

The ratio  $\frac{dM}{dT}$  was analyzed in terms of five different theoretical models, two of which are based on nonequilibrium thermodynamics (NET) and three on classical thermodynamics. All models require sorption isotherm and heat of sorption data; and in some cases, the activation energy for moisture transport through wood. Adsorption and desorption isotherm data were obtained at 30°C for both species. Heat of sorption and moisture transport activation energy data used in testing the models were taken from the literature.

The two NET models provided the best agreement with the experimental values of  $\frac{dM}{dT}$ . The Siau model gave the next best prediction, followed by the Stanish model, with the Skaar-Siau model giving the poorest agreement with the experimental results.

The heat of transfer was also computed using the two NET models as well as those of Stanish and Siau. Values ranged from 5500 to 17000  $\frac{\text{cal}}{\text{mol}}$  for the general NET model and from 8100 to 9900  $\frac{\text{cal}}{\text{mol}}$  based on the Nelson model. The corresponding values for the Stanish model range from 15200 to 16500; while those of the Siau model varied between 11700 to 13600  $\frac{\text{cal}}{\text{mol}}$ .

Calculations of other quantities from the information generated in these experiments revealed that at the steady state, vapor pressure and spreading pressure were not constant across the thickness of the material; the chemical potential of water vapor and sorbed water were equal at all points indicating local equilibrium; and that the sorbed water and water vapor entropies were more or less constant across the thickness of the sample.

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A special acknowledgement must go to my Mama, and my brothers and sisters for their constant prayers and abiding love.

Dedication: To my Papa, who would have been proud

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# Introduction

One of the major characteristics of wood is its hygroscopicity. It has a very strong affinity to moisture that slight changes in the amount of water present in the atmosphere causes it to gain or lose moisture. The interaction of wood with water is both a surface and internal phenomenon. While moisture addition to and removal from the wood occur on the surface, water must move in and out of the material during the adsorption and desorption process. The mechanism of moisture movement through wood has been extensively studied because of its importance in understanding the behavior of the material both during drying and when it is in service. Yet despite the wealth of experimental and theoretical studies devoted to it, it is neither well-characterized nor well-understood.

Most analyses of moisture transport in wood have used Fick's law for quantifying the process. The steady-state form of this law expresses the rate of water diffusion as the product of a diffusion coefficient and a driving force. However, the identification of the proper driving force has been a source of controversy for many years. Many investigators assumed that the potential which causes moisture movement is the

concentration gradient, expressed either as mass of moisture per unit volume or as mass of moisture per unit mass of dry wood. This approach was successfully applied to many moisture transport experiments, however, the diffusion coefficients obtained were strong functions of moisture content, temperature, or wood properties. Other researchers suggested that a gradient of a more fundamental potential than concentration is involved and proposed such driving forces as gradient in vapor pressure, spreading pressure, chemical potential, concentration of activated moisture molecules, and osmotic pressure as the actual potential.

The controversy over the driving force also led to a consideration of the nonisothermal moisture transfer through wood. Some investigators proposed that provided the driving force is properly identified, an equation of the form of Fick's law can quantitatively describe moisture movement in wood for both the isothermal and nonisothermal conditions. Subsequent studies, however, have proven that this is not true. Fick's law was shown to be inadequate in quantifying moisture movement in wood subjected to a temperature gradient.

In most drying processes and when wood is in service, temperature as well as moisture content gradients are present in the material and, therefore, it is important to consider moisture flow under the influence of both these gradients. It is widely recognized that a gradient of temperature can cause mass movement, while conversely a concentration gradient can cause the transfer of heat. This coupling between the flow of heat and the flow of mass has been demonstrated to occur in many systems, particularly the thermal diffusion or Soret effect which is defined as the transport of mass in the direction of decreasing temperature even in the absence of a concentration gradient. A number of studies have also confirmed the occurrence

of the Soret effect in wood, these studies showing that water can move through wood in the reverse direction to the moisture gradient under the influence of a reverse temperature gradient of sufficient magnitude.

Several theoretical models have been proposed to quantify coupled heat and mass transport through wood under nonisothermal conditions. One approach involves the principles of nonequilibrium thermodynamics (NET), a branch of macroscopic physics dealing with irreversible phenomena. This methodology has found applications in the treatment of many coupled phenomena such as thermoelectricity, electrokinetics, thermoosmosis, galvanomagnetism, and other irreversible processes of greater or lesser complexity. It has been used extensively in the analysis of thermal diffusion in biological membranes, soil, and other porous media; and, therefore, should also find important application in moisture movement in wood subjected to a temperature gradient.

The NET treatment proves to be a very elegant solution, but it is not the only available tool for the treatment of thermal diffusion in wood. Over the years several theoretical solutions to the problem of nonisothermal moisture movement in wood have been forwarded. Some of these are modifications of the NET equation while some are mechanistic in nature.

This study was conducted with the objective of measuring experimentally the uniaxial temperature and moisture content profiles in wood samples whose opposite faces were maintained at different but constant temperatures. With these experiments, a sufficiently large database was generated to calculate the appropriate transport coefficients as functions of temperature and moisture content. The parameters in the NET model were thus determined; and the applicability of several the-

oretical models which have been proposed to quantify the coupling between heat and moisture transfer through wood were evaluated.

# Theoretical Background and Review of Literature

## A. Thermodynamics of Sorption

At temperatures above the melting point of water, moisture in wood may coexist in three different forms, namely, as water vapor in the lumina and cell spaces, as free or capillary water in the cell cavities, and as bound or hygroscopic water in the cell wall. Conversion from one form of water to another involves energy changes. For instance, to evaporate free water in the cell cavities energy must be supplied to these molecules. This energy is called the molar heat of vaporization  $\Delta H_o$ . Since the vapor pressure of capillary water is lower than that of ordinary liquid water,  $\Delta H_o$  of free water is slightly higher than that of liquid water. The difference, however, is so small that it can be neglected. To evaporate bound water from the cell wall, energy equal to the molar heat of vaporization of sorbed water  $\Delta H_v$  must be supplied to the bound water molecules. Compared to the heat of vaporization,  $\Delta H_v$  is always greater by a quantity  $\Delta H_s$ , called the differential molar heat of sorption:

$$\Delta H_v = \Delta H_o + \Delta H_s \quad [1]$$

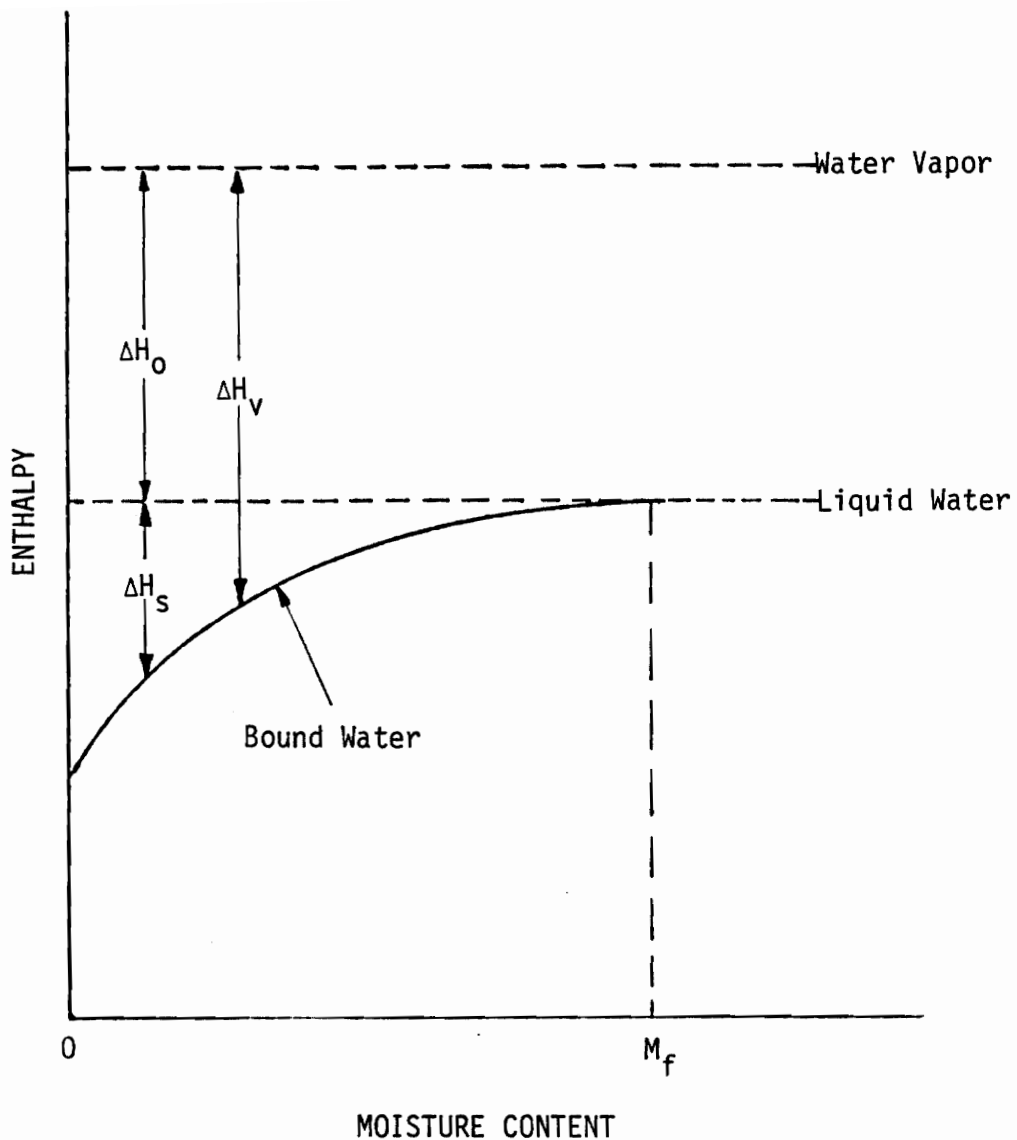
$\Delta H_b$  is thought of as the additional energy over and above that of the heat of vaporization of free water which must be supplied to evaporate water from the cell wall, and is a measure of the bond strength between the sorbed water and the wood substrate (Rees, 1960). The energy level of bound water in the cell wall depends on the moisture content of the wood since the sorbed water molecules are held with varying degrees depending on the wood moisture content. This is reflected in Figure 1 which shows a schematic diagram of the energy level of bound water  $H_b$  as a function of moisture content  $M$ , relative to those of water vapor  $H_v$  and liquid water  $H_w$ . To determine the heat of vaporization of liquid water, it is necessary to have information about the variation of the vapor pressure of liquid water with temperature and use this in the Clausius-Clapeyron equation:

$$\Delta H_o = -R \frac{d(\ln p_o)}{d(1/T)} \quad [2]$$

where  $R$  is the gas constant,  $p_o$  the vapor pressure of water, and  $T$  the Kelvin temperature. A similar approach can be taken to calculate the molar heat of vaporization of bound water. In this case, the variation of the vapor pressure of sorbed water  $p$  with temperature is needed to solve the equation:

$$\Delta H_v = -R \left[ \frac{d(\ln p)}{d(1/T)} \right]_M \quad [3]$$

The subscript  $M$  indicates that the quantity inside the bracket must be determined at a constant moisture content since the vapor pressure of sorbed water varies with  $M$ . The behavior of  $\Delta H_v$  with  $M$  can then be obtained by evaluating the above equation at different moisture content levels.



**Figure 1. Schematic diagram of enthalpy  $H$  as a function of moisture content  $M$ :**  $H_v$ ,  $H_w$ , and  $H_s$  are the enthalpies of water vapor, liquid water, and sorbed water, respectively; while  $\Delta H_v$ ,  $\Delta H_o$ , and  $\Delta H_s$  are the heat of vaporization of bound water, heat of vaporization of liquid water, and differential heat of sorption, respectively.  $M_f$  refers to the moisture content at fiber saturation point.

Since  $\Delta H_s = \Delta H_v - \Delta H_o$ , the two equations above may be combined to yield an expression for the differential molar heat of sorption:

$$\Delta H_s = -R \left[ \frac{d \left( \ln \frac{p}{p_o} \right)}{d(1/T)} \right]_M \quad [4]$$

Thus given the sorption data at two or more different temperatures,  $\Delta H_s$  can be calculated from the values of the relative vapor pressure  $h$  ( $= p/p_o$ ) and the absolute temperature  $T$  (Stamm, 1964; Skaar, 1972, 1988). Stamm and Loughborough (1935) were the first to apply the above equation to calculate the  $\Delta H_s$  of wood at different moisture contents and temperatures. Their values for Sitka spruce were in excellent agreement with experimental values for klinki pine determined by Kelsey and Clarke (1956).

The differential heat of sorption is composed of two parts, namely, the differential free energy component  $\Delta G_s$  and the differential unavailable energy component  $T\Delta S_s$ :

$$\Delta H_s = \Delta G_s + T\Delta S_s \quad [5]$$

where  $\Delta S_s$  is the differential entropy of sorption. The differential free energy of sorption which can be calculated using the equation

$$\Delta G_s = -RT \ln \left( \frac{p}{p_o} \right) \quad [6]$$

represents the energy change involved in doing work reversibly when one mole of water is taken up by wood at a given moisture content and temperature. On the other hand, the unavailable energy  $T\Delta S_s$  is interpreted as an excess energy, showing by how much the binding strength between a sorbed water molecule and the wood

substrate exceeds the energy of attraction between a water molecule and a free water surface (Rees, 1960).

Once the differential heat of sorption is known, the enthalpy of sorbed water  $H_s$  relative to the enthalpy of water at absolute zero  $H^0$  may then be determined to construct the diagram in Figure 1:

$$\Delta H_s = H_w - H_s \quad [7]$$

or

$$H_s = H_w - \Delta H_s \quad [8]$$

where  $H_w$  is the enthalpy of ordinary water at any temperature  $T$  and can be calculated relative to the enthalpy of water at absolute zero  $H^0$  by using the equation (Eisenberg and Kauzmann, 1969):

$$H_w = H^0 + \Delta H_{pc} + \int_0^T C_p dT \quad [9]$$

The symbol  $\Delta H_{pc}$  in the above equation represents the sum of all enthalpy changes for phase transitions occurring between 0 and  $T^\circ K$ . Since the temperature range of main interest here is that between the melting point and boiling point of water,  $\Delta H_{pc}$  is equal to the heat of fusion. The last term in equation (9) may be evaluated by numerically integrating the molar heat capacity at constant pressure  $C_p$  vs. temperature data for water, which can be obtained from steam tables. Thus substituting equation (9) in equation (8) results in:

$$H_s - H^0 = \Delta H_{pc} - \Delta H_s + \int_0^T C_p dT \quad [10]$$

The entropy of sorbed water  $S_s$  at temperature  $T$  relative to that of water at absolute zero  $S^0$  may be calculated as follows:

$$S_s - S^0 = \Delta S_{pc} - \Delta S_s + \int_0^T \frac{C_p}{T} dT \quad [11]$$

and by difference, the free energy of sorbed water  $G_s$  at temperature  $T$  relative to that at absolute zero  $G^0$  is given by

$$G_s - G^0 = H_s - H^0 - TS_s \quad [12]$$

where  $\Delta S_{pc}$  is the sum of entropy changes for all phase transitions occurring between 0 and  $T^\circ\text{K}$ .

## B. Isothermal Moisture Diffusion

The mathematical theory of diffusion is based on the hypothesis that the rate of transfer of the diffusing substance through a unit area of a section is proportional to the concentration gradient measured normal to the section (Crank, 1975). This theory was first forwarded by Adolf Fick in 1855 and can be expressed as follows:

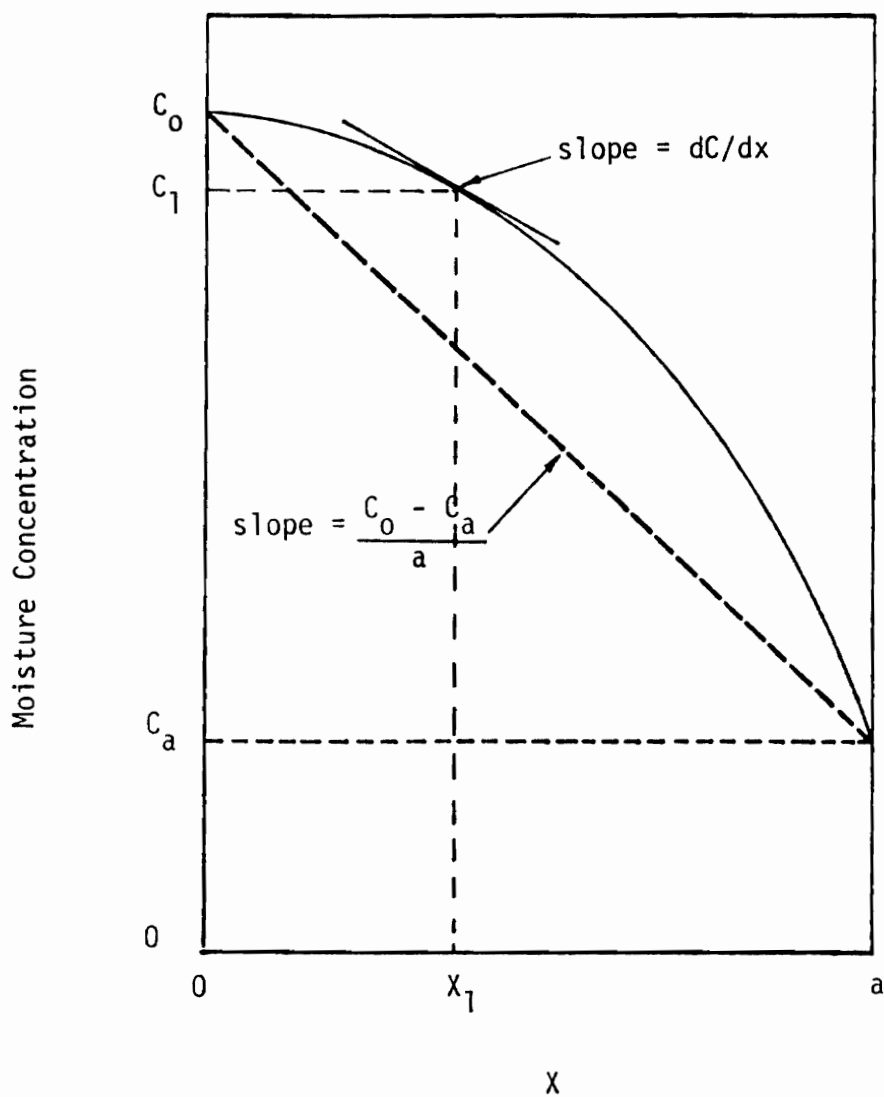
$$J = -D \frac{dC}{dx} \quad [13]$$

where  $J$  is the steady-state flux, or the rate of transfer (g/s) per unit area ( $\text{cm}^2$ ) of the section;  $D$  is the diffusion coefficient ( $\text{cm}^2/\text{s}$ ); and  $dC/dx$  is the gradient of concentration  $C$  ( $\text{g}/\text{cm}^3$ ) at the point  $x$  (cm). The negative sign in the above equation indicates that movement is in the direction of decreasing gradient.

Most of the studies of moisture movement in wood below the fiber saturation point have been based on this mathematical expression called Fick's law of diffusion. For instance, if two opposite faces of a board are subjected to different relative humidities but constant temperature and total pressure such that the equilibrium moisture concentration at each face is different, moisture will flow from the high moisture concentration side to the low concentration side. A moisture distribution will be established in the material and eventually a steady-state condition will be attained in which the rate of moisture flow through the wood is constant. If the diffusion coefficient is independent of moisture concentration, the moisture distribution will be linear and the diffusion coefficient can be calculated by dividing the product of the steady-state flux and the thickness of the material by the difference between the surface moisture concentrations. For instance referring to Figure 2, the diffusion coefficient can be obtained by dividing the moisture flux by the slope of the secant line joining the point  $(0, C_0)$  and  $(a, C_a)$ , or

$$D = \frac{J}{\frac{C_0 - C_a}{a}} \quad [14]$$

Studies, however, have shown that the diffusion coefficient of wood is a function of moisture content (Skaar, 1958; Stamm, 1960; Choong, 1965; Comstock, 1963; McNamara, 1969; Martin and Moschler, 1970). In this case moisture distribution in the material described above will not be linear, the degree of nonlinearity reflecting the



**Figure 2. Hypothetical steady-state moisture distribution curve for wood:** The slope of the curve for the case where the diffusion coefficient increases with increasing moisture concentration is shown for the location  $x_1$ ; while the mean secant slope of the curve between the concentrations at the surfaces is shown by the broken line connecting  $C_0$  and  $C_a$ .

extent of the moisture content dependence of the diffusion coefficient. Referring to the hypothetical nonlinear moisture distribution in Figure 2, the diffusion coefficient at a certain point, say  $x_1$ , is given by the ratio of the flux and the slope  $dC/dx$  of the line tangent to the curve at  $x = x_1$ :

$$(D)_{x=x_1} = - \frac{J}{\left( \frac{dC}{dx} \right)_{x=x_1}} \quad [15]$$

If the actual moisture distribution in the interior of a test sample can not be determined conveniently but the surface moisture concentrations  $C_o$  and  $C_s$  are known, the apparent or mean diffusion coefficient  $\bar{D}$  can be calculated using equation (14), where in this case the coefficient is a mean value between the values effective at the faces. The moisture concentration corresponding to this apparent diffusion coefficient is not that of the arithmetic mean of the two surface moisture concentrations (Siau, 1984b), but instead as pointed out by Stamm (1959), if the moisture concentration profile is assumed parabolic, it should be that of the moisture concentration which is two-thirds of the difference between the surface concentrations plus the moisture concentration at the surface in equilibrium with the lower relative vapor pressure.

The experimental measurement of the diffusion coefficient by the steady-state method involves the use of a vapometer or diffusion cup (Siau, 1984b). In this technique, water or a saturated salt solution is placed inside the cup to maintain the desired relative vapor pressure on one side of the wood specimen which is used to cover the mouth of the cup. By placing the assembled cup in a humidity chamber where the relative vapor pressure is constant but different from that inside the cup, a moisture concentration gradient is set up in the material causing moisture to flow. The moisture flux may be monitored by weighing the cup assembly at suitable time

intervals, a constant rate of weight change indicating steady state has been attained. The steady-state flux is then calculated as the ratio of the rate of weight change and the area of the specimen exposed to moisture movement. The details of this experiment together with the mathematical computations involved are described in the works of Skaar (1957), Choong (1962), and Comstock (1962).

In the foregoing discussion, the steady-state form of Fick's law was expressed in terms of the concentration gradient. Oftentimes, it is more convenient to use the moisture content gradient  $dM/dx$ . This is made possible by the fact that

$$\frac{dC}{dx} = \left( \frac{G_M \rho_w}{100} \right) \left( \frac{dM}{dx} \right) \quad [16]$$

where  $\frac{dM}{dx}$  is the moisture content gradient,  $G_M$  the specific gravity of wood at moisture content  $M$ , and  $\rho_w$  the density of water. Therefore,

$$J = - D \left( \frac{G_M \rho_w}{100} \right) \left( \frac{dM}{dx} \right) \quad [17]$$

or

$$J = - K_M \left( \frac{dM}{dx} \right) \quad [18]$$

where  $K_M = \frac{D G_M \rho_w}{100}$  is the moisture transport coefficient based on a moisture content gradient. The use of the coefficient  $K_M$  and the associated moisture gradient  $\frac{dM}{dx}$  to describe moisture movement in wood is, therefore, the same as using Fick's law in its original form.

As mentioned earlier, a point of controversy in applying Fick's law to moisture transport is the assumption that the driving force which causes movement is the concentration gradient. Potentials other than concentration or moisture content gradient have been proposed as the actual force which drives moisture through wood. These alternative transport equations are listed in Table 1 in derivative form (Siau, 1984b; Skaar, 1988). It can be shown that each of the transport coefficients  $K$  is related to the Fick's law coefficient  $D$  if the rate of change of the assumed potential with respect to  $C$  is known. These relationships are shown on the last column of Table 1. Skaar (1957) obtained the relationship between  $D$ ,  $K_M$ , and  $K_p$  and showed that isothermal transport calculations may be made using concentration, moisture content, or vapor pressure gradients with identical results. For example, for  $K_p$ ,

$$J = - K_p \left( \frac{dp}{dx} \right) \quad [19]$$

or

$$- D \left( \frac{dC}{dx} \right) = - K_p \left( \frac{dp}{dx} \right) \quad [20]$$

Solving for  $K_p$ ,

$$K_p = D \left( \frac{dC}{dp} \right) \quad [21]$$

This equation may also be written in terms of the relative vapor pressure  $\frac{p}{p_o}$ :

$$K_p = D \left[ \frac{dC}{p_o d\left(\frac{p}{p_o}\right)} \right] \quad [22]$$

**Table 1. Tabulation of some moisture transport equations for wood.**

| Assumed Potential<br>(units)                      | Transport Coefficient<br>(units)         | Transport Equation             | Relationship of<br>the Coefficient<br>to D |
|---------------------------------------------------|------------------------------------------|--------------------------------|--------------------------------------------|
| Moisture Concentration, C<br>$(\frac{g}{cc})$     | D<br>$(\frac{cm^2}{s})$                  | $J = -D \frac{dC}{dx}$         | $D = D$                                    |
| Moisture Content, M<br>(%)                        | $K_M$<br>$(\frac{g}{cm\ s\ \%})$         | $J = -K_M \frac{dM}{dx}$       | $K_M = D \frac{dC}{dM}$                    |
| Vapor Pressure, P<br>$(\frac{dyne}{cm^2})$        | $K_p$<br>$(\frac{g\ cm}{dyne\ s})$       | $J = -K_p \frac{dp}{dx}$       | $K_p = D \frac{dC}{dp}$                    |
| Water Activity, a<br>(ratio)                      | $K_a$<br>$(\frac{g}{cm\ s})$             | $J = -K_a \frac{da}{dx}$       | $K_a = D \frac{dC}{da}$                    |
| Chemical Potential, $\mu$<br>$(\frac{cal}{mol})$  | $K_\mu$<br>$(\frac{g\ mol}{cm\ s\ cal})$ | $J = -K_\mu \frac{d\mu}{dx}$   | $K_\mu = D \frac{dC}{d\mu}$                |
| Osmotic Pressure, $\pi$<br>$(\frac{dyne}{cm^2})$  | $K_\pi$<br>$(\frac{g\ cm}{dyne\ s})$     | $J = -K_\pi \frac{d\pi}{dx}$   | $K_\pi = D \frac{dC}{d\pi}$                |
| Spreading Pressure, $\phi$<br>$(\frac{dyne}{cm})$ | $K_\phi$<br>$(\frac{g}{dyne\ s})$        | $J = -K_\phi \frac{d\phi}{dx}$ | $K_\phi = D \frac{dC}{d\phi}$              |

where  $p_o$  is the saturated vapor pressure of the atmosphere at the temperature at which the diffusion is taking place. But since the relative humidity  $H$  is equal to the relative vapor pressure times 100,

$$K_p = \left( \frac{100 D}{p_o} \right) \left( \frac{dC}{dH} \right) \quad [23]$$

Or substituting moisture content for concentration,

$$K_p = \left( \frac{D G_M \rho_w}{p_o} \right) \left( \frac{dM}{dH} \right) \quad [24]$$

It is clear from the above equation that the sorption isotherm of wood is needed to relate  $K_p$  to  $D$ . The term  $\frac{dC}{dp}$  which is equal to  $\left( \frac{G_M \rho_w}{p_o} \right) \left( \frac{dM}{dH} \right)$  is not constant since  $\frac{dM}{dH}$  varies in a complex manner with relative humidity, wood moisture content, and temperature. In addition, the specific gravity  $G_M$  decreases with increasing moisture content below the fiber saturation point.

Similar expressions can be derived for the calculation of the other diffusion coefficients. It is apparent that the bound water transport coefficient for wood can be obtained by applying gradients of moisture content, vapor pressure, chemical potential, osmotic pressure, etc. These coefficients can be used in obtaining Fick's diffusion coefficient  $D$ , giving the same result in all cases. One interesting and useful property of the coefficient  $D$  is that it appears in unmodified form in the unsteady-state differential equation of diffusion, whereas all other transport coefficients  $K$  appear in combination with other parameters.

## **C. Nonisothermal Moisture Transport**

Although there is hardly a situation where wood is in an isothermal state, most investigations on moisture movement have been performed under constant temperature conditions. In most drying processes and when wood is in service, temperature gradients are present and there is some coupling between heat and water transport. One such heat-mass coupling phenomenon is known as the thermal-diffusion or Soret effect wherein mass is transported through a medium in the direction of decreasing temperature, even in the absence of a concentration gradient. A reciprocal phenomenon called the diffusion-thermo or Dufour effect occurs when heat is transported under the influence of a concentration gradient (Bird et al, 1960). This coupling between the flow of heat and the flow of mass has been demonstrated to occur in many systems (Jost, 1960), the Soret effect being better documented and easier to measure than the Dufour effect.

Nonisothermal moisture movement experiments on solid wood were first performed by Voigt et al (1940) on European beech, and by Choong (1963) on western white fir. Both studies were carried out on prismatic solid wood samples sealed on all faces to prevent moisture exchange with the surroundings. After sealing, each of two opposite faces were maintained in continuous contact with a constant-temperature platen such that a constant temperature gradient was established. This caused a redistribution of moisture throughout the thickness of the specimen as the moisture migrated away from the warm surface and towards the cool surface of the specimen because of the thermo-diffusion effect. Eventually, steady-state temperature and moisture profiles were obtained in the thickness direction of the specimen. Thermocouples were used to measure the temperature profiles and the samples

were sectioned serially in the thickness direction to determine the final or equilibrium moisture profiles.

Bramhall (1976a, 1979) in trying to identify the proper driving force for moisture movement in wood attempted to explain the experimental results obtained by Voigt et al (1940) and Choong (1963) using the steady-state form of Fick's law but with vapor pressure gradient as the driving force. The analysis, however, showed that at the end of the experiment, there was a vapor pressure gradient opposite to that of the moisture content gradient, indicating that vapor pressure is not the driving force for moisture movement. Bramhall then made a correction to the original computation by taking into consideration the effect of sorption hysteresis, and showed that the vapor pressure was more or less constant in some samples but not in others. He reasoned out that the existence of a vapor pressure at the end of the experiment in some samples despite correcting for sorption hysteresis is probably due to the samples not yet having attained the steady state when the study was terminated. The hypothesis forwarded by Bramhall resulted in a lively exchange of ideas (Rosen, 1976; Bramhall, 1976b; Babbitt, 1977a; Bramhall, 1977; Wengert, 1977; Babbitt, 1977b; Bramhall, 1979; Siau, 1980a; Bramhall 1980) and led to a renewed interest in the subject of nonisothermal moisture movement in wood.

Lately, Siau and coworkers (Siau and Babiak, 1983; Siau and Jin, 1985; Siau et al, 1986; Avramidis et al, 1987; and Avramidis and Siau, 1987) performed a series of experiments to investigate moisture movement under the influence of a temperature gradient. They employed a steady-state method but this time only the edges of the wood samples were moisture sealed. The opposite faces were each exposed to a different but constant humidity as well as temperature, and the moisture flux through

the sample was measured. A given set of experimental conditions were maintained on opposite faces of the sample until a steady-state moisture flux was attained, after which the conditions on one side of the sample were changed and the process repeated for each of several sets of surface conditions. The studies showed that Fick's law does not apply under nonisothermal conditions. Moisture content or partial pressure gradient alone could not explain the observed results, but when a combination of moisture content and thermal gradients was considered, a relatively good agreement was obtained between the experimental and theoretical fluxes.

The mathematical treatment of thermal diffusion can generally be categorized into two: the irreversible thermodynamics approach (Prigogine, 1967; de Groot and Mazur, 1962; Katchalsky and Curran, 1965); and the mechanistic approach (Philip and de Vries, 1957; Luikov, 1966). In the first approach, attempts are made to relate the entropy production in the system to the heat and mass transfer rate so that relevant driving forces and fluxes can be identified and related through a number of phenomenological coefficients. In the second approach, a physical model for the system is theorized and macroscopic description of mass movement is derived. The mathematical models for nonisothermal moisture movement in wood proposed by Siau (1980b) and Nelson (1986b) fall under the first category; while those forwarded by Skaar and Siau (1981), Siau (1983, 1984a) and Stanish (1986) can be grouped under the second category.

### ***1. NET Models for Nonisothermal Moisture Transport in Wood***

Classical thermodynamics, despite its usefulness in describing many observable phenomena, is essentially applicable to systems in equilibrium or undergoing

reversible processes. Most of the usual physicochemical processes such as conduction of heat, diffusion, conduction of electricity, and chemical reactions are, however, irreversible processes and in such cases the laws of classical thermodynamics provide a set of inequalities describing only the direction of change. A branch of macroscopic physics called nonequilibrium thermodynamics (NET) considers such irreversible phenomena and provides a numerical treatment and quantitative description of systems which are not in equilibrium. It has made possible the replacement of the inequalities of classical thermodynamics with equalities (Katchalsky and Curran, 1965).

A brief sketch of the theory of nonequilibrium thermodynamics and a simple explanation of the principles on which it is based will be given below. More detailed discussion of the theory can be obtained from several standard works on the subject (Prigogine, 1967; de Groot and Mazur, 1962). Although nonequilibrium thermodynamics has been extended to nonlinear problems, the following discussion limits itself to linear regimes.

The entropy change for any system may be written as

$$dS = d_e S + d_i S \quad [25]$$

where  $d_e S$  is the change in entropy due to the interaction of the system with the surrounding; and  $d_i S$  the change in entropy due to production inside the system. According to the second law of thermodynamics,  $d_i S$  is zero when the system undergoes reversible changes but is positive if the system undergoes irreversible changes:

$$d_i S = 0 \quad (\text{reversible}) \quad [26a]$$

$$d_i S > 0 \quad (\text{irreversible}) \quad [26b]$$

Classical thermodynamics is concerned with the study of reversible processes for which (26a) holds. On the other hand, nonequilibrium thermodynamics tries to relate  $d_i S$  to various irreversible phenomena occurring within the system.

Consider for instance the flow of heat in a system consisting of two closed phases 1 and 2, maintained respectively at uniform temperatures  $T_1$  and  $T_2$  (Figure 3). Since entropy is an extensive variable, the entropy for the whole system is given by

$$dS = dS_1 + dS_2 \quad [27]$$

If we separate the heat received by each phase into two parts

$$dq_1 = dq_{1e} + dq_{1i} \quad [28a]$$

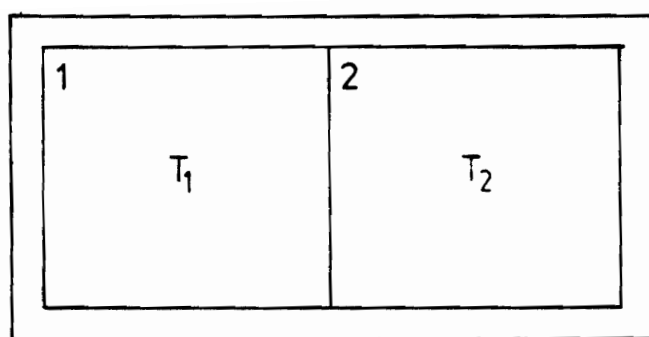
$$dq_2 = dq_{2e} + dq_{2i} \quad [28b]$$

where  $dq_{1e}$  is the heat supplied to phase 1 from the outside, and  $dq_{1i}$  the heat received by phase 1 from phase 2. The symbols  $dq_{2e}$  and  $dq_{2i}$  have similar interpretations. Since  $dS = \frac{dq_1}{T_1} + \frac{dq_2}{T_2}$  then

$$dS = \frac{dq_{1i}}{T_1} + \frac{dq_{1e}}{T_1} + \frac{dq_{2i}}{T_2} + \frac{dq_{2e}}{T_2} \quad [29a]$$

$$dS = \frac{dq_{1e}}{T_1} + \frac{dq_{2e}}{T_2} + \frac{dq_{1i}}{T_1} - \frac{dq_{1i}}{T_2} \quad [29b]$$

$$dS = \frac{dq_{1e}}{T_1} + \frac{dq_{2e}}{T_2} + dq_{1i} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad [29c]$$



**Figure 3.** Hypothetical closed system consisting of phases 1 and 2 maintained at uniform temperatures  $T_1$  and  $T_2$  , respectively.

The entropy change as given by equation (29c) consists of two parts: one due to the exchange of heat with the exterior given by the first two terms; and the other due to the irreversible heat flow inside the system given by

$$d_i S = dq_{ii} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad [30]$$

Notice in equation (30) that  $dq_{ii}$  is positive when  $(1/T_1 - 1/T_2)$  is positive; while  $dq_{ii}$  is negative when  $(1/T_1 - 1/T_2)$  is negative. Thus  $d_i S$  is always positive whenever a temperature difference exists. The entropy production can only be zero when thermal equilibrium is established, that is, when  $T_1 = T_2$ .

de Groot and Mazur (1962) showed that for a system in which the densities of the extensive properties are continuous functions of space and time, equation (25) may be rewritten in the form

$$\rho \left( \frac{ds}{dt} \right) = - \nabla \cdot \vec{J}_s + \sigma \quad [31]$$

where  $\rho = \sum_{i=1}^n \rho_i$  is the total density,  $ds/dt$  is the substantial time derivative of entropy per unit mass  $s$ ,  $\nabla$  the del or nabla operator,  $\vec{J}_s$  the entropy flux, the dot product  $\nabla \cdot \vec{J}_s$  is called the divergence of  $\vec{J}_s$ , and  $\sigma$  the rate of entropy production per unit volume.

To have an expression for the rate of entropy production per unit volume  $\sigma$ , a relationship between the specific entropy  $s$  and other thermodynamic variables must be obtained. This requires that the theory of NET must be treated as a continuum theory which considers a system to be in local equilibrium. That is, it will be assumed that the system under study can be divided into cells so that the thermodynamic

properties within a cell are constant while at the same time allowing these properties to vary from cell to cell in such a way that the thermodynamic variables are continuous functions of space and time. This implies that Gibb's equation is valid locally (Kreuzer, 1981):

$$T dS = dU + PdV - \sum_{i=1}^n \mu_i dm_i \quad [32]$$

where  $S$  is the entropy,  $T$  the absolute temperature,  $U$  the internal energy,  $V$  the volume,  $P$  the pressure,  $\mu_i$  the chemical potential per gram of the  $i$ th component,  $m_i$  the mass of the  $i$ th component, and  $n$  the number of chemical components. Dividing equation (32) by the total mass and taking the substantial time derivative results in:

$$T \frac{ds}{dt} = \frac{du}{dt} + P \frac{dv}{dt} - \sum_{i=1}^n \mu_i \frac{dC_i}{dt} \quad [33]$$

where  $C_i = m_i/m$  is the mass fraction of the  $i$ th component,  $s$  the specific entropy,  $u$  the specific internal energy, and  $v$  the specific volume. To reduce equation (33) to a form similar to equation (31), expressions for  $dC_i/dt$  and  $du/dt$  must be obtained using the equation of continuity and the equation of energy.

The equation of continuity for component  $i$  which in vector symbolism can be written as follows is derived in Appendix A:

$$\rho \frac{dC_i}{dt} = -\nabla \cdot \vec{J}_i \quad [34]$$

Also shown in Appendix A is the derivation of the equation of energy which can be written as follows:

$$\rho \frac{du}{dt} = -\nabla \cdot \vec{J}_q - P \nabla \cdot \vec{v} - \tau : \nabla \vec{v} + \sum_{i=1}^n F_i \cdot \vec{J}_i \quad [35]$$

Combining these two equations with equation (33) results in the entropy balance equation:

$$T \frac{ds}{dt} = -\frac{1}{\rho} (\nabla \cdot \vec{J}_q) - \frac{1}{\rho} (\tau : \nabla \vec{v}) + \frac{1}{\rho} \sum_{i=1}^n F_i \cdot \vec{J}_i + \frac{1}{\rho} \sum_{i=1}^n \mu_i (\nabla \cdot \vec{J}_i) \quad [36]$$

or

$$\rho \frac{ds}{dt} = -\frac{\nabla \cdot \vec{J}_q}{T} - \frac{\tau : \nabla \vec{v}}{T} + \frac{\sum_{i=1}^n F_i \cdot \vec{J}_i}{T} + \frac{\sum_{i=1}^n \mu_i (\nabla \cdot \vec{J}_i)}{T} \quad [37]$$

Equation (37) can be recast into the form of equation (31) to obtain (Kreuzer, 1981):

$$\rho \frac{ds}{dt} = -\nabla \cdot \frac{\vec{J}_q - \sum_{i=1}^n \mu_i \vec{J}_i}{T} - \frac{1}{T^2} \vec{J}_q \cdot \nabla T - \frac{1}{T} \sum_{i=1}^n \vec{J}_i \cdot T \nabla \left( \frac{\mu_i}{T} \right) - F_i - \frac{1}{T} \tau : \nabla \vec{v} \quad [38]$$

where the entropy flux  $\vec{J}_s$  and the rate of entropy production per unit volume  $\sigma$  are given by:

$$\vec{J}_s = \frac{\vec{J}_q - \sum_{i=1}^n \mu_i \vec{J}_i}{T} \quad [39]$$

$$\sigma = -\frac{1}{T^2} \vec{J}_q \cdot \nabla T - \frac{1}{T} \sum_{i=1}^n \vec{J}_i \cdot \left[ T \nabla \left( \frac{\mu_i}{T} \right) - F_i \right] - \frac{1}{T} \tau : \nabla \vec{v} \quad [40]$$

Equation (40) may also be rewritten as follows:

$$\Phi = T\sigma = -\frac{1}{T} \vec{J}_q \cdot \nabla T - \sum_{i=1}^n \vec{J}_i \cdot \left[ T \nabla \left( \frac{\mu_i}{T} \right) - F_i \right] - \tau : \nabla \vec{v} \quad [41]$$

where the product  $T\sigma$  has the dimensions of energy per unit volume per unit time and thus  $\Phi$  is called the energy dissipation function. Notice that equation (41) is of the form

$$\Phi = \sum_j \vec{J}_j \cdot X_j \quad [42]$$

where  $\vec{J}_j$  and  $X_j$  are the independent fluxes and thermodynamic forces.

Having obtained the expressions for the fluxes and thermodynamic forces, what needs to be done next is to find equations relating the fluxes to the thermodynamic forces. One possibility is to assume that the fluxes are linear functions of the forces. Some of the linear phenomenological theories of irreversible processes that are generally known are: Fourier's law which expresses a linear relationship between heat flux and temperature gradient, Ohm's law between electrical current and electrical potential gradient, Fick's law between the flux of a component of a mixture and its concentration gradient, Newton's law between shearing stress and velocity potential gradient, and Darcy's law between the flux of a liquid and its hydraulic potential gradient (Taylor, 1963). Also included among these linear processes are the cross phenomena when two or more of the irreversible processes occur simultaneously in the same system. Examples of these are given by the thermoelectric effects, thermal-diffusion effect, and diffusion-thermo effect. In the linear regime, we can write the flux of any component  $\vec{J}_j$  as the sum of the forces times an appropriate coefficient:

$$\vec{J}_j = \sum_k L_{jk} X_k \quad [43]$$

where the  $L_{jk}$ 's are called the phenomenological coefficients. When  $j=k$ , the coefficients are related to the ordinary conductivities like heat conductivity, electrical conductivity, diffusion coefficient, etc.; while when  $j \neq k$ , the coefficients are connected with the interference or linked phenomena. According to Onsager (1931a,b), for  $j \neq k$ ,

$$L_{jk} = L_{kj} \quad [44]$$

The equality expressed by (44) is called the Onsager reciprocity relation which states that when a flux corresponding to the irreversible process  $j$  is influenced by the potential  $X_k$  of the irreversible process  $k$ , then the flux corresponding to  $k$  is also influenced by the potential  $X_j$  through the same interference coefficient.

#### a. NET Thermal Diffusion Model:

The fluxes and driving forces as defined by equation (41) can be used for the description of the uniaxial (say,  $x$  direction) simultaneous flow of water and heat in wood:

$$\Phi = -J_q \left( \frac{1}{T} \frac{dT}{dx} \right) - J_w \left( T \frac{d\left(\frac{\mu_w}{T}\right)}{dx} - F_w \right) \quad [45]$$

where  $J_w$  is the moisture flux,  $F_w$  the external force (usually the gravitational force is the only one operating), and  $\mu_w$  the chemical potential per gram of water. If we assume  $F_w$  to be negligible, equation (45) reduces to

$$\Phi = -J_q \left( \frac{1}{T} \frac{dT}{dx} \right) - J_w \left( T \frac{d\left(\frac{\mu_w}{T}\right)}{dx} \right) \quad [46]$$

The second term of the right hand side of equation (46) contains the chemical potential of water and temperature as part of the space derivative. It is possible to remove the temperature  $T$  from the gradient as follows (de Groot, 1950):

$$\frac{d\left(\frac{\mu_w}{T}\right)}{dx} = \frac{1}{T} \frac{d\mu_w}{dx} + \mu_w \frac{d\left(\frac{1}{T}\right)}{dx} \quad [47]$$

The specific water potential  $\mu_w$  is a function of temperature, pressure, and concentration so that

$$\frac{d\mu_w}{dx} = \left( \frac{\partial \mu_w}{\partial T} \right)_{P,m} \frac{dT}{dx} + \left( \frac{\partial \mu_w}{\partial P} \right)_{T,m} \frac{dP}{dx} + \frac{d\mu_{wc}}{dx} \quad [48]$$

where  $\mu_{wc}$  is the concentration-dependent part of the water potential. Since the system is considered to be in mechanical equilibrium (or  $dP/dx = 0$ ), and the partial specific entropy  $\bar{s} = - \left( \frac{\partial \mu_w}{\partial T} \right)_{P,m}$  then

$$\frac{d\mu_w}{dx} = -\bar{s} \frac{dT}{dx} + \frac{d\mu_{wc}}{dx} \quad [49]$$

Equation (47) can therefore be written as

$$\frac{d\left(\frac{\mu_w}{T}\right)}{dx} = \frac{1}{T} \left( \bar{s} \frac{dT}{dx} + \frac{d\mu_{wc}}{dx} \right) + \mu_w \frac{d\left(\frac{1}{T}\right)}{dx} \quad [50]$$

Considering that the partial specific enthalpy  $\bar{h} = T\bar{s} + \mu$ , equation (50) becomes

$$\frac{d\left(\frac{\mu_w}{T}\right)}{dx} = \frac{1}{T} \frac{d\mu_{wc}}{dx} + \bar{h}_w \frac{d\left(\frac{1}{T}\right)}{dx} \quad [51]$$

which when substituted in equation (46) gives

$$\Phi = - J_q \left( \frac{1}{T} \frac{dT}{dx} \right) - J_w T \left( \frac{1}{T} \frac{d(\mu_{wc})}{dx} - \bar{h} \frac{d\left(\frac{1}{T}\right)}{dx} \right) \quad [52a]$$

Or since  $\frac{d(1/T)}{dx} = \frac{-1}{T^2} \frac{dT}{dx}$

$$\Phi = J_q T \left( \frac{d\left(\frac{1}{T}\right)}{dx} \right) - J_w T \left( \frac{1}{T} \frac{d(\mu_{wc})}{dx} - \bar{h} \frac{d\left(\frac{1}{T}\right)}{dx} \right) \quad [52b]$$

$$\Phi = (J_q - \bar{h} J_w) \left( -\frac{1}{T} \frac{dT}{dx} \right) - J_w \frac{d(\mu_{wc})}{dx} \quad [52c]$$

$$\Phi = -\frac{J'_q}{T} \left( \frac{dT}{dx} \right) - J_w \frac{d(\mu_{wc})}{dx} \quad [52d]$$

where  $J'_q = J_q - \bar{h} J_w$ , called the reduced heat flow, is the difference between the total heat flow and the heat flow caused by the flow of water. Equation (52d) may then be written in the same form as equation (42) as follows:

$$\Phi = J'_q X'_q + J'_w X'_w \quad [53a]$$

where

$$J'_w = J_w \quad [53b]$$

$$X'_q = -\frac{1}{T} \frac{dT}{dx} \quad [53c]$$

$$X'_w = -\frac{d\mu_{wc}}{dx} \quad [53d]$$

Thus from equation (43), the moisture and heat flux equations are given by

$$J'_w = L'_{ww} X'_w + L'_{wq} X'_q \quad [54a]$$

$$J'_q = L'_{qq} X'_q + L'_{qw} X'_w \quad [54b]$$

Or

$$J'_w = -L'_{ww} \frac{d\mu_{wc}}{dx} - \frac{L'_{wq}}{T} \frac{dT}{dx} \quad [54c]$$

$$J'_q = -\frac{L'_{qq}}{T} \frac{dT}{dx} - L'_{qw} \frac{d\mu_{wc}}{dx} \quad [54d]$$

Under isothermal condition, equation (54c) reduces to

$$J'_w = -L'_{ww} \frac{d\mu_{wc}}{dx} \quad [55]$$

Since  $\frac{d\mu_{wc}}{dx} = \frac{\partial \mu_w}{\partial C} \frac{dC}{dx}$  then

$$J'_w = -L'_{ww} \frac{\partial \mu_w}{\partial C} \frac{dC}{dx} \quad [56a]$$

or

$$J'_w = -D \frac{dC}{dx} \quad [56b]$$

which is Fick's law of diffusion with the diffusion coefficient  $D$  being equal to  $\left( L'_{ww} \frac{\partial \mu_w}{\partial C} \right)$ .

It is also convenient to define a thermal-diffusion coefficient  $D_T$  by the relation (Katchalsky and Curran, 1965):

$$D_T = \frac{L'_{wq}}{T C} \quad [57]$$

where  $C$  is the concentration of the diffusing substance. Thus, equation (54c) may also be written as

$$J'_w = -D \frac{dC}{dx} - C D_T \frac{dT}{dx} \quad [58]$$

Equation (58) shows that the total flow of water under nonisothermal condition is composed of two terms: the ordinary diffusional flow proportional to the concentration gradient; and the thermal-diffusion flow dependent on the temperature gradient.

In the absence of a concentration gradient, equation (54d) may also be shown to reduce to the form

$$J'_q = -K_q \frac{dT}{dx} \quad [59]$$

which is Fourier's law for heat transport with the thermal conductivity coefficient  $K_q$  being equal to  $\left( \frac{L'_{ww}}{T} \right)$ .

Thermal diffusion may also be discussed in terms of a quantity  $Q^*$ , called the heat of transfer (Katchalsky and Curran, 1965; Prigogine, 1967; de Groot and Mazur, 1962). For the isothermal case, the temperature gradient  $\frac{dT}{dx}$  and the potential  $X'_q$  are zero. If the ratio of the reduced heat flow to the moisture flow is taken, the quantity  $Q^*$  is defined:

$$Q^* = \left[ \frac{J'_q}{J'_w} \right]_T = \frac{L'_{wq}}{L'_{ww}} \quad [60]$$

In terms of the quantity  $Q^*$ , the moisture flux and the reduced heat flux equations (54c) and (54d) become

$$J'_w = -L'_{ww} \left( \frac{d\mu_{wc}}{dx} + Q^* \frac{d(\ln T)}{dx} \right) \quad [61a]$$

$$J'_q = -L'_{qq} \frac{d(\ln T)}{dx} - L'_{ww} Q^* \frac{d\mu_{wc}}{dx} \quad [61b]$$

Equations (61a) and (61b) will hereon be called the NET moisture flux equation and the NET reduced heat flux equation, respectively. Taylor and Cary (1964) were the first to use these equations in quantitatively describing the simultaneous flow of moisture and heat in a soil system. Equation (61a) is the same equation given by Briggs (1967) in a monograph on the movement of water in plants and which was adopted by Siau (1980b) to quantify the nonisothermal movement of moisture in wood.

Another quantity of transfer called the energy of transfer  $U^*$  is often encountered in the literature. It represents the total energy transported under isothermal conditions and is mathematically expressed by the ratio of the total energy flux  $J_q$  and the moisture flux  $J_w$ . It is related to the heat of transfer through the partial molar enthalpy  $h$

$$U^* = \left[ \frac{J_q}{J_w} \right]_T = \frac{L_{qw}}{L_{ww}} = Q^* + h \quad [62]$$

For the isothermal condition, the moisture flux equation (61a) becomes

$$J'_w = -L'_{ww} \frac{\partial \mu_w}{\partial M} \frac{dM}{dx} \quad [63]$$

where  $M$  is the moisture content based on the oven-dry weight of the wood. This can be combined with the steady-state form of Fick's law which, as shown by Skaar (1957, 1988), can be expressed in terms of the fractional moisture content gradient as

$$J'_w = -K_M \frac{dM}{dx} \quad [64]$$

resulting in

$$K_M = -L'_{ww} \frac{\partial \mu_w}{\partial M} \quad [65]$$

where  $K_M$  is the moisture conductivity coefficient related to the diffusion coefficient  $D$  by  $K_M = D \frac{dC_w}{dM}$ ,  $C_w$  being the mass concentration of water (i.e. mass of water per unit gross volume of wood). Substituting equation (65) in equation (54c) results in

$$J'_w = -K_M \frac{dM}{dx} - L'_{wq} \frac{d(\ln T)}{dx} \quad [66]$$

The heat of transfer  $Q^*$  may be incorporated in this equation to obtain

$$J'_w = -K_M \left[ \frac{dM}{dx} + \frac{Q^*}{\left( \frac{\partial \mu_w}{\partial M} \right)} \frac{d(\ln T)}{dx} \right] \quad [67]$$

The variation of the water potential with moisture content is given by

$$\frac{\partial \mu_w}{\partial M} = \frac{\partial(\mu_1^0 + RT \ln a)}{\partial M} = RT \frac{\partial \ln a}{\partial M} \quad [68]$$

where  $a$  is the activity of the sorbed water essentially equal to the equilibrium relative vapor pressure;  $\mu_1^0$ , a constant, is the chemical potential of pure water at atmospheric pressure; and  $R$  the gas constant. Combining equations (67) and (68) gives

$$J'_w = -K_M \left[ \frac{dM}{dx} + \frac{Q^*}{RT \left( \frac{\partial \ln a}{\partial M} \right)} \frac{d(\ln T)}{dx} \right] \quad [69]$$

which further reduces to the following equation after replacing  $a$  by  $\frac{H}{100}$ ,  $H$  being the relative humidity:

$$J'_w = -K_M \left[ \frac{dM}{dx} + \frac{Q^* H}{RT \left( \frac{\partial H}{\partial M} \right)} \frac{d(\ln T)}{dx} \right] \quad [70]$$

If an experiment is performed wherein a closed wood system is subjected to a uniaxial temperature gradient, the moisture flux at steady state becomes zero and by using equation (66) allows us to define a transfer quantity  $Q_2$  analogous to the heat of transfer  $Q^*$  defined in equation (60):

$$\frac{dM}{d(\ln T)} = -\frac{L'_{wq}}{K_M} = -Q_2 \quad [71]$$

This quantity  $Q_2$  is similar to the quantity  $\beta^*$  defined by Taylor and Cary (1964). In fact  $Q_2 = 100(\beta^*)$ . When  $Q_2$  is substituted in equation (66) we obtain

$$J'_w = -K_M \left[ \frac{dM}{dx} + Q_2 \frac{d(\ln T)}{dx} \right] \quad [72]$$

From the following equation derived by Briggs (1967)

$$\frac{Q^*}{RT^2} = \frac{d(\ln D_{gT})}{dT} \quad [73]$$

where  $D_{gT}$  is the diffusion coefficient of water vapor through wood, Siau (1980b) showed that if the coefficient  $D_{gT}$  is expressed by an Arrhenius-type equation  $D_{gT} = D_0 [\exp(-E_A/RT)]$  and if  $D_0$  and  $E_A$  are assumed to be constant then  $Q^*$  is equal

to the activation energy  $E_A$ . He then proceeded to express the phenomenological coefficient  $L'_{ww}$  in terms of the coefficient  $D_{gT}$  to finally obtain the following equation:

$$J'_w = \frac{D_{gT} G_M \rho_w}{100} \frac{dM}{d\mu_w} \left( \frac{d\mu_w}{dx} + \frac{E_A}{T} \frac{dT}{dx} \right) \quad [74]$$

#### b. Nelson Modification of the NET Model:

Starting with equation (61a), Nelson (1986b) proposed another mathematical model for the movement of moisture in wood under the influence of a temperature gradient. Arguing that the heat of transfer is different from the activation energy, he obtained the following expression for  $Q^*$

$$Q^* = \Delta H_o + \Delta H_s - C_p^v T \quad [75]$$

which when substituted in equation (61a) results in the following expression for the moisture flux:

$$J'_w = -L'_{ww} \left( \frac{d\mu_{wc}}{dx} + \frac{\Delta H_o + \Delta H_s - C_p^v T}{T} \frac{dT}{dx} \right) \quad [76]$$

where:  $C_p$  is the average heat capacity of water vapor from the reference temperature to temperature  $T$ . For convenience, Nelson rewrote the above equation in terms of the fractional moisture content gradient  $dm/dx$  as follows:

$$J'_w = -L'_{ww} \left( B_n \Delta \mu \frac{dm}{dx} + \frac{\Delta H_o + \Delta H_s - C_p^v T}{T} \frac{dT}{dx} \right) \quad [77]$$

where  $B_n$  is the slope of the equation ( $\ln \Delta \mu = A - B_n m$ ) relating the natural logarithm of the change in the molar free energy of adsorbed water with fractional moisture

content  $m$  (Nelson, 1983). Substituting an expression for  $L_{ww}$  obtained from an earlier publication (Nelson, 1986a), Nelson's model finally takes the form:

$$J'_w = - \frac{\rho_c n m D B_n \Delta\mu}{R T} \left[ \frac{-(\Delta H_o + \Delta H_s - C_p^v T)}{B_n \Delta\mu T} \frac{dT}{dx} + \frac{dm}{dx} \right] \quad [78]$$

where:  $\rho_c$  = density of the cell wall at the fractional moisture content  $m$ ;  $D$  = diffusion coefficient under isothermal conditions; and  $n$  = dimensionless exponent relating spreading pressure to vapor pressure.

## 2. Mechanistic Models for Nonisothermal Moisture Transport in Wood

### a. Skaar-Siau Activated Molecule Model:

Skaar and Siau (1981) proposed a theoretical expression for bound water flux based upon a gradient of activated water molecules:

$$J'_w = - A_o \left( \frac{dM^*}{dx} \right) \quad [79]$$

where  $A_o$  is a constant of proportionality, and  $M^*$  is the content of activated water molecules in the cell wall. Considering that the gradient  $\frac{dM^*}{dx}$  is a function of moisture content  $M$  and temperature  $T$

$$\frac{dM^*}{dx} = \frac{\partial M^*}{\partial M} \frac{dM}{dx} + \frac{\partial M^*}{\partial T} \frac{dT}{dx} \quad [80]$$

and assuming that the concentration of activated molecules in the cell wall follows a Boltzmann temperature distribution

$$M^* = M \exp\left(\frac{-E_s}{RT}\right) \quad [81]$$

where  $E_s$  is the activation energy for bound water diffusion, they arrived at the following expression for moisture flux:

$$J'_w = -\frac{A_o M^*}{RT} \left[ \left( \frac{RT}{M} - \frac{\partial E_s}{\partial M} \right) \frac{dM}{dx} + \frac{E_s}{T} \frac{dT}{dx} \right] \quad [82]$$

By introducing the bound water conductivity coefficient  $K_b$ , the above equation was further modified resulting in the final form of the equation for bound water flux shown below:

$$J'_w = -\frac{K_b M}{\left( RT - M \frac{\partial E_s}{\partial M} \right)} \left[ \left( \frac{RT - M \frac{\partial E_s}{\partial M}}{M} \right) \frac{dM}{dx} + \frac{E_s}{T} \frac{dT}{dx} \right] \quad [83]$$

If it is assumed that  $E_s$  is constant with moisture content  $M$ , the above equation reduces to

$$J'_w = -K_b \left( \frac{dM}{dx} + \frac{M E_s}{RT^2} \frac{dT}{dx} \right) \quad [84]$$

and further reduces to the following equation if it is assumed that the sorption isotherm is linear and  $E_s = Q^*$ :

$$J'_w = -K_b \frac{dM}{d\mu} \left( \frac{d\mu}{dx} + \frac{Q^*}{T} \frac{dT}{dx} \right) \quad [85]$$

Using the values of the diffusion coefficient obtained by Stamm (1959), the activation energy was approximated as (9200-70M) cal/mol, simplifying equation (83) to

$$J'_w = -K_b \left[ \frac{dM}{dx} + \left( \frac{M}{RT + 70M} \right) \left( \frac{9200 - 70M}{T} \right) \frac{dT}{dx} \right] \quad [86]$$

#### b. Siau Water Potential Model:

An alternate theoretical model was proposed by Siau (1983) by defining moisture flux in terms of the water potential gradient

$$J'_w = -K_\mu \frac{d\mu_w}{dx} \quad [87]$$

where  $\mu_w$  is the water potential, and  $K_\mu$  is the conductivity coefficient based on the chemical potential gradient. Taking into consideration the moisture content and temperature dependence of the water potential

$$\frac{d\mu_w}{dx} = \frac{\partial \mu_w}{\partial H} \frac{\partial H}{\partial M} \frac{dM}{dx} + \frac{\partial \mu_w}{\partial T} \frac{dT}{dx} \quad [88]$$

and expressing  $K_\mu$  in terms of the bound water conductivity coefficient  $K_b$ ,

$$K_\mu = K_b \frac{\partial H}{\partial \mu_w} \frac{\partial M}{\partial H} \quad [89]$$

Siau obtained the following expression for moisture flux

$$J'_w = -K_b \left( \frac{dM}{dx} + \frac{\partial H}{\partial \mu_w} \frac{\partial M}{\partial H} \frac{\partial \mu_w}{\partial T} \frac{dT}{dx} \right) \quad [90]$$

Since the water potential is defined as

$$\mu_w = \mu_1^0 + R T \ln(H/100) \quad [91]$$

Siau showed that the moisture flux equation may also be written as

$$J'_w = -K_b \left[ \frac{dM}{dx} + \frac{H}{RT} \frac{\partial M}{\partial H} \left( \frac{\partial \mu_1^0}{\partial T} + R T \frac{\partial \ln(\frac{H}{100})}{\partial T} + R \ln(\frac{H}{100}) \right) \frac{dT}{dx} \right] \quad [92]$$

and reduced to the following expression if the differential heat of sorption  $\Delta H_s$  is substituted for the term  $\left( R T^2 \frac{\partial \ln(H/100)}{\partial T} \right)$

$$J'_w = -K_b \left[ \frac{dM}{dx} + \frac{H}{RT} \frac{\partial M}{\partial H} \left( \frac{\partial \mu_1^0}{\partial T} + \frac{\Delta H_s}{T} + R \ln(H/100) \right) \frac{dT}{dx} \right] \quad [93]$$

Considering the fact that the chemical potential of water must decrease with increasing temperature, Siau (1984a) presented a modification to the above equation as follows

$$J'_w = -K_b \left[ \frac{dM}{dx} + \frac{H}{RT} \frac{\partial M}{\partial H} \left( \frac{\partial \mu_1^0}{\partial T} + \frac{\Delta H_o + \Delta H_s + E_s}{T} + R \ln(\frac{H p_o}{7600}) \right) \frac{dT}{dx} \right] \quad [94]$$

where  $p_o$  is the saturated vapor pressure in (cmHg).

### c. Stanish Model:

Stanish (1986) reviewed several equations used to characterize moisture transport through wood, including most of those noted above. He then developed a mathematical expression for the net migration rate through wood of water in the bound and vapor phases where it was assumed that the diffusion of bound water is driven by the gradient in the chemical potential of the bound water molecules, while water

vapor diffusion is driven by the gradient in the mole fraction of water in the gas phase. Thus the total flux of moisture through wood was defined as

$$J'_w = n_b + n_v \quad [95]$$

where  $n_b$  and  $n_v$  are the flux of bound water through the cell wall and flux of water vapor through the gas phase, respectively. Taking the bound water flux as being directly proportional to the chemical potential of the bound water molecules  $\mu_b$  and to the fractional volume occupied by the cell wall  $(1 - \varepsilon)$ , Stanish presented the following expression for  $n_b$

$$n_b = -K_\mu (1 - \varepsilon) \frac{d\mu_b}{dx} \quad [96]$$

where  $K_\mu$  is the bound water diffusion coefficient with chemical potential as the driving force. Assuming local thermodynamic equilibrium between bound water and water vapor in the wood, an expression for the gradient  $d\mu_b/dx$  in terms of the temperature and water vapor pressure gradients was obtained:

$$\frac{d\mu_b}{dx} = \frac{1}{m_v} \left( -s_v \frac{dT}{dx} + \frac{R T}{p} \frac{dp}{dx} \right) \quad [97]$$

where  $s_v$  is the molar entropy and  $m_v$  is the molecular weight of water vapor. The molar entropy term was further evaluated using thermodynamic principles resulting in the following expression

$$s_v = 187 + c_p \ln\left(\frac{T}{298.15}\right) - R \ln\left(\frac{p}{101325}\right) \quad [98]$$

with units of  $\frac{J}{mol K}$ , where 187 J/(mol K) is the average of the statistical and third law entropies of water vapor at 298.15 K and one atmosphere pressure;  $c_p$  is the heat

capacity in J/(mol K) and  $p$  is the water vapor pressure in Pa. When these two expressions are substituted in equation (96), the bound water flux component is obtained

$$n_b = -K_\mu \frac{(1-\varepsilon)}{m_v} \left[ - \left( 187 + c_p \ln \frac{T}{298.15} - R \ln \frac{p}{101325} \right) \frac{dT}{dx} + \frac{RT}{p} \frac{dp}{dx} \right] \quad [99]$$

The equation for water vapor flux was also derived based on Fick's law of diffusion in a binary mixture of gases:

$$n_v = m_v N_A \quad [100]$$

where  $N_A$  is the molar flux of water vapor relative to stationary coordinates in a mixture of water vapor and air, and is given by the expression

$$N_A = - \frac{\frac{p_t}{R T} D_{eff} \frac{d\left(\frac{p}{p_t}\right)}{dx}}{1 - \frac{p}{p_t}} \quad [101]$$

if the net flux of air is zero. The term  $D_{eff}$  in the above equation denotes the effective vapor diffusivity in wood, while the ratio  $\frac{p}{p_t}$  is the mole fraction of water vapor in air. Taking  $D_{eff}$  as being equal to the product of an attenuation factor  $\alpha$  and the coefficient of interdiffusion of water vapor in air  $D_a$  (Dushman and Lafferty, 1962):

$$D_{eff} = \alpha D_a = \alpha \left[ 2.20 \times 10^{-5} \left( \frac{T}{273.15} \right)^{1.75} \left( \frac{101325}{p_t} \right) \right] \quad [102]$$

the vapor flux component was obtained

$$n_v = -1.21 \times 10^{-4} \frac{m_v \alpha T^{0.75}}{R \left(1 - \frac{p}{p_t}\right)} \frac{d\left(\frac{p}{p_t}\right)}{dx} \quad [103]$$

### 3. Steady-state Form of the Theoretical Models

Consider a prismatic wood sample, initially at a uniform temperature and moisture content, and sealed so that it can not exchange moisture with the environment. If the two opposite faces are suddenly exposed to two different but constant temperatures, a temperature profile will develop in a relatively short time. The initial uniform moisture profile will also commence to change to some intermediate profile. This moisture distribution will continue to change as it approaches a steady-state condition. Under steady-state condition, both temperature and moisture content profiles will remain invariant with time, and there will be no further net moisture flux. However, there will be a constant heat flux provided the two temperatures are maintained constant.

The equations for nonisothermal moisture movement presented above may be used to estimate the relationship between the temperature and moisture content profiles in wood under the steady-state condition with zero net moisture flux. Equation (70), for instance, can be shown to reduce to the following form at  $J'_w = 0$  :

$$\left(\frac{dM}{dT}\right)_s = - \frac{H Q^*}{R T^2 \left(\frac{\partial H}{\partial M}\right)_T} \quad [104]$$

It can similarly be shown that the equations of Nelson(1986b), Skaar and Siau (1981), and Siau (1984a) reduce to the following forms, respectively:

$$\left( \frac{dM}{dT} \right)_s = \frac{\Delta H_o + \Delta H_s - C_p^v T}{B_n T \Delta \mu} \quad [105]$$

$$\left( \frac{dM}{dT} \right)_s = - \frac{9200 - 70 M}{\frac{R T^2}{M} + 70 T} \quad [106]$$

$$\left( \frac{dM}{dT} \right)_s = - \frac{H \left( T \frac{d\mu_1^o}{dT} + \Delta H_s + \Delta H_o + E_s + R T \ln \frac{H p_o}{7600} \right)}{R T^2 \left( \frac{\partial H}{\partial M} \right)_T} \quad [107]$$

At steady state condition with zero net moisture flux, the ratio of the temperature and vapor pressure gradients for the bound water diffusion equation (99) of Stanish (1986) is given by

$$\left( \frac{dp}{dT} \right)_s = - \frac{p s_v}{R T} \quad [108]$$

In terms of the moisture content gradient, the above equation can be rewritten as:

$$\left( \frac{dM}{dT} \right)_s = - \frac{H T s_v}{R T^2 \left( \frac{\partial H}{\partial M} \right)_T} \quad [109]$$

The parameter  $Q^*$ , the heat of transfer, arising from the principles of irreversible thermodynamics, may be calculated using equation (104) if the sorption isotherms are known. It should be equivalent to equation (75), to the term  $(T s_v)$  of equation (109), and to the following expression obtained from equation (107):

$$\left(T \frac{d\mu_1^\circ}{dT}\right) + \Delta H_s + \Delta H_o + E_s + (R T \ln \frac{H p_o}{7600}) \quad [110]$$

## Materials and Methods

### A. Specimen Preparation

The species used in this research were yellow poplar (*Liriodendron tulipifera* L.) and hard maple (*Acer* spp.). These species were chosen because of their uniform structure thereby minimizing wood variability which otherwise would have affected uniformity of moisture flow. The yellow poplar samples were obtained from seven quarter-sawn boards with dimensions of about 3.8 cm (T) x 20 cm (R) x 3 m (L), selected from a pile of lumber used in a lumber-grading class at the Brooks Forest Products Center, Virginia Tech. These boards, which were marked as boards A, B, C, E, F, H and J, were free of defects and composed mainly of heartwood (Table 2). The hard maple samples, on the other hand, were obtained from a log with a diameter of about 55 cm at the butt end. The log was sawn into boards using a 52-inch circular saw. Immediately after sawing, wane was removed from the boards using a two-saw edger. The size of the boards after edging was approximately 3.8 cm (T) x 13 cm (R) x 3 m (L). Four quarter-sawn boards, mostly sapwood, were obtained and were

**Table 2. Percentage of heartwood and oven-dry specific gravity of yellow poplar and hard maple boards used in the research.**

| Species       | Board ID | Percent Heartwood | Oven-dry Specific Gravity <sup>1</sup> |
|---------------|----------|-------------------|----------------------------------------|
| Yellow Poplar | A        | 98%               | 0.441 (2)                              |
|               | B        | 60%               | 0.403 (2)                              |
|               | C        | 80%               | 0.466 (4)                              |
|               | E        | 90%               | 0.554 (2)                              |
|               | F        | 90%               | 0.531 (2)                              |
|               | H        | 80%               | 0.384 (4)                              |
|               | J        | 40%               | 0.569 (2)                              |
| Hard Maple    | W        | 10%               | 0.706 (2)                              |
|               | X        | 0%                | 0.710 (2)                              |
|               | Y        | 5%                | 0.722 (2)                              |
|               | Z        | 5%                | 0.722 (2)                              |

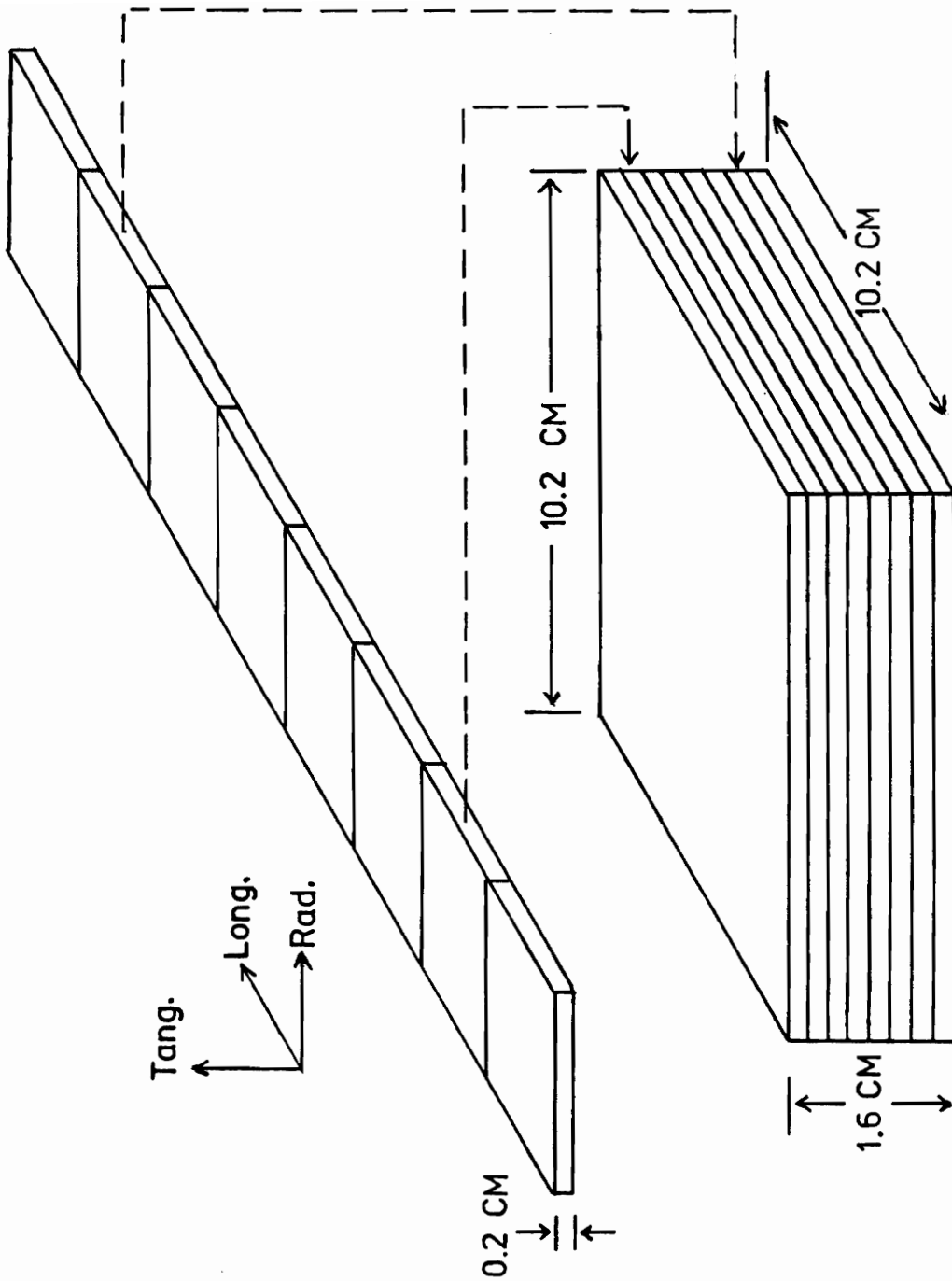
<sup>1</sup> The number in parenthesis refers to the number of replicates obtained from a given board for the specific gravity determination.

marked as boards W, X, Y and Z (Table 2). When the research was started, the yellow poplar samples had been sitting in the sawmill for several months and so had dried considerably. In order for the two sets of samples to have more or less the same drying history, the hard maple samples were also left in the sawmill to air dry. This lasted for several weeks while preliminary experiments were being conducted.

After removing about 30 cm of materials from each board for specific gravity determination and sorption studies, each board was sawn into "veneers" about 0.7-cm thick in a band saw. Each veneer was surfaced on both sides in a planer to about 0.2-cm thickness producing several flat strips of quarter-sawn veneer. Each strip was then trimmed into 11 cm-long pieces producing several wafers. Eight end-matched wafers were combined to form an assembly of about 1.6 cm thickness. The width and the length of the assembly were further reduced on a belt sander to 10.2 cm for yellow poplar and 8.9 cm for hard maple, finally resulting in experimental units of 1.6 cm thick, 10.2 cm wide and 10.2 cm long for yellow poplar, and 1.6 cm thick, 8.9 cm wide and 8.9 cm long for hard maple (Figure 4). A total of 24 assemblies were generated from the seven yellow poplar boards, while 20 sets were formed from the four hard maple boards.

## **B. Specific Gravity Determination**

The specific gravity on an oven-dry volume and weight basis was measured using Method B of ASTM D2395-83 (American Society for Testing and Materials, 1989). A total of 18 replicates were used for yellow poplar, and eight for hard maple. The average specific gravity of each board and of each species are shown in Table 2, where



**Figure 4.** Dimensions of the yellow poplar assembly obtained from end-matched wafers cut from a single veneer strip: The corresponding dimensions of the hard maple assembly were 1.6 cm x 8.9 cm x 8.9 cm.

the number in parenthesis refers to the number of replicates obtained from a given board.

### **C. Determination of Sorption Isotherms**

From the 30-cm sample removed from each board, sorption specimens about 0.60 cm thick were taken. The cross section of the samples varied in dimensions but on the average the area of the yellow poplar and hard maple specimens were 15 sq. cm and 20 sq. cm, respectively. The thickness was chosen to be in the longitudinal direction so as to allow rapid attainment of equilibrium at a given temperature and relative humidity condition.

Different specimens were used for adsorption and desorption determinations. Matching of samples was, however, observed by having end-matched specimens from a given board equally represented in the adsorption and desorption studies. A total of 18 and 12 replicates for yellow poplar and hard maple, respectively, were employed in the adsorption phase of the study. These were reduced to 12 and eight, respectively, during the desorption cycle to facilitate weight measurements. This decision to bring down the number of replicates was arrived at after careful examination of the adsorption results revealed that differences in calculated moisture content values did not vary much between the samples.

Sample moisture equilibrations were performed in an insulated chamber supplied by a PCG Climate-Lab-AA conditioned air generator. This generator which is equipped with electronic controls was designed to maintain a dry-bulb temperature within  $\pm 0.2^{\circ}\text{C}$  and a relative humidity within  $\pm 0.5\%$ . For accurate measurement of

the temperature and relative humidity inside the chamber, in addition to the generator controls, a Vaisala temperature/humidity probe was inserted into the chamber through a small access port. When this probe broke down, it was replaced by another one manufactured by Omega Co., Inc.. All weight measurements were performed by removing the sample from the chamber and weighing it on a Mettler balance placed near the chamber. The balance allowed weights to be taken to the nearest 0.001 g. Thus, since the lowest oven-dry weight was 5.083 g, the error was no greater than 0.02%. It required 30 sec to remove a sample from the controlled chamber, weigh it in the analytical balance and then put it back into the chamber.

All adsorption samples were oven dried overnight at  $103 \pm 2^\circ\text{C}$  before being placed into the controlled chambers. The specimens were first exposed to a relative humidity of 28% and dry-bulb temperature of  $30^\circ\text{C}$ . When weight changes could no longer be detected, after about 9 to 11 days, the samples were weighed individually to get their equilibrium weights,  $W_m$ . While maintaining the same temperature, the relative humidity was changed to the next higher level and the process of equilibration and weight measurement repeated at relative humidity conditions of 41.2%, 61.8%, 66.5%, 76.6% and 83.8%.

For the desorption phase of the study, the other group of samples were first moistened with liquid water to a minimum moisture content of 40%. They were then wrapped in plastic for two days to permit moisture equilibration without loss of moisture prior to being placed in the controlled environment chamber. The equilibrium weights  $W_m$  of the samples were then taken at chamber conditions of successively lower relative humidities of 82%, 68%, 61.8%, 40.5% and 33.6% all at  $30^\circ\text{C}$ .

After the last step, the samples were placed in an oven maintained at  $103 \pm 2^\circ\text{C}$  for about 24 h to get their oven-dry weights,  $W_o$ .

## **D. Nonisothermal Steady-state Experiments**

In this part of the research, constant but different temperatures were maintained on opposite faces of a closed wood assembly in order to obtain the steady-state distribution of moisture content and temperature in the material.

### **1. Preliminary Experiments**

A number of preliminary test runs were carried out in order to develop the apparatus and the experimental techniques used in the bulk of the nonisothermal experiments. There were three specific objectives in these test runs. The first was to develop a suitable method for minimizing moisture loss from the samples during the experiment. The second was to determine the most suitable moisture and temperature ranges for the study. The third was to estimate the time required for the test assemblies to attain moisture equilibrium.

One of the problems encountered in this investigation was in finding a way of preventing the wood from exchanging moisture with the environment. Different coatings were first tested by applying several layers of a given sealant to a piece of wood and then clamping this to a vapometer cup half-filled with water. Several sealants performed well but based on a combination of factors, like water impermeability, ease of handling and relative safety, a vinylidene chloride-

methylethacrylate-acrylonitrile polymer dispersion in water (Daran SL 112 distributed by W.R. Grace and Co.) was chosen. By itself, this coating could not prevent moisture loss from the sample so it was reinforced with an aluminum foil sheet and a 100% solids polyisobutylene-butyl preformed sealant (Tremco 440). The results of test runs using flat-sawn balsa (*Ochroma pyramidale*) and yellow poplar assemblies indicated good performance since a moisture balance analysis yielded less than 1% moisture loss when a sample initially at 12% MC was subjected to temperatures of 56°C and 19°C on opposite faces for three weeks. Other samples exhibited lower moisture loss while others showed a slight increase in moisture content.

Another objective in performing the preliminary experiments on balsa and yellow poplar was to have an idea as to the levels of the factors (initial moisture content, and temperature difference between the hot and cold plates) to use in the final experiments. It was foreseen that if the initial moisture content and the temperature difference were high, the moisture content near the cold plate would go beyond the fiber saturation point causing some complications in the analysis. This is demonstrated in Choong's nonisothermal data (Choong, 1962) where some samples had moisture contents as high as 100%. Some investigators (Siau, 1980b; Nelson, 1986b), in analyzing the data often disregarded the high MC values. While it is informative to have such samples where some parts go beyond the fiber saturation point, it unduly complicates a study whose main objective is to characterize moisture movement in the hygroscopic range. Thus, since the preliminary experiments were done at hot and cold face temperatures of approximately 55 and 15°C, respectively, on samples with initial MC of about 12% and since at these conditions large moisture content values developed near the cold face, it was decided that the temperature difference be reduced to 20°C and that the initial MC must not exceed 15%. Thus two temperature

ranges (15 to 35°C and 25 to 45°C) and three moisture content levels (9, 12 and 15%) were chosen for the final studies. The two temperature ranges also dictated the temperature used in the sorption studies, 30°C being midway between the two temperature extremes of 15 and 45°C. The reasoning behind the choice of the two temperature ranges lies in the fact that if two samples, A and B, are from the same species and are of the same initial MC but A is subjected to the 15 to 35°C temperature difference, while B is exposed to the 25 to 45°C temperature difference, then if it is supposed that the temperature profile across the thickness of the material is linear, the temperature gradient is the same in both materials but at a given location along the axis of decreasing temperature, the temperature in A will be lower than the temperature in B. Thus significant statements/comparisons can be made concerning the effect of temperature on the property being investigated.

The preliminary experiments also provided information on the duration of a given experiment. It took at least three weeks for the samples to reach steady state. If one week extension is allowed just to be certain that the steady state has indeed been attained, and assuming a one-week down time between runs, it would have taken at least 15 months to do just the nonisothermal steady-state phase of the research at the then existing set-up of four samples per run. Based on this projection, efforts were made to expand the capacity of the existing facilities (see next section).

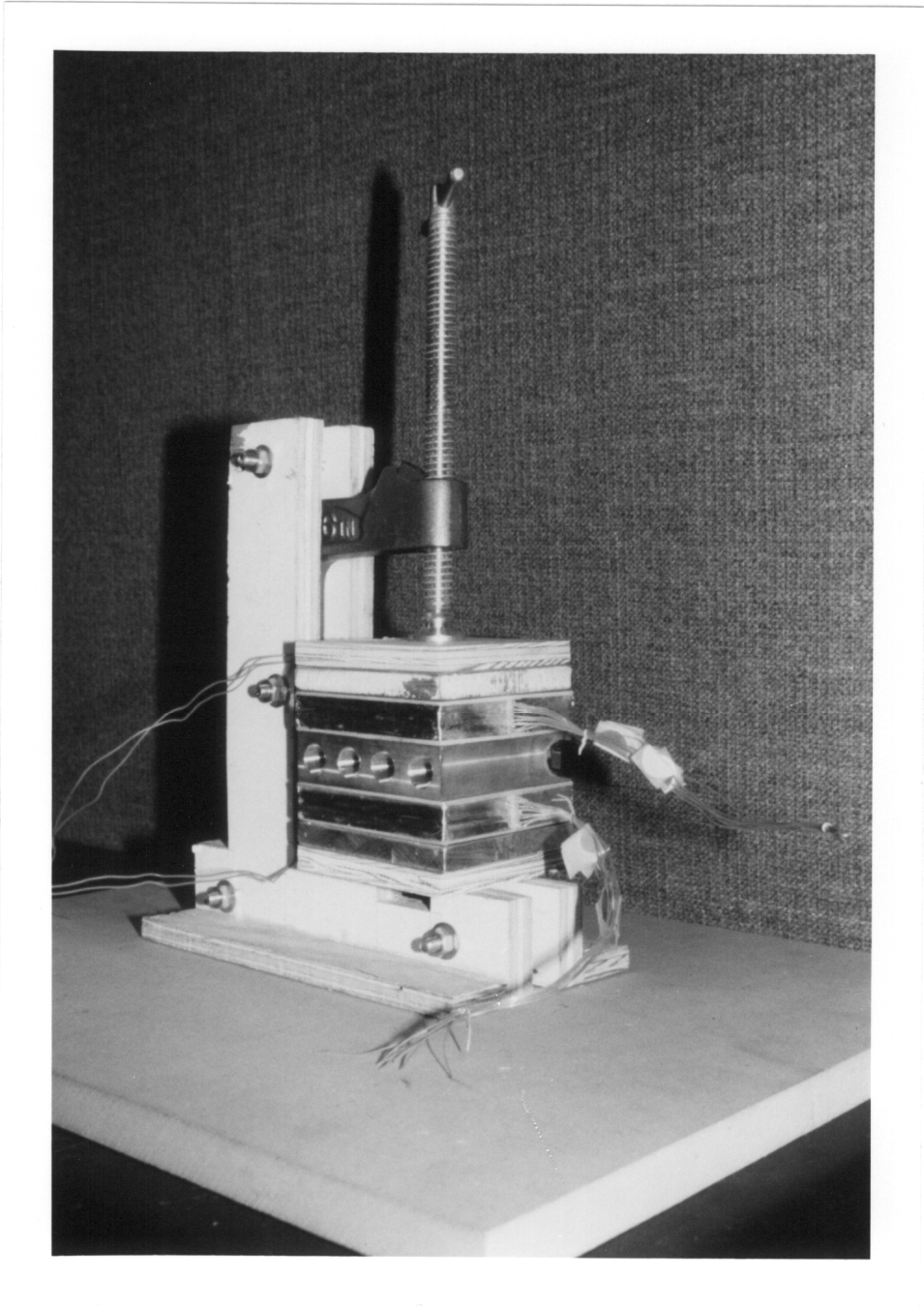
## ***2. Hardware Preparation***

The set-up consisted of a wood assembly clamped between temperature controlled platens such that constant but different temperatures were maintained on opposite faces. C-clamps were used to hold the wood assembly and the plates

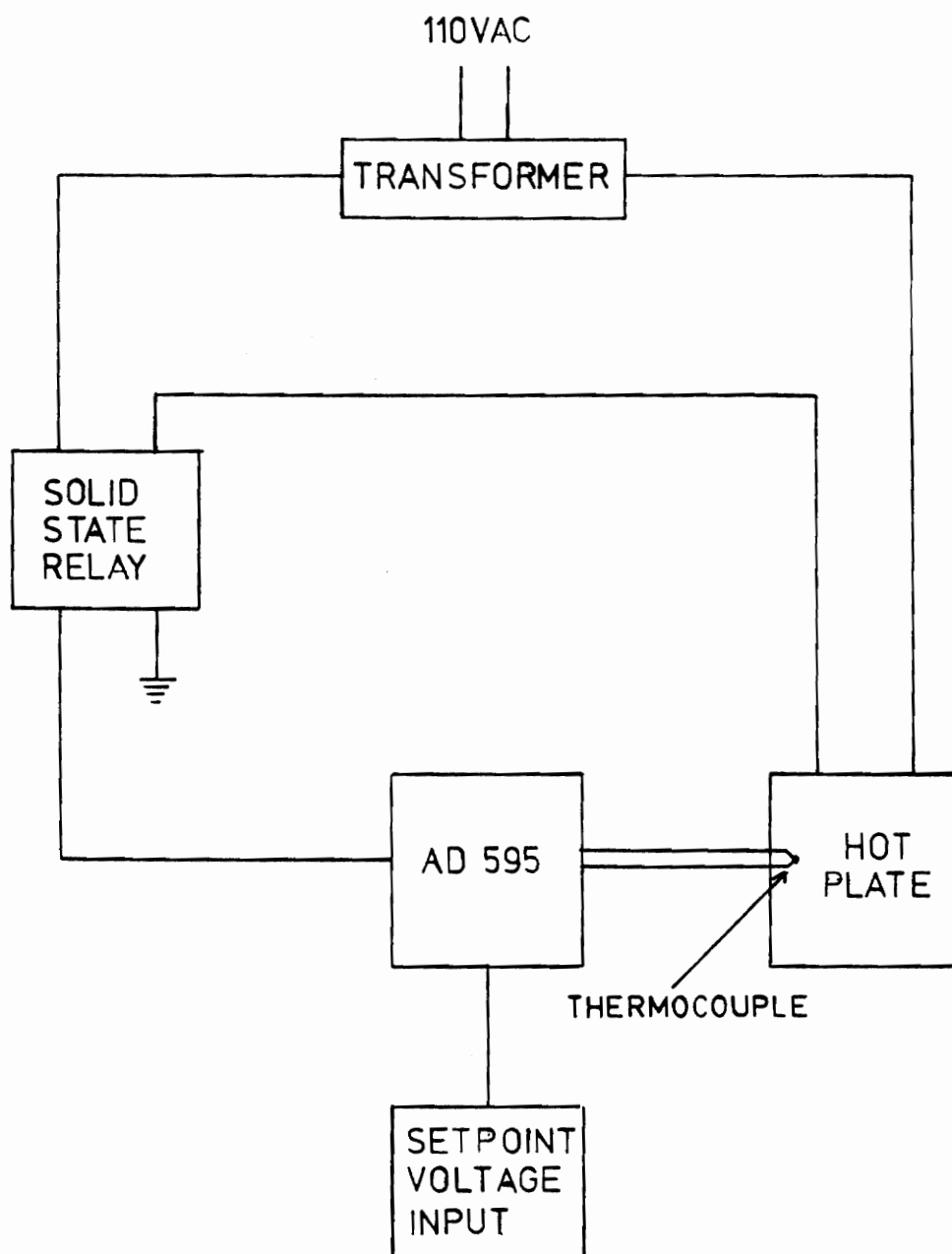
together. For each C-clamp, two assemblies were accommodated (Figure 5). The cold plate was placed between the two samples which in turn were sandwiched between the two hot plates. The 10.2 cm x 10.2 cm hot plate was made of 1.3 cm thick aluminum sheet bonded to an etched-foil heating element (Minco Thermofoil). A total of 16 rough aluminum plates were finished in the machine shop and each was mounted with a heater. A small groove was run along the face which was to be in contact with the wood so that a 30 gage thermocouple can be accommodated. The hot plate thermofoil was connected to a temperature controller which was built in the electronic shop. It essentially consisted of a monolithic thermocouple amplifier (AD595) used as a set-point controller. Its input was fed from the thermocouple inserted in the hot plate groove while its output operated a solid state relay which controlled the flow of electricity to the heater (Figure 6).

The 10.2 cm x 10.2 cm cold platen, on the other hand, was prepared from a 1.9 cm thick aluminum sheet. Four parallel holes were drilled at the side of the plate to allow cooling water to flow through. These holes were connected through a plastic tubing to a Fisher Scientific isotemp refrigerated circulator equipped with a thermoregulator and water stirrer. Through the circulation of water, the temperature of the cold plate was kept uniform and constant.

A total of eight C-clamps were prepared allowing 16 experiments to be performed simultaneously (Figure 7). To reduce load and maintain more uniform and constant temperature, two refrigerated circulators were used with each one controlling four cold plates. This also provided flexibility to a given experimental run since the two circulators can be set to maintain different temperatures in each group of four cold plates.



**Figure 5.** Photograph of an assembly showing the two wood samples, and the hot and cold plates held by a c-clamp.



**Figure 6.** Schematic diagram of the hot-plate temperature-control system.

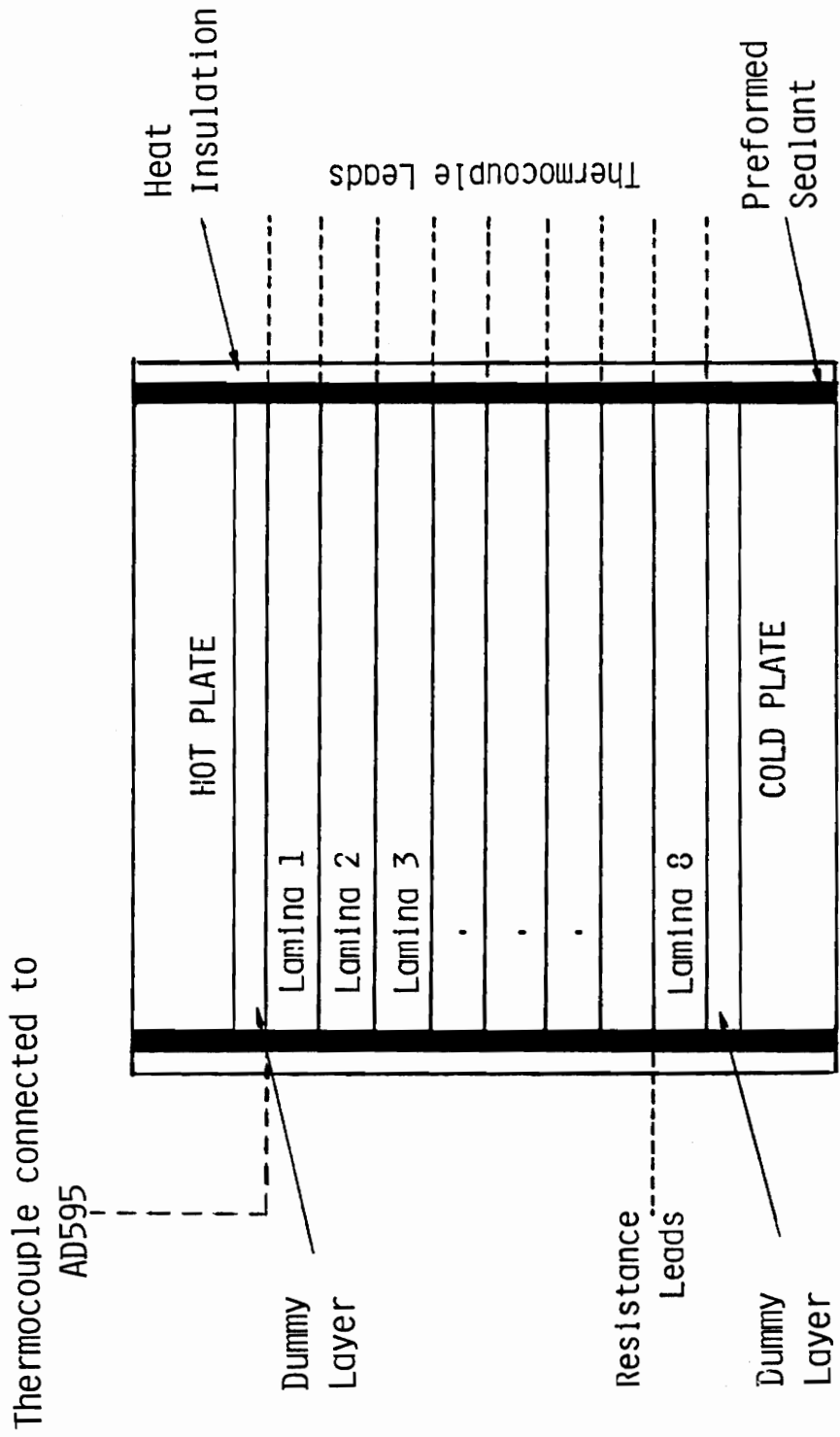


Figure 7. Photograph of the experimental set-up.

### **3. Test Procedure**

The samples were obtained from the wood assemblies described earlier. The different layers of the composite were first conditioned in a controlled environment chamber to the desired initial average moisture content. Once the equilibrium MC was attained, the composite was reassembled. A copper-constantan thermocouple (30 gage) was inserted between each layer of wood in order to allow monitoring of temperature profile in the wood when it was later pressed between the cold and hot plates. With the thermocouples in place, and while applying pressure on the assembly together with dummy layers put on the wide faces, the edges were glued with Duco cement. The dummy layers were 2-mm thick wafers bonded with aluminum foil on the face in contact with the wood assembly, and were added so that the two outermost laminae were not coated with the vapor barrier. After gluing, the assembly was removed from the clamp and was painted on the surface with six layers of Daran SL 112. One layer of aluminum foil was bonded to the edges and then six more layers of the vapor barrier were applied. Once the last coating had dried, the sample was clamped between temperature-controlled plates where opposing longitudinal-radial faces were subjected to different but constant temperatures. This was then the time when the polyisobutylene-butyl preformed sealant was wrapped around the set-up to further reduce moisture loss. To minimize the effect of environmental temperature, the whole set-up was covered with a heat insulator (Figure 8).

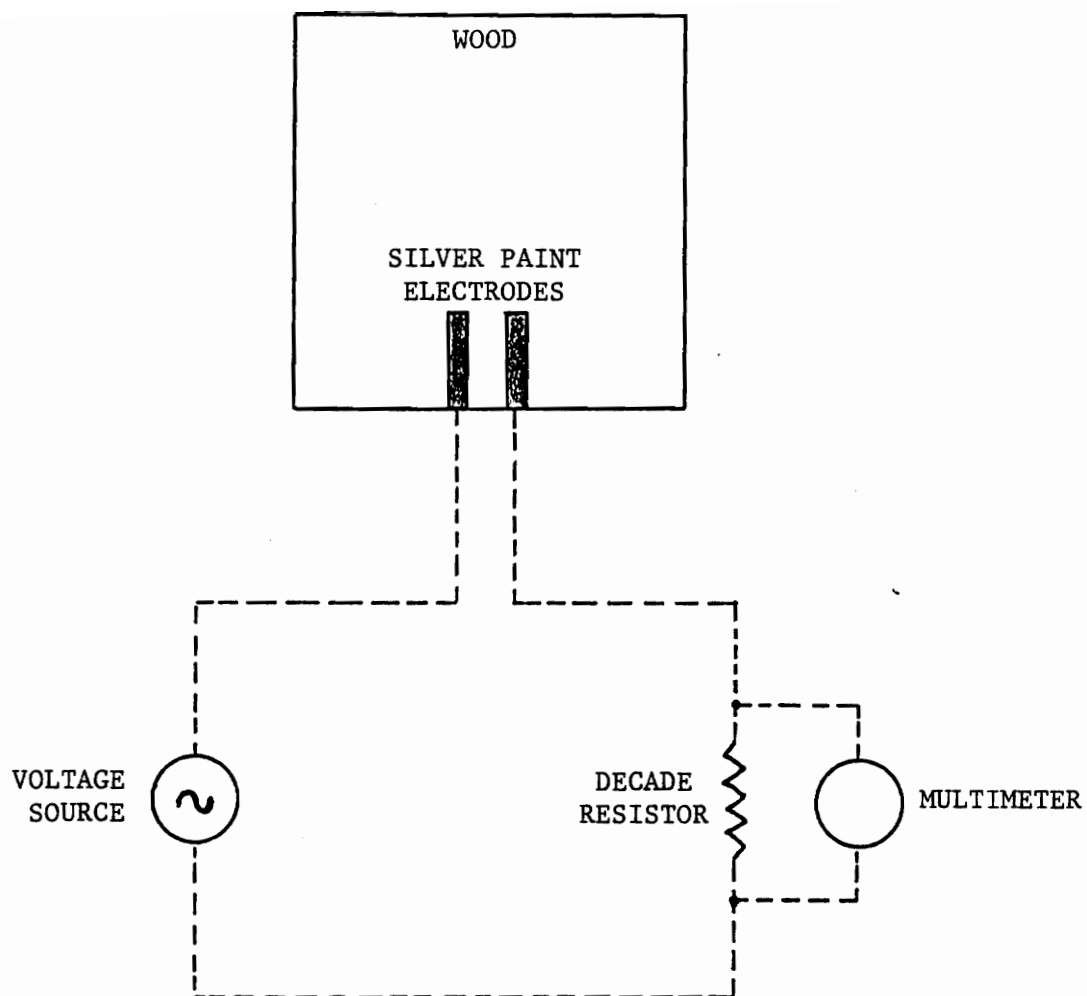
The assembly was left in the set-up until steady state was attained (about 4 to 5 weeks). To determine whether this condition has been reached, the moisture content of the veneer closest to the cold plate was monitored. This was done using electrical resistance electrodes consisting of thin parallel strips of silver paint applied on one



**Figure 8.** Diagram of a wood sample during a given experimental run: Shown are the different wood layers, the sealant and heat insulation wrapped around the sample, and the location of the thermocouple and resistance leads.

surface of the last lamina before the sample was assembled. These electrodes were connected to electrical terminals leading to the measuring instrument (Figure 9). It is very difficult to determine accurately the moisture content based on resistance measurements because of the effect of temperature, spacing of the electrodes, and species. This is complicated by the high electrical resistance of wood (in the megohm range) which presents problems on the range and resolution of the measuring instrument. Thus the main function of the electrodes was just to determine constancy of moisture content to indicate that the steady-state condition had been reached. Gravimetric determination after disassembly was used to obtain actual moisture contents.

Once successive electrical resistance measurements were constant, another week was allowed for the samples to remain in the set-up to be certain that the steady-state condition had indeed been attained. Then the final temperature values at the different layers were taken. (The temperatures were monitored continuously from the start of the experiment by a Hewlett-Packard 3421 data acquisition system in conjunction with an HP Model 75 computer). After removing the sample from the set-up, the edges of the material were sawn to remove the glue and the seal and to separate the different layers. Each lamina was then weighed and the thickness measured, after which it was placed in an oven set at  $103 \pm 2^{\circ}\text{C}$  for at least 24 h to obtain the oven-dry weight. All weights were taken to within 0.001 g while the thickness were measured to within 0.001 inch resulting in percent errors of 0.02% and 1.4% for the weight and thickness, respectively. From the oven-dry weight and the weight measured immediately after disassembly, the moisture content of each lamina was calculated, hence the moisture profile across the thickness was determined.



**Figure 9.** Circuit for monitoring the resistance between two silver-paint electrodes applied on one surface of the veneer closest to the cold plate.

The temperature profile was obtained from the values of the temperature at the different layers just prior to disassembly.

The procedure described above differs from that used by Voigt et al (1940) and Choong (1963), both of whom used solid wood blocks. The use of an assembly of laminae has several advantages over that of a solid block of wood. First is that the moisture distribution upon completion of an experiment can be measured more quickly and accurately since the individual laminae can be removed and isolated rapidly, compared with the sectioning procedures required for a solid wood sample. Secondly, the same samples can be used in several different experiments, thus minimizing the variability in the material among experiments. Thirdly, temperature probes can be located easily in the test samples so that temperature profile can be determined conveniently. If a moisture sensor is available, it can also be inserted in the assembly to allow 'in situ' moisture content determinations. Lastly, a given test assembly consisting of a number of end-matched laminae, all from similar growth increments, will generally be more homogeneous than a single block containing wood from a large number of growth increments.

The primary disadvantage of the laminate assembly is the presence of discontinuities in the wood at the interfaces between laminae. This is not a serious disadvantage, however, since the faces are in close contact because of the pressure applied to the assembly. Furthermore, moisture movement between laminae is much faster than through the wood itself, vapor transport in air being so much more rapid than transport through wood. There may be a greater effect on heat transport since this is more rapid through wood than through still air. This effect can be minimized

by use of sufficiently high pressure on the assembly to assure good thermal contact between adjacent laminae.

#### ***4. Experimental Variables and Design***

The three experimental variables investigated in this research were species, initial moisture content, and temperature range. The two species were, as mentioned earlier, yellow poplar and hard maple; while the two temperature range levels were 15 to 35°C , and 25 to 45°C. The actual temperatures on the cold and hot faces of the samples varied slightly from the target values. The error, however, was very small, the deviation being no more than 2°C from the temperatures cited above.

The three moisture content levels were, nominally 9, 12 and 15%. Again, there were variations among samples because of the inherent heterogeneity of wood. In conditioning the materials to a given moisture content, all the samples were placed in a controlled environment chamber set to the dry-bulb temperature and relative humidity conditions which gave an equilibrium moisture content as close to the desired level as possible. Apparently, hard maple is slightly more hygroscopic than yellow maple (see results of sorption studies) that the moisture contents of the hard maple samples were higher than those of the yellow poplar specimens.

All 44 assemblies obtained from the seven yellow poplar and four hard maple boards were used in this study. Randomization was used in allocating the 44 assemblies among the different combinations of the three factors, resulting in the treatment assignment shown in Table 3. Because of the smaller number of samples obtained from the hard maple boards, the number of replications per treatment com-

**Table 3. Allocation of the experimental units among the different treatment combinations in the nonisothermal steady-state experiments.**

| <b>Species</b>   | <b>Temperature Range<br/>(C)</b> | <b>Initial Moisture<br/>Content (%)</b> | <b>Experimental Units<sup>1</sup></b>     |
|------------------|----------------------------------|-----------------------------------------|-------------------------------------------|
| Yellow<br>Poplar | 15 - 35                          | 9                                       | A5, B4, C4, A7                            |
|                  | 15 - 35                          | 12                                      | H1, C1, F1, E1                            |
|                  | 15 - 35                          | 15                                      | B3, H2, A3 <sup>2</sup> , C2 <sup>2</sup> |
|                  | 25 - 45                          | 9                                       | A6, B5, E3, C5                            |
|                  | 25 - 45                          | 12                                      | B1, A2, E2, A1                            |
|                  | 25 - 45                          | 15                                      | B2, A4, C3, J1                            |
| Hard<br>Maple    | 15 - 35                          | 9                                       | X1, Z1, X3, Y1                            |
|                  | 15 - 35                          | 12                                      | W3, X7, X9                                |
|                  | 15 - 35                          | 15                                      | X5, Z4, W2                                |
|                  | 25 - 45                          | 9                                       | X2, Z2, X4, W1                            |
|                  | 25 - 45                          | 12                                      | W4, Y2, X8                                |
|                  | 25 - 45                          | 15                                      | Z3, Y3, X6                                |

<sup>1</sup> The letter in the experimental unit identification tag refers to the board from which it was taken.

<sup>2</sup> These two samples were not included in later analyses because moisture balance tests revealed that considerable moisture loss occurred in these samples during the experiment.

bination involving this species was reduced in some cases from four to three resulting in an unbalanced experimental design. This study was then performed as a three-factor factorial experiment in a completely randomized design. An end-of-experiment mass balance test revealed that considerable moisture loss occurred in two samples (A3 and C2) so they were excluded in subsequent analyses.

## Results and Discussion

The two basic experiments in this study are the development of moisture sorption isotherms and the nonisothermal moisture transport experiments. The sorption studies are discussed first, followed by consideration of the transport experiments.

### A. Sorption Studies

The equilibrium moisture content values  $M$  of each sample at the different relative humidity conditions  $H$  were calculated using the equation

$$M = \frac{W_M - W_o}{W_o} 100 \quad [111]$$

where  $W_M$  is the weight of the sample at the moisture content in equilibrium with the given relative humidity; and  $W_o$  is the oven-dry weight of the sample. The adsorption and desorption values for yellow poplar are shown in appendix Tables A1 and A2, while those for hard maple are shown in Tables A3 and A4, respectively.

Subsequent parts of this work rely heavily on the interconversion between moisture content and relative humidity, therefore, a convenient way of expressing the relationship between these two quantities must be obtained for the data in Tables A1 to A4. The literature is full of empirical, quasi-empirical, and theoretical equations forwarded to describe sorption data. Van den Berg and Bruin (1981), for instance, listed as many as 75 equations which have been applied to the sorption of water by biological materials. The different mathematical models have their own advantages and disadvantages, and the adoption of a particular equation depends on the purpose for selecting a model. Thus if the objective is for predicting thermodynamic variables, a particular equation may perform very well but it may perform poorly if used for instance to predict the mechanical properties of the adsorbent. For this study, the objective is mainly to obtain a mathematical equation whose parameters fit the experimental data well, thereby facilitating handling of the moisture content - relative humidity data in future work. For its simplicity and proven good performance when fitted to wood sorption data (Spalt, 1958; Simpson, 1971, 1973, 1980; Okoh, 1976), the Hailwood-Horrobin single-hydrate model was used here. The theory assumes that water in the cell wall exists in two states, viz, as water which forms a hydrate with the wood and as water in solution with the polymer; and that the three species present - dissolved water, unhydrated polymer, and hydrated polymer - form an ideal solid solution (Hailwood and Horrobin, 1946). Mathematically, the model can be expressed as follows:

$$M = \frac{1800}{M_p} \left( \frac{K_1 K_2 H}{100 + K_1 K_2 H} + \frac{K_2 H}{100 - K_2 H} \right) \quad [112]$$

where  $M_p$  is the molecular weight of wood per mole of sorption sites;  $K_1$  the equilibrium constant between the reaction product (hydrated wood) and the two reactants

(water and dry wood); and  $K_2$  the equilibrium constant between water vapor and dissolved water. To obtain these parameters, nonlinear regression analyses were performed on the sorption data (Myers,1986). The statistical model is written as

$$M_i = \frac{1800}{M_p} \left( \frac{K_1 K_2 H_i}{100 + K_1 K_2 H_i} + \frac{K_2 H_i}{100 - K_2 H_i} \right) + \varepsilon_i \quad [113]$$

for  $i = 1, 2, \dots, n$ .

where  $\varepsilon_i$  is the model error and  $n$  the number of observations. The Marquardt option (Marquardt, 1963) of the NLIN procedure in the Statistical Analysis System package (SAS, 1985) was used to obtain the parameter values. Since this procedure requires starting estimates for the parameters, the values reported by Simpson (1973) for the Wood Handbook data (U.S. Forest Products Laboratory, 1955) were used as the initial quantities. In all cases convergence was achieved in five iterations. The results of the analyses are summarized in Table 4, while the graphs of the isotherms fitted to the data points are shown in Figures 10 and 11. To gain insight into the quality of the fit, the predicted moisture content values ( $\hat{M}$ ) using the parameters in Table 4, together with the residual ( $M - \hat{M}$ ), are included in Tables A1 to A4.

If equation (112) is solved for  $H/M$ , the theory predicts a quadratic relationship between  $H/M$  and  $H$  of the form

$$\frac{H}{M} = A + B H - C H^2 \quad [114a]$$

where

$$A = \frac{M_p}{18} \left( \frac{1}{K_2 (K_1 + 1)} \right) \quad [114b]$$

**Table 4. Hailwood-Horrobin sorption coefficients at 30 C for yellow poplar and hard maple; and for various woods studied by different investigators.**

| Kind of Wood <sup>1</sup>   | M <sub>p</sub> | $\frac{1800}{M_p}$ | K <sub>1</sub> | K <sub>2</sub> | A    | B    | C                     |
|-----------------------------|----------------|--------------------|----------------|----------------|------|------|-----------------------|
| Yellow poplar, A            | 349.99         | 5.14               | 5.49           | 0.81           | 3.71 | 0.13 | 1.33x10 <sup>-3</sup> |
| Yellow poplar, D            | 217.36         | 8.28               | 5.08           | 0.69           | 2.88 | 0.08 | 6.97x10 <sup>-4</sup> |
| Hard maple, A               | 319.03         | 5.64               | 4.72           | 0.78           | 3.97 | 0.12 | 1.14x10 <sup>-3</sup> |
| Hard maple, D               | 210.79         | 8.54               | 4.95           | 0.69           | 2.85 | 0.08 | 6.72x10 <sup>-4</sup> |
| Spalt's data <sup>2</sup>   |                |                    |                |                |      |      |                       |
| Basswood, A                 | 364.14         | 4.94               | 9.49           | 0.83           | 2.32 | 0.16 | 1.52x10 <sup>-3</sup> |
| Basswood, D                 | 235.55         | 7.64               | 5.17           | 0.76           | 2.80 | 0.09 | 8.31x10 <sup>-4</sup> |
| Softwoods, A                | 294.07         | 6.12               | 8.30           | 0.76           | 2.36 | 0.13 | 1.10x10 <sup>-3</sup> |
| Softwoods, D                | 221.46         | 8.13               | 7.83           | 0.71           | 2.00 | 0.09 | 7.77x10 <sup>-4</sup> |
| Avramidis' data             |                |                    |                |                |      |      |                       |
| W. white pine, A            | 388            | 4.64               | 5.76           | 0.80           | 3.97 | 0.15 | 1.47x10 <sup>-3</sup> |
| W. white pine, D            | 271            | 6.64               | 7.63           | 0.72           | 2.41 | 0.12 | 9.64x10 <sup>-4</sup> |
| Wd. Hdbk. data <sup>3</sup> | 260.89         | 6.90               | 5.72           | 0.75           | 2.87 | 0.10 | 9.28x10 <sup>-4</sup> |

<sup>1</sup> The letters A and D after the name of the species stand for adsorption and desorption, respectively.

<sup>2</sup> These are values reported at 90°F. The softwood values are the average for 8 softwood species.

<sup>3</sup> Values were computed at 86°F using the equations given by Simpson (1981).

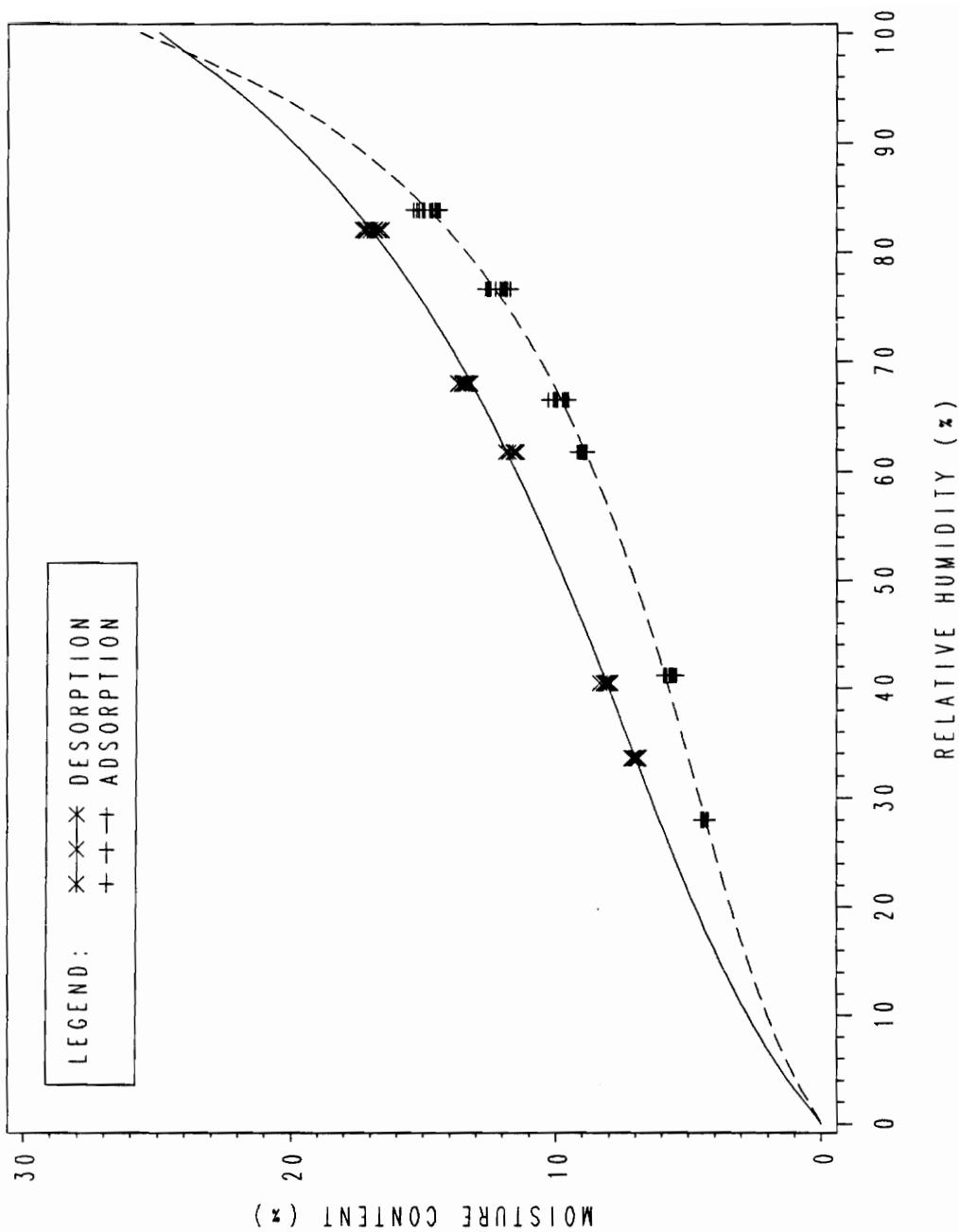


Figure 10. Desorption and adsorption curves fitted to the yellow poplar sorption data.

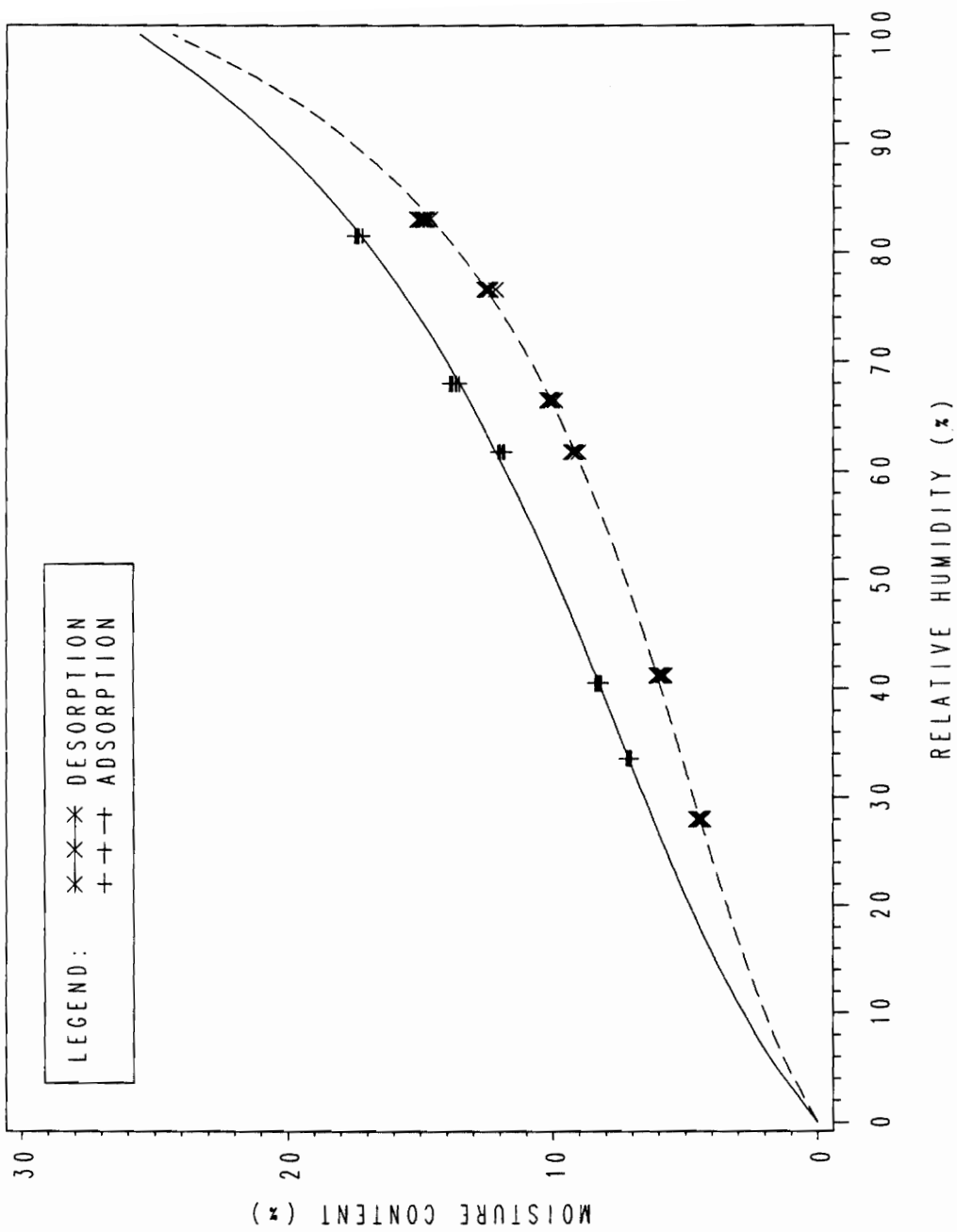


Figure 11. Desorption and adsorption curves fitted to the hard maple sorption data.

$$B = \frac{M_p}{1800} \left( \frac{K_1 - 1}{K_1 + 1} \right) \quad [114c]$$

$$C = \frac{M_p K_1 K_2}{180000 (K_1 + 1)} \quad [114d]$$

The coefficients A, B, and C in equation (114a) were calculated from the values of  $M_p$ ,  $K_1$ , and  $K_2$  and are included in Table 4. Also shown in Table 4 are the values of the Hailwood-Horrobin coefficients obtained by other investigators for various woods (Spalt, 1958; Simpson, 1971; and Avramidis, 1986). The moisture content at different levels of relative humidity were computed using the parameters in Table 4 and are presented in Figures 12, 13, and 14.

Sorption hysteresis is often measured by taking the ratio of the adsorption-to-desorption moisture content (AD) at a given relative humidity. The values presented in Figure 15 were obtained for the relative humidity range (25% to 85%) used in this study at 5% intervals. To obtain an average value ( $\overline{AD}$ ), the equations for the isotherms were integrated between the limits of RH=25% and RH=85%, and then the result for adsorption was divided by the result for desorption:

$$\overline{AD} = \frac{\left[ \int_{25}^{85} \frac{H}{A + B H - C H^2} dH \right]}{\left[ \int_{25}^{85} \frac{H}{A + B H - C H^2} dH \right]} \quad [115]$$

The nonlinear regression analyses showed that the Hailwood-Horrobin sorption model gives a good fit to the data over the experimental range of humidities. Absolute

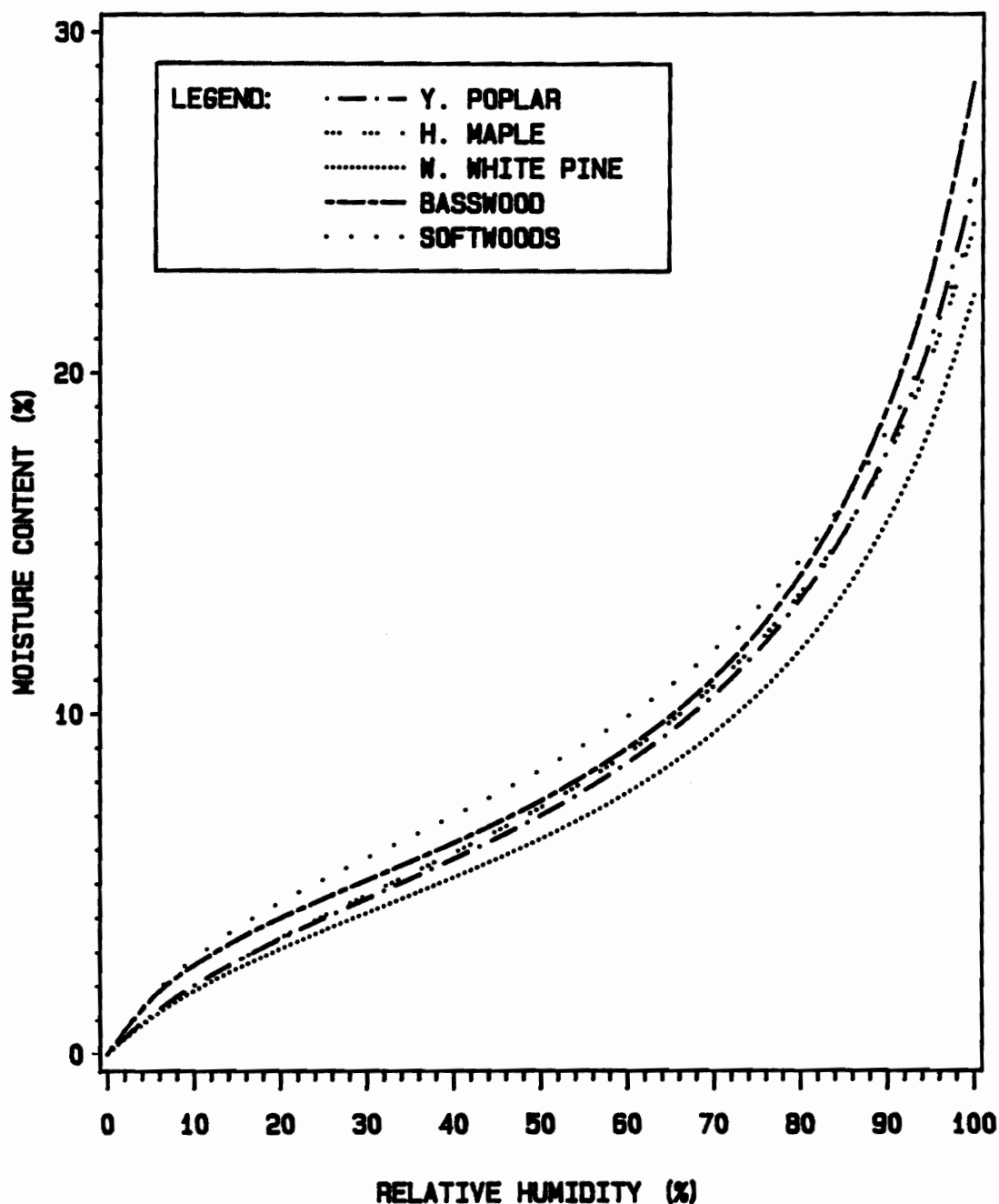


Figure 12. Adsorption isotherms for various woods obtained using the Hailwood-Horrobin parameters in Table 4.

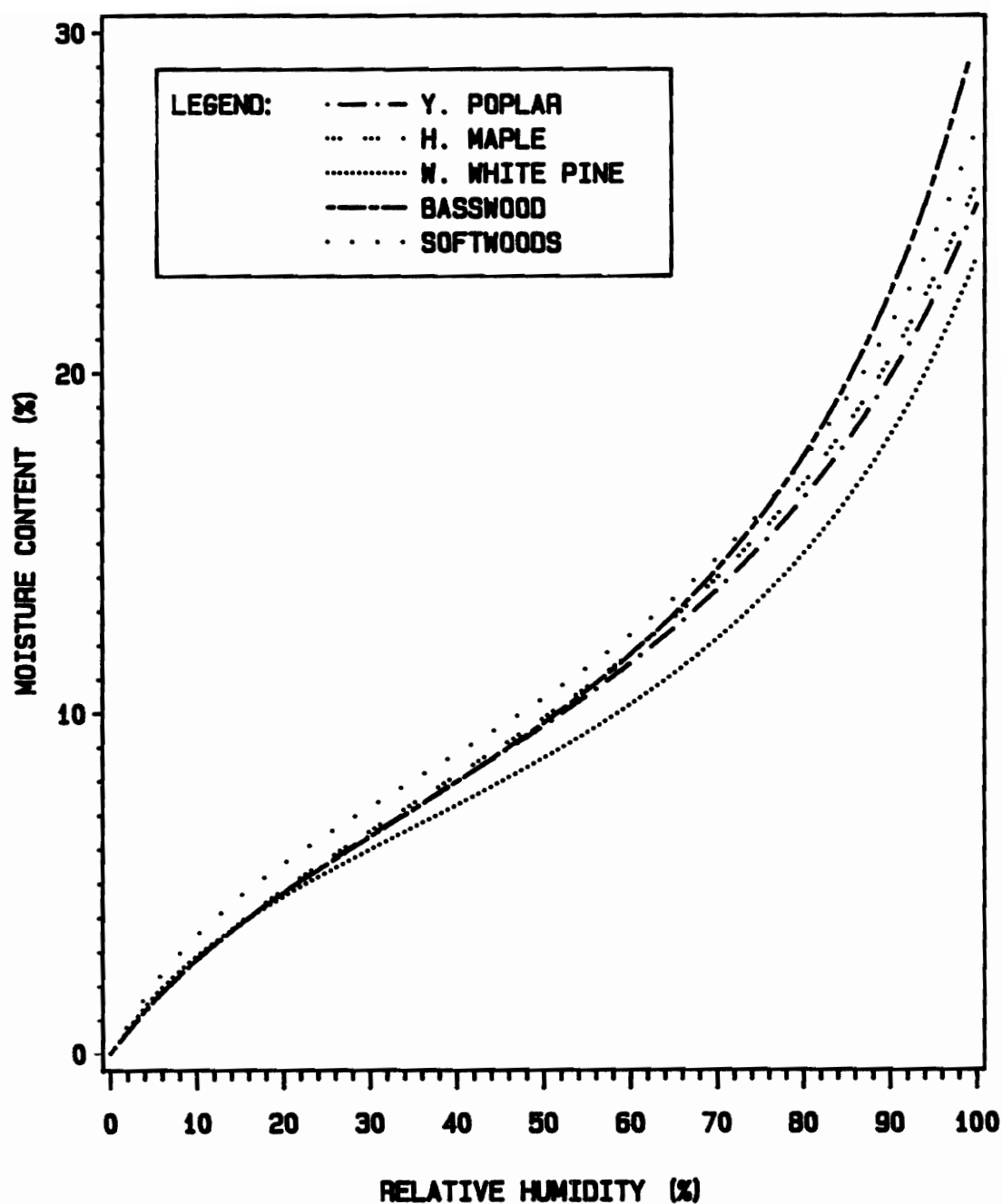


Figure 13. Desorption isotherms for various woods obtained using the Hailwood-Horrobin parameters in Table 4.

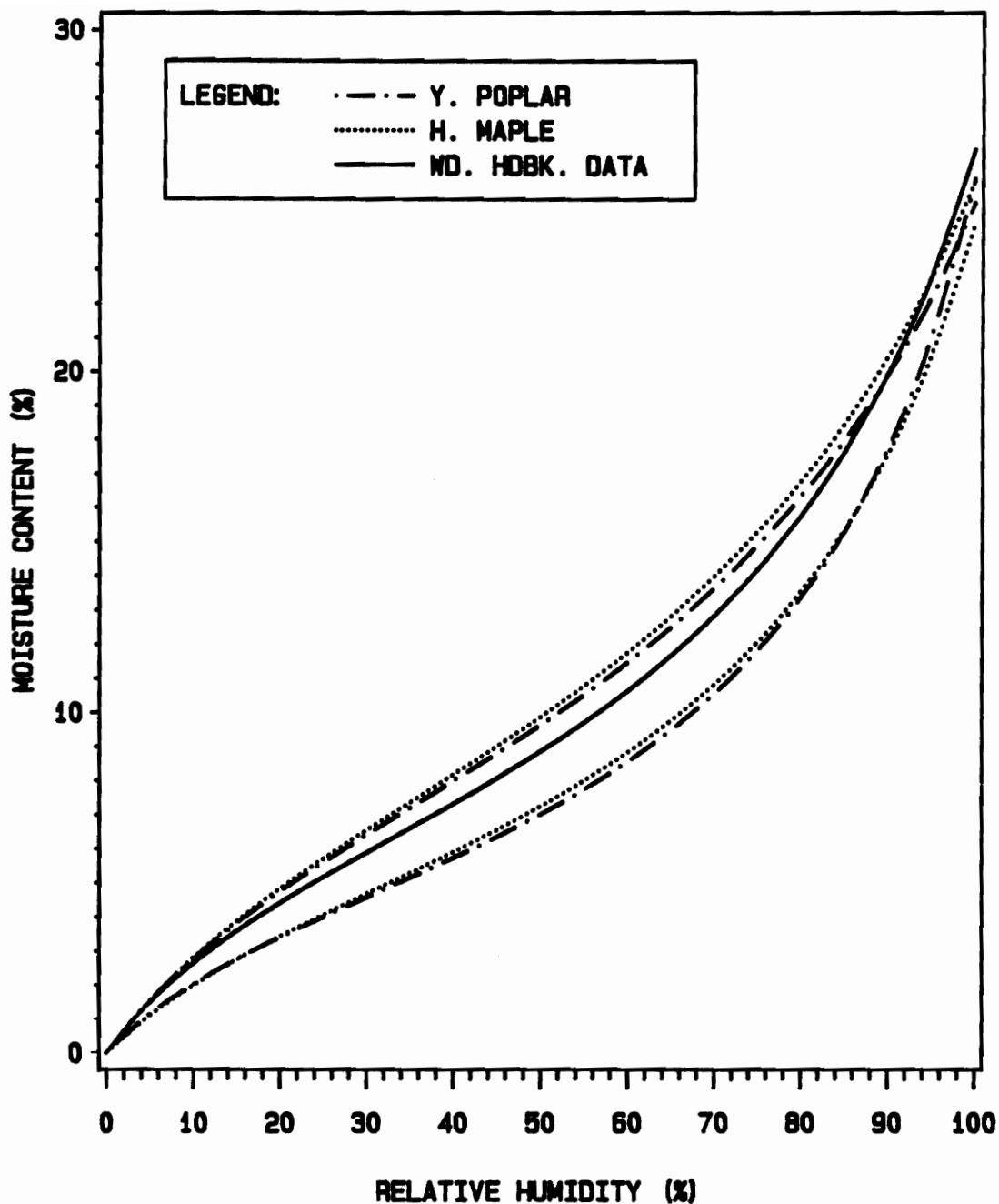


Figure 14. Adsorption and desorption isotherms at 30 C of yellow poplar and hard maple, together with the Wood Handbook isotherm.

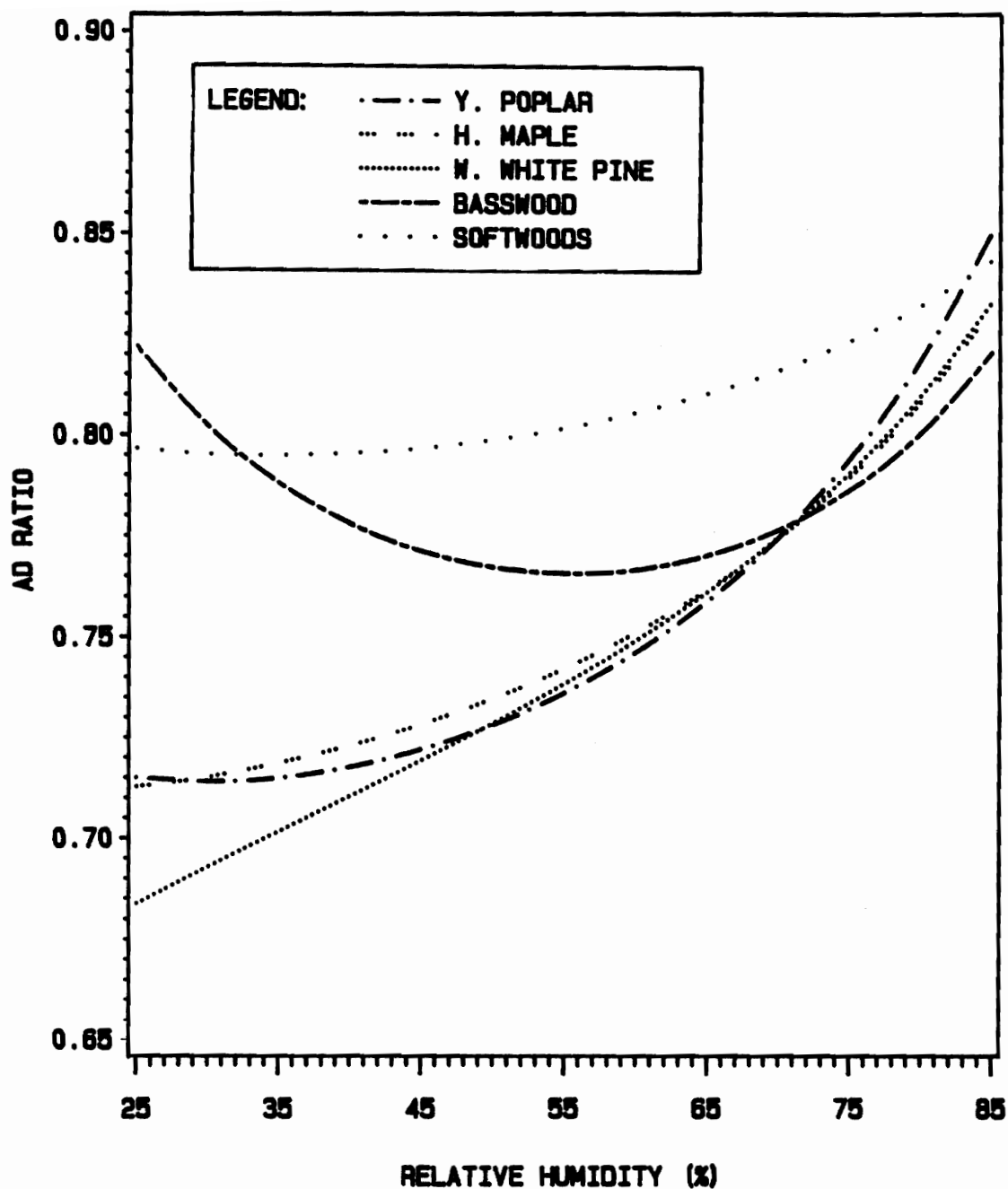


Figure 15. Graphs of the adsorption-to-desorption moisture content ratio of yellow poplar and hard maple at different relative humidity values: Also included are those of Avramidis' data for western white pine, and of Spalt's data for basswood and various softwoods.

deviations of less than 0.60% were obtained for all four curves, reflecting the theory's ability to reasonably describe the sorption process for wood. The model adequately showed the sigmoid shape of the isotherm and the expected moisture content corresponding to complete monolayer coverage of all available sorption sites ( $1800/M_p$ ).

Comparison of the sorption curves of the two species used in this study shows that hard maple is more hygroscopic than yellow poplar but the difference is very small, the maximum difference being no greater than 0.5% MC. Also, looking at the values of  $(1800/M_p)$  in Table 4, a quantity which indicates the amount of sorption sites available for bonding with water, the calculated values for hard maple were higher than those for yellow poplar both in desorption and adsorption, the difference though is again negligible. This is not entirely unexpected since the chemical compositions of the two species, especially the extractives content, are not so different; the amount of sapwood and heartwood in the samples were about the same; and the samples used in the study had more or less the same sorption history.

The parameters obtained in this experiment compare reasonably well with those obtained by other investigators. Particular attention is given to the quantities obtained by Spalt (1958) for basswood since this species is the only hardwood in the reference group and, therefore, should have a sorption curve close to those of the two hardwood species used in this study. Spalt actually studied 7 more hardwood species but these were of tropical origin and, therefore, were no longer included in this comparison. Various investigators have observed temperate zone woods to be more hygroscopic than tropical woods, and this is attributed mainly to the higher average extractives content of the latter (Okoh, 1976; Wangaard and Granados, 1967). Notice in Figures 12 and 13 that the sorption curves for basswood closely follow those

of yellow poplar and hard maple in the relative humidity range used in this study. A divergence though may be observed at high relative humidities (85% to 100%), attributed most likely to uncertainties associated with extrapolation. It is not expected that the sorption curves for the three hardwood species be similar since definitely for a variable material like wood, there should be some differences in the hygroscopicities between species, and even within a given species (Wengert and Mitchell, 1979). Of interest in this comparison is to show that the experimental values do not deviate radically from those reported in the literature.

The generally observed lowering of the equilibrium moisture content at a given relative humidity on adsorption relative to that on desorption was also apparent in this study (Figures 10 and 11). In the humidity range investigated, the adsorption moisture content was always lower than the desorption moisture content. In the case of yellow poplar (Figure 10), there was a crossing over of the sorption curves at about 98.5% relative humidity, again most likely a result of uncertainty associated with extrapolation beyond the experimental range. Several explanations have been forwarded to account for hysteresis effect. These have been classified by Skaar (1979) into three categories: (a) the capillary theory which states that hysteresis is caused primarily by the lower contact angle of water within the cell wall capillaries during adsorption than during desorption (Zsigmondy, 1911; Chen and Wangaard, 1968); (b) the sorption site availability theory which postulates that hysteresis is due to a reduction in available hydroxyl sorption sites in the material after it has been dried (Urquhart, 1960); and (c) the thermodynamic hysteresis theory which says that wood is not a perfectly elastic material and, thus, is capable of assuming irreversible deformations under stress as in the case of drying (Barkas, 1945, 1949).

The lower values of  $(1800/M_p)$  for adsorption in Table 4 indicate that lesser sorption sites are available for bonding during adsorption than during desorption. This is explained by Skaar (1972) as mainly the result of the crosslinking of hydroxyl groups in the wood after it has been dried. Another measure of sorption hysteresis, the adsorption-to-desorption moisture content ratio ( $\overline{AD}$ ) is shown in Figure 15. The ratio varies with relative humidity and ranges from 0.71 to 0.85 ( $\overline{AD} = 0.76$ ), values comparable to those obtained by Avramidis (1986) and Spalt (1958). Okoh and Skaar (1980) also obtained, for 10 U.S. hardwoods, hysteresis ratios (0.79 to 0.83) of the same magnitude as the ones observed in this study but caution should be taken in making a comparison since they performed their experiments at a temperature slightly lower than the one used in this investigation. Sorption hysteresis in wood has been found to decrease with increase in temperature (Kelsey, 1957), and may in fact disappear at very high temperatures (Weichert, 1963).

Stamm (1964) pointed out that large wood specimens should have sorption isotherms falling within the hysteresis loop obtained from experiments performed on small specimens. This intermediate curve should be followed by materials subjected to industrial drying conditions. For this reason, the MC vs RH data in the Wood Handbook (U.S. Forest Products Laboratory, 1987) were based on experiments performed on large samples (Stamm and Loughborough, 1935). The existence of an intermediate curve is due to the simultaneous occurrence of desorption and adsorption in the large specimen. During the drying process, the moisture that is desorbed from the center is re-adsorbed near the surface resulting in an oscillating curve that falls within the hysteresis loop (Stamm, 1964). This behavior is reflected in Figure 14 where the sorption curve obtained by plotting moisture content vs. relative humidity using the Hailwood-Horrobin parameters computed by Simpson (1971) for

the Wood Handbook data falls within the hysteresis loop for yellow poplar and hard maple.

## **B. Nonisothermal Steady-state Experiments**

### **1. Moisture Content and Temperature Profiles**

The moisture contents and temperatures of the samples at different locations along the thickness of the specimen are shown in appendix Table A5. The temperature vs distance data were fitted with a model of the form:

$$T = A_T + B_T x \quad [116a]$$

while the moisture content vs distance data were fitted with an equation of the form

$$M = A_M + B_M x + C_M \exp(-D_M x) \quad [116b]$$

The linear regression analyses were performed using the REG procedure while the nonlinear regression analyses were done using the Marquardt option of the NLIN procedure of the SAS statistical package (SAS,1985). A strong linear relationship was obtained between the temperature and distance from the cold face with a square sample correlation coefficient  $r^2$  of at least 0.995 in all linear regression runs, with the linear model being found to be highly significant at the 1% level. Included in Table A5 are the predicted values of temperature ( $\hat{T}$ ) together with the residuals ( $T - \hat{T}$ ). A maximum absolute residual of only 0.96 K was obtained indicating the appropriateness of the linear model in predicting the temperature at different locations along the thickness of the material. The nonlinear model presented in equation (116b) also gave

a very good description of the variation of moisture content with distance from the cold face. This is reflected in the values of  $\hat{M}$  which are very close to the actual values resulting in small residuals, the maximum absolute value being only 0.45% (Table A5). Estimates of the temperature and moisture content coefficients are summarized in appendix Table A6, while three representative graphs showing the temperature and moisture content variation across the thickness of the material are presented in Figures 16 to 18. The temperature and moisture content profiles for the 42 samples were more or less the same as reflected in Figures 16 to 18, the temperature increasing linearly; and the moisture content decreasing exponentially at low values of  $x$ , and linearly at large values of  $x$  with increasing distance from the cold face. For the samples with high initial moisture content (15% MC), the moisture content at locations near the cold face exceeded the fiber saturation point indicating that the temperatures at these locations were below the dew point temperature causing condensation in the cell lumina.

From the equations describing the moisture content and temperature variation with distance from the cold face, the derivatives with respect to location were taken and the ratio of these derivatives  $\frac{dM/dx}{dT/dx}$  was computed for each sample to obtain the experimental value of the quantity  $\frac{dM}{dT}$ . These ratios at different locations where temperatures and moisture contents were measured are presented in Figure 19 for three yellow poplar samples of different initial moisture contents. In order to compare the effect of the different experimental variables (species, temperature range, and initial moisture content) on the final values of  $\frac{dM}{dT}$ , several analyses of variance (ANOVA) were performed. Since  $\frac{dM}{dT}$  as shown in Figure 19 varies with location, the ANOVA were made at 3 different locations: 25%, 50%, and 75% of the thickness. The results of these analyses are summarized in Table 5. The values of  $\frac{dM}{dT}$  at  $x = 0$  (cold

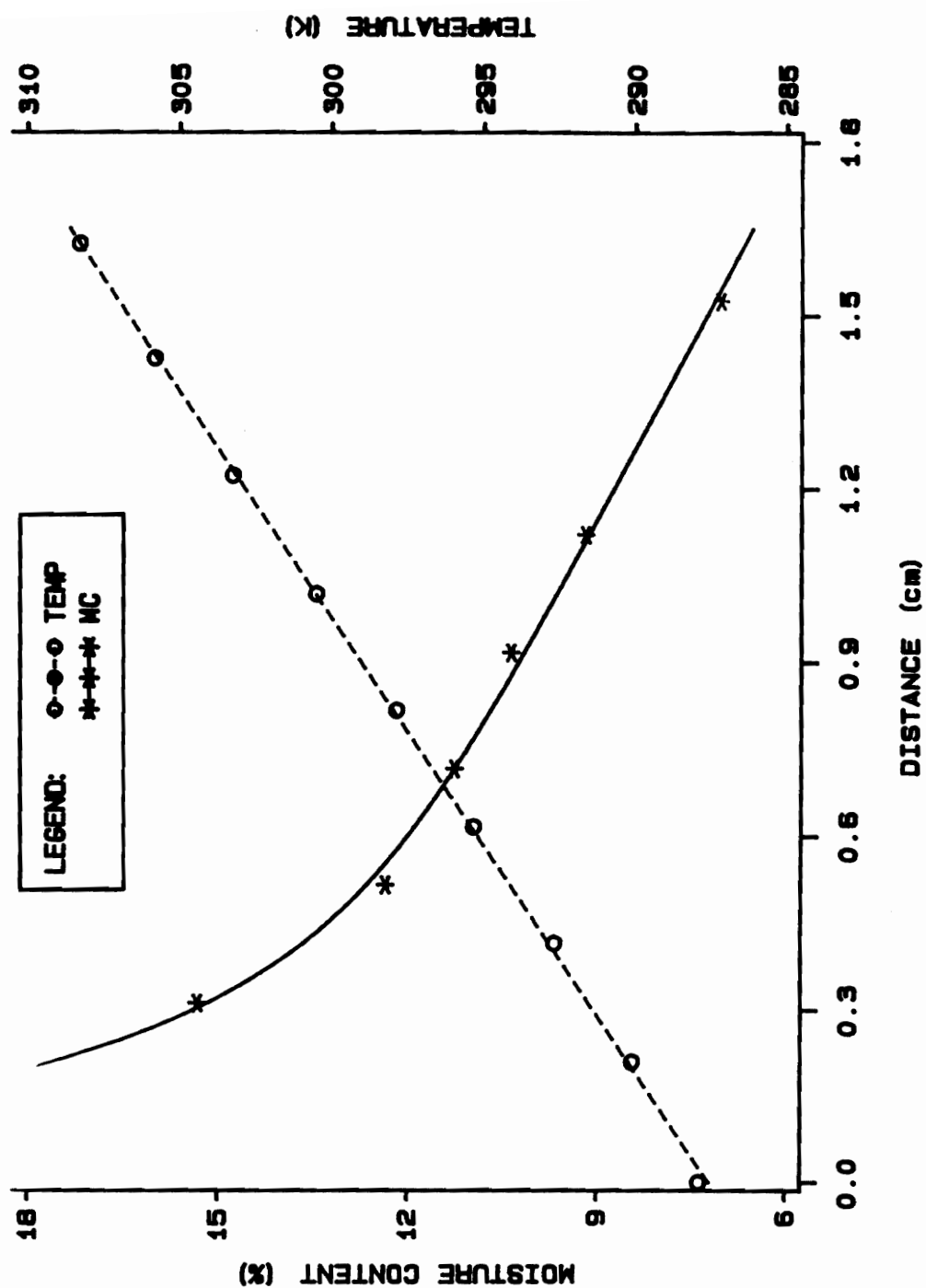


Figure 16. Steady-state temperature and moisture content profiles in a yellow poplar sample: The material had an initial moisture content of 9% and was subjected to temperatures of 15°C and 35°C on opposite faces.

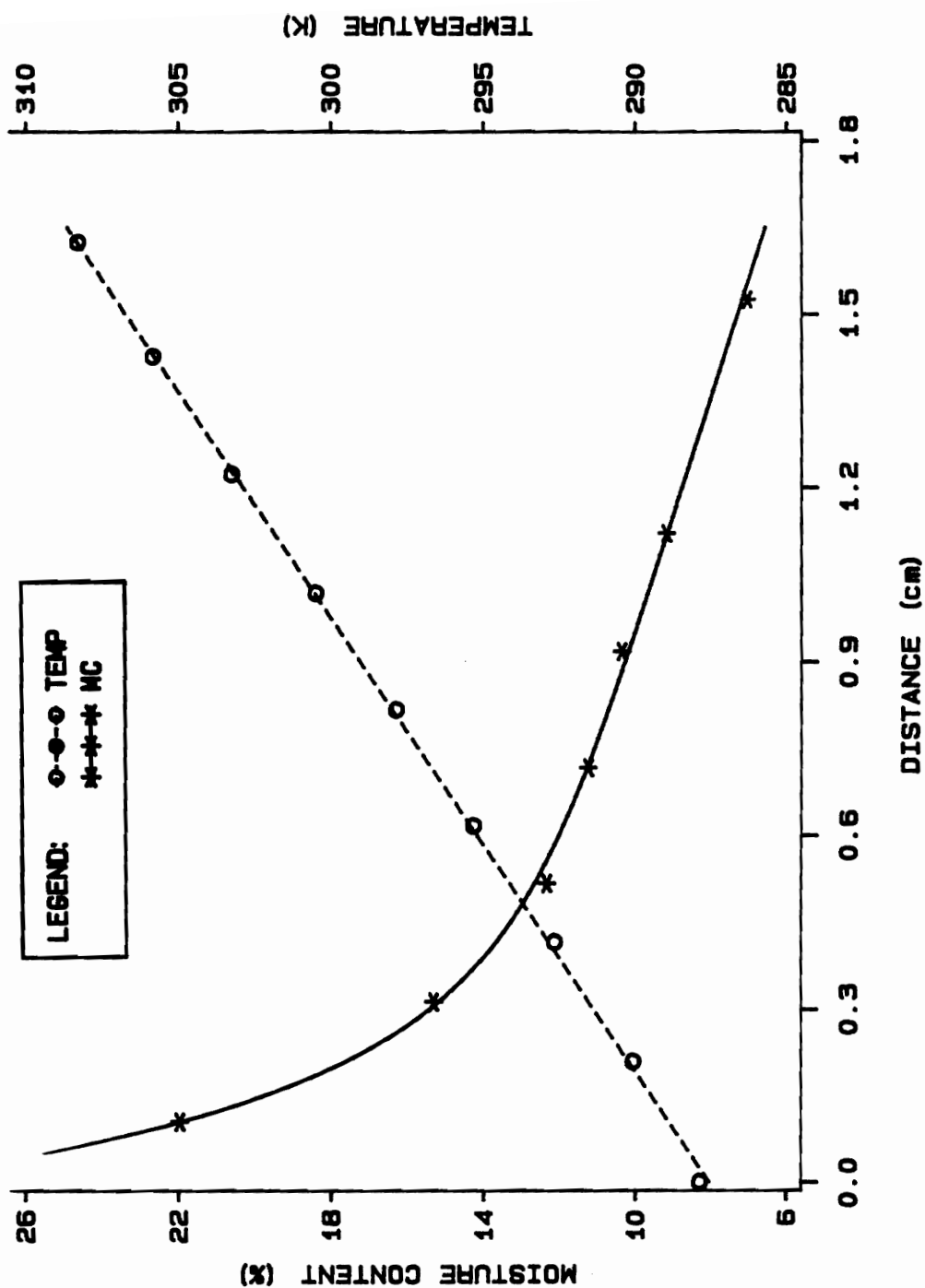


Figure 17. Steady-state temperature and moisture content profiles in a yellow poplar sample: The material had an initial moisture content of 12% and was subjected to temperatures of 15°C and 35°C on opposite faces.

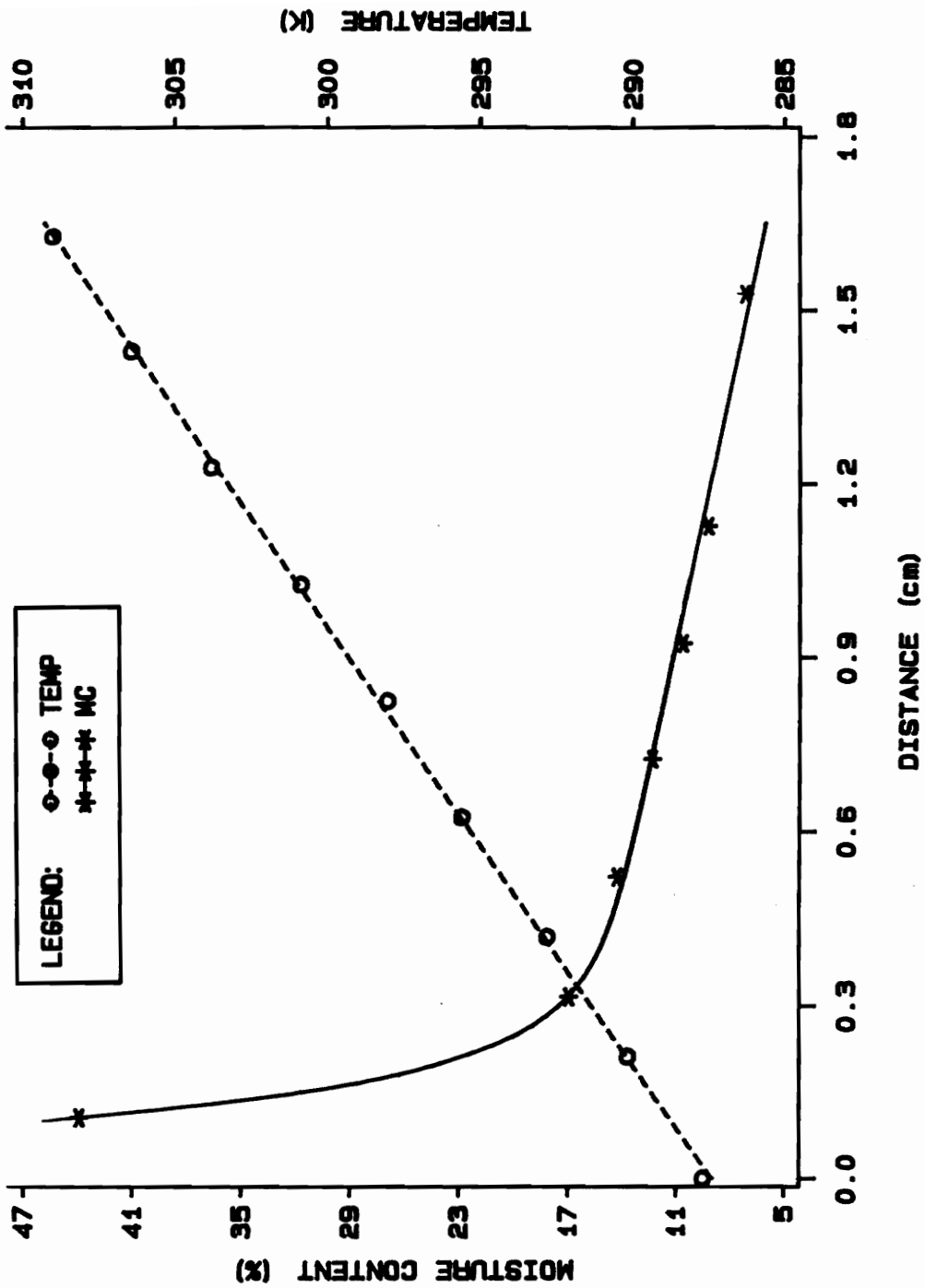


Figure 18. Steady-state temperature and moisture content profiles in a yellow poplar sample: The material had an initial moisture content of 15% and was subjected to temperatures of 15°C and 35°C on opposite faces.

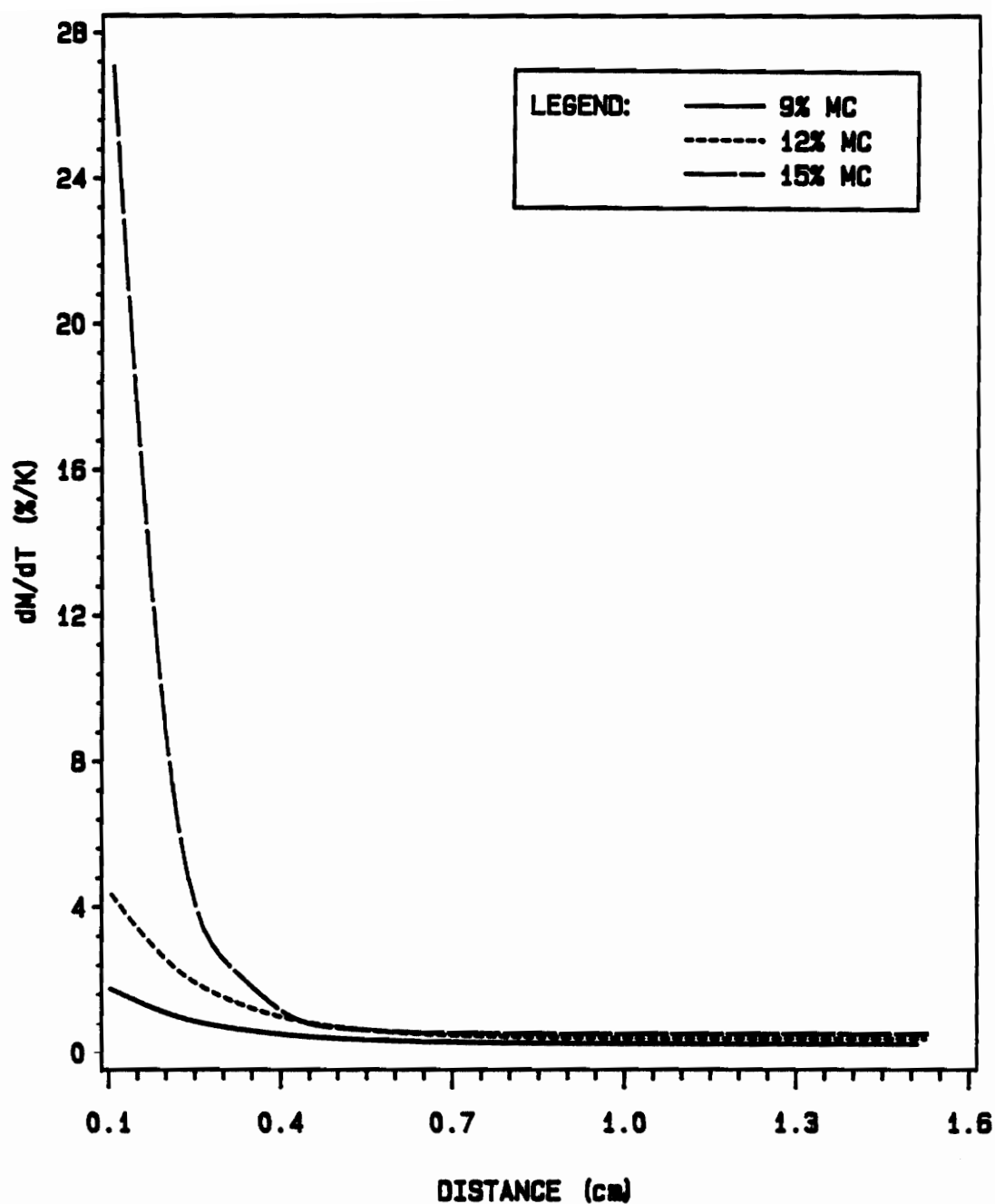


Figure 19.  $dM/dT$  ratio at different locations along the thickness of a nonisothermal steady-state sample: The graphs are those of yellow poplar of different initial moisture contents subjected to 15 C and 35 C on opposite faces.

**Table 5. Analyses of variance for the effect of species (SPEC), temperature range (TEMP), and initial moisture content (MC) on dM/dT.**

| Location              | SV           | DF | SS     | F       | PR     |
|-----------------------|--------------|----|--------|---------|--------|
| 0.25 of the thickness | SPEC         | 1  | 0.0076 | 1.44    | 0.2391 |
|                       | TEMP         | 1  | 0.4524 | 86.23   | 0.0001 |
|                       | MC           | 2  | 4.3023 | 410.00  | 0.0001 |
|                       | SPECxTEMP    | 1  | 0.0018 | 0.35    | 0.5595 |
|                       | SPECxMC      | 2  | 0.1014 | 9.66    | 0.0006 |
|                       | TEMPxMC      | 2  | 0.1153 | 10.98   | 0.0003 |
|                       | SPECxTEMPxMC | 2  | 0.0042 | 0.40    | 0.6723 |
| 0.50 of the thickness | SPEC         | 1  | 0.0043 | 13.00   | 0.0011 |
|                       | TEMP         | 1  | 0.0140 | 42.02   | 0.0001 |
|                       | MC           | 2  | 0.5148 | 769.99  | 0.0001 |
|                       | SPECxTEMP    | 1  | 0.0003 | 1.07    | 0.3090 |
|                       | SPECxMC      | 2  | 0.0074 | 11.15   | 0.0002 |
|                       | TEMPxMC      | 2  | 0.0014 | 2.18    | 0.1304 |
|                       | SPECxTEMPxMC | 2  | 0.0005 | 0.78    | 0.4677 |
| 0.75 of the thickness | SPEC         | 1  | 0.0037 | 15.03   | 0.0005 |
|                       | TEMP         | 1  | 0.0025 | 10.22   | 0.0033 |
|                       | MC           | 2  | 0.5574 | 1117.72 | 0.0001 |
|                       | SPECxTEMP    | 1  | 0.0003 | 1.38    | 0.2487 |
|                       | SPECxMC      | 2  | 0.0006 | 1.31    | 0.2855 |
|                       | TEMPxMC      | 2  | 0.0003 | 0.53    | 0.5921 |
|                       | SPECxTEMPxMC | 2  | 0.0005 | 1.14    | 0.3335 |

face) and at  $x=100\%$  (hot face) of the thickness were not included because of questions as to the validity of the values at these locations. To obtain them, extrapolation of the moisture content and temperature profiles must be done and this introduces some error in the obtained quantities.

The ratio  $\frac{dM}{dT}$  is interpreted as the moisture content gradient which causes a flux of moisture equal and opposite to that due to an applied unit temperature gradient. Figure 19 shows that this value is highest at  $x=0$  cm, decreases with distance and then remains more or less constant near the hot face. This pattern of  $\frac{dM}{dT}$  is mainly the result of moisture content variation across the thickness of the material. Although the temperature gradient was uniform throughout the sample, the moisture content near the cold face was high and, therefore, a unit temperature gradient at these locations was able to maintain a high moisture content gradient compared to that near the hot face where the moisture content was low. It means that it is easier to cause movement of moisture by a thermal gradient when the moisture is high than when the moisture content is low. For instance, in the case of yellow poplar sample H1, the  $\frac{dM}{dT}$  ratio at 25% of the thickness was  $-0.96 \frac{\%}{K}$  while at  $x=75\%$  of the thickness, this ratio was  $-0.38 \frac{\%}{K}$ . Thus near the cold face where the moisture content was about 14%, a moisture content gradient of about  $1 \frac{\%}{cm}$  was needed to counterbalance the flow of moisture caused by a temperature gradient of  $1 \frac{K}{cm}$ . On the other hand, a moisture content gradient of only  $0.4 \frac{\%}{cm}$  was sufficient to cause movement of moisture as when applying a unit temperature gradient near the hot face where the moisture content was only 8.7%. From a theoretical point of view, the ease of moisture flow should increase with increase in moisture content. Wood is thought to hold water by polymolecular adsorption. Since the force of attraction between the sorption sites and water decreases rapidly with increase in distance, the mobility of

the adsorbed water increases with an increase in the polymolecularity with which it is held (Stamm, 1964). In addition, at high moisture contents, the cell wall is swollen to a greater degree causing the wall structure to open up, thus, facilitating moisture movement which otherwise would have been restricted if the moisture content is low and the microfibrils are close to each other. The temperature variation across the thickness of the material should also affect the magnitude of  $\frac{dM}{dT}$  at different locations in the sample. Studies on moisture diffusion in wood show that the diffusion coefficient is higher at higher temperatures, meaning that moisture movement is faster if the wood is at an elevated temperature. If this factor were the only one operating, then  $\frac{dM}{dT}$  would have decreased with distance from the cold face, not the other way around as observed here. The inference we can make from this is that the effect of the moisture content variation in the material on  $\frac{dM}{dT}$  is more pronounced than that of the temperature variation.

The moisture content and temperature dependence of  $\frac{dM}{dT}$  will be pursued further as the effect of the different experimental variables (species, temperature range, and initial moisture content) on the magnitude of this quantity is evaluated. Table 5 shows that two-factor interaction effects are significant at  $x=0.25$  and  $0.50$  of the thickness. In the case of  $\frac{dM}{dT}$  at  $x=0.25$  of the thickness, for instance, the (SPEC x MC) interaction is significant at the 1% probability level indicating that there is a difference in the  $\frac{dM}{dT}$  between the two species investigated but this difference depends on the level of the initial moisture content. The same thing can be said concerning the (TEMP x MC) interaction.

Since interaction effects were not present in the mean  $\frac{dM}{dT}$  at  $x=0.75$  of the thickness, it is instructive to first look at  $\frac{dM}{dT}$  at this location. Comparison of the

means revealed that  $\frac{dM}{dT}$  increased with increase in the initial moisture content, as expected. At a given location, the moisture content was high for the samples with high initial moisture content and, thus, as explained above, a unit temperature gradient was able to cause greater moisture flow in these samples. With regard to the effect of temperature, the ratio was found to be higher in samples subjected to the (25 to 45°C) temperature range than in the materials exposed to the (15 to 35°C) temperature range. This is equivalent to saying that  $\frac{dM}{dT}$  was greater at higher temperatures because although the temperature difference was the same (20°C) in the two temperature range levels studied, the temperature at a particular location was higher in samples subjected to the (25 to 45°C) range. Thus, to cause moisture to flow with the same magnitude as applying a  $1 \frac{K}{cm}$  gradient, a higher moisture content gradient must be imposed on a material which is at a higher temperature. The reason for this is that in a sample which is at a higher temperature, a greater fraction of the water molecules have enough energy to overcome the potential energy barrier which keeps them bound to a particular site in wood (Choong, 1965). Since the rate of movement is directly proportional to the number of molecules with energy in excess of the bonding energy, then a smaller temperature gradient must be applied to the sample which is at a higher temperature to obtain the same flux as the sample which is at a lower temperature.

With regard to species, the average  $\frac{dM}{dT}$  was higher in hard maple samples compared to the yellow poplar assemblies. The difference though was very slight (0.39 %/K for hard maple vs. 0.38 %/K for yellow poplar) that it may be attributed to experimental and curve-fitting error. Based on density, the  $\frac{dM}{dT}$  ratio should have been greater for yellow poplar where, because of the greater fraction of void volume, more of the transport of moisture would have occurred in the vapor phase through the

air spaces. From the experimental results it seems other material properties were affecting moisture flow in the two species.

Going back to the evaluation of treatment effects on  $\frac{dM}{dT}$  at  $x=0.25$  and  $x=0.50$  of the thickness, follow-up analyses (plot of means and mean comparisons) showed that the same conclusions reached for  $x=0.75$  of the thickness regarding the effect of initial moisture content and temperature range on  $\frac{dM}{dT}$  also apply to the other two locations. That is,  $\frac{dM}{dT}$  was also found to increase with increase in initial MC, and that the ratio was higher for the (25 to 45°C ) temperature range. The interaction effect was caused mainly by the average  $\frac{dM}{dT}$  of the two species at the different moisture content levels. The (SPEC x MC) interaction is evident in Figure 20 where the average  $\frac{dM}{dT}$  at  $x=0.25$  of the sample thickness is plotted against initial moisture content level for the two species subjected to 15°C on one face and 35°C on the other. At the 9% and the 12% initial moisture content levels, the mean  $\frac{dM}{dT}$  was higher for yellow poplar than for hard maple; but at 15% MC, the average value was higher for hard maple.

## **2. Thermal Diffusion Parameters**

The observed build-up of a moisture gradient opposite to the imposed temperature gradient is a manifestation of the occurrence of thermal diffusion. This phenomenon is often characterized by the Soret coefficient  $S_T$  which is defined as the ratio of the thermal diffusion coefficient  $D_T$  to the ordinary diffusion coefficient  $D$ . At the steady state when the net moisture flux in a closed system is zero, the coefficient may also be written as follows from equation (58) (Katchalsky and Curran, 1965):

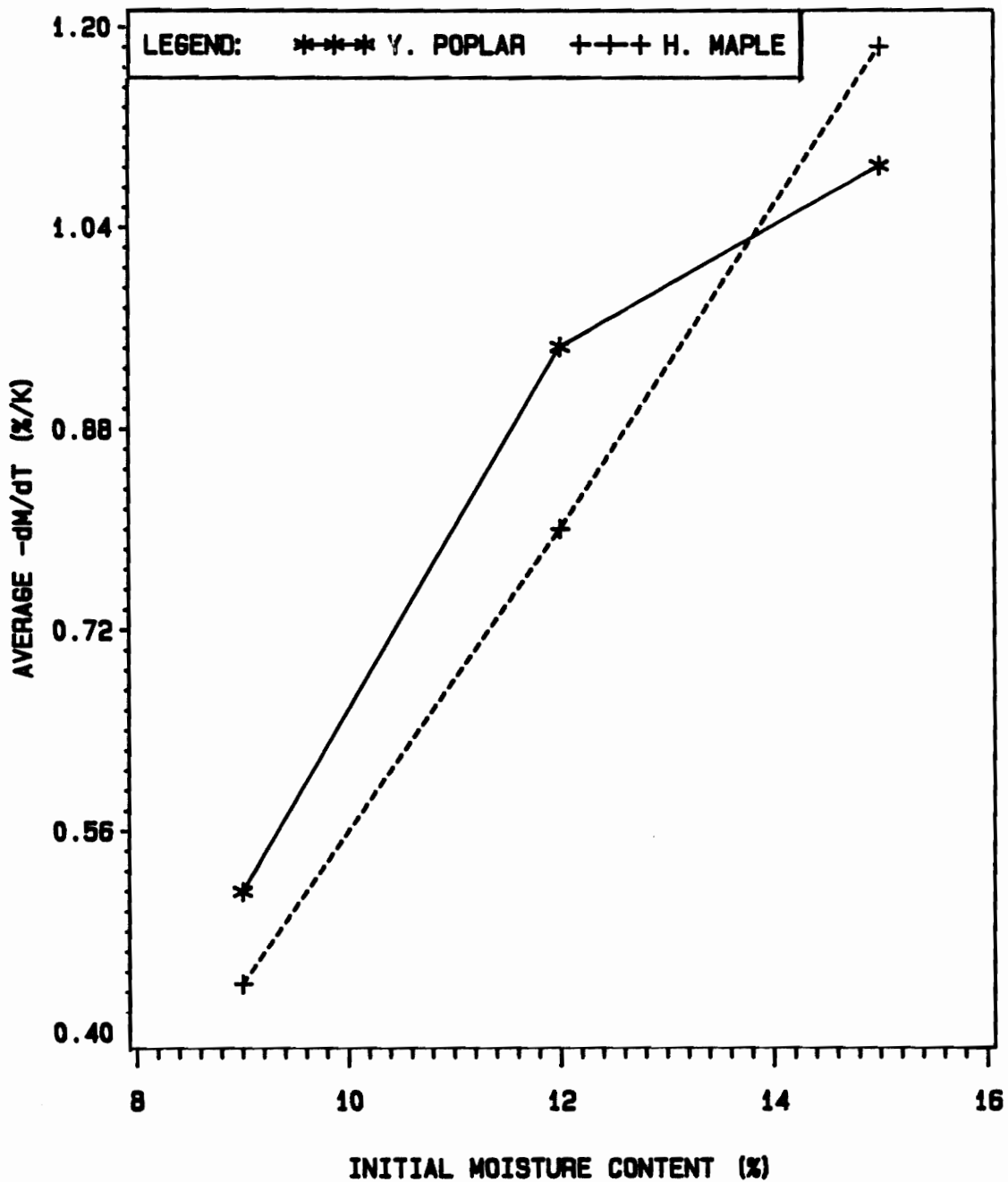


Figure 20. Plot of the average  $dM/dT$  ratio against the initial moisture content level: The two curves are those of yellow poplar and hard maple subjected to 15 C and 35 C on opposite faces.

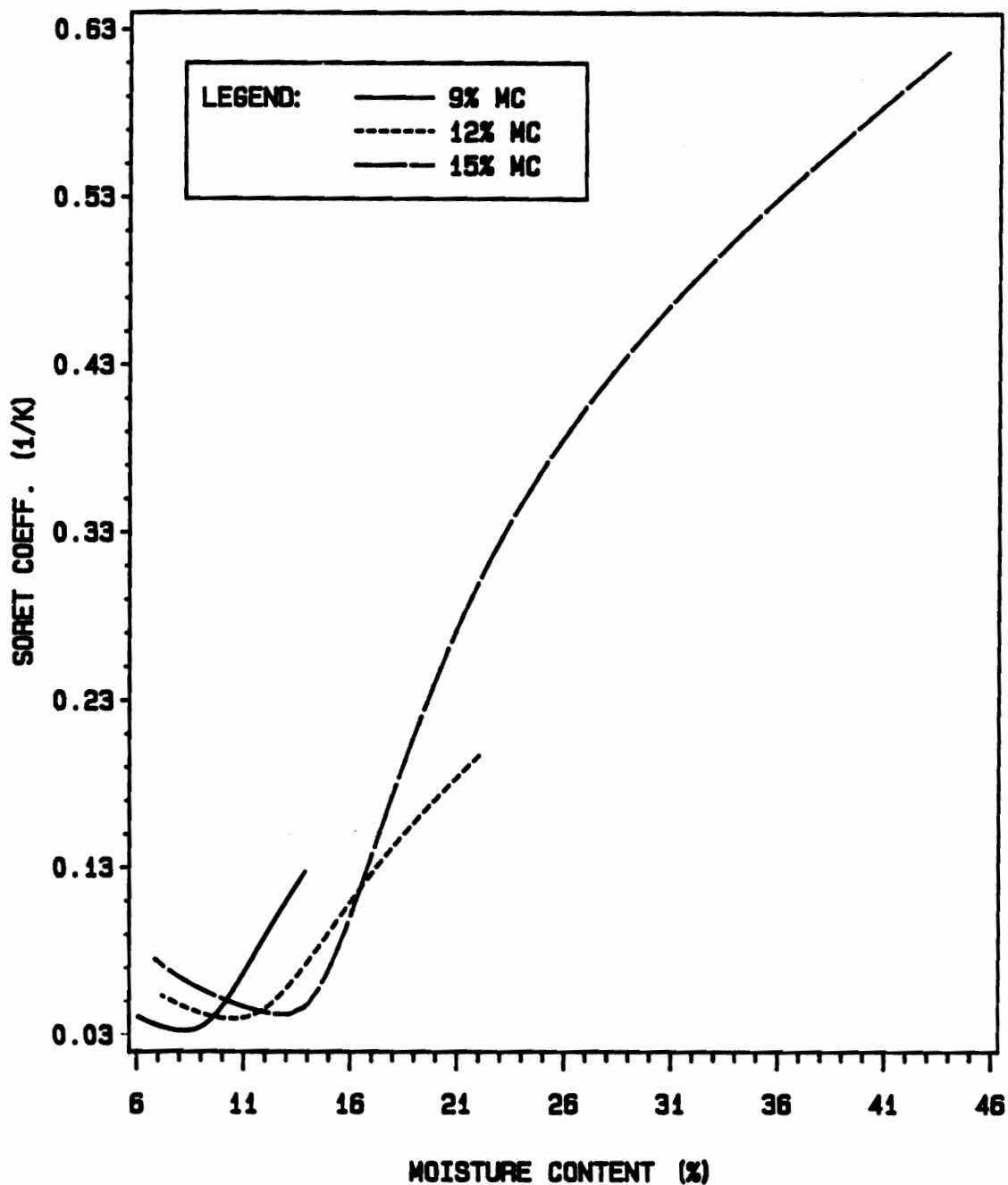
$$S_T = \frac{D_T}{D} = -\frac{1}{C} \frac{dC}{dT} \quad [117a]$$

For moisture transport in wood, this can be approximated by the expression

$$S_T = -\frac{1}{M} \frac{dM}{dT} \quad [117b]$$

The Soret coefficient was calculated for each sample at different locations along the thickness of the material. Graphs of the coefficient as a function of the moisture content at a particular location in the sample are presented in Figure 21 for three representative samples of yellow poplar subjected to 15°C on one face and 35°C on the other. Each curve corresponds to a given initial moisture content level (9%, 12%, and 15 % MC). The profiles obtained for the rest of the experimental units were more or less the same as those presented. Initially the Soret coefficient decreased slightly with increase in moisture content, reached a minimum at about 8% to 12% MC, and then increased rapidly with increase in moisture content. The value of  $S_T$  ranged from  $0.028 \frac{1}{K}$  to  $0.650 \frac{1}{K}$ , with most of the data falling within the  $0.03$  to  $0.05 \frac{1}{K}$  region. The unusually high Soret coefficient values were observed in the samples with high initial moisture content. In these materials, the moisture content near the cold face exceeded the fiber saturation point, and it is possible that capillary forces contributed to the large value of  $S_T$ .

The Soret coefficient is a measure of the relative moisture content change per degree change in temperature (Jost, 1960; Skaar, 1988). The slight dip in the  $S_T$  profile in Figure 21 indicates that at low moisture contents, the increase in moisture content did not significantly increase the rate of thermal diffusion such that at the constant temperature gradient imposed on the material, the opposite moisture content gradi-



**Figure 21.** Soret coefficient as a function of moisture content at different locations along the thickness of a material.: The graphs are those of yellow poplar samples of three different initial moisture contents whose opposite faces were maintained at 15 C and 35 C.

ent needed to balance the flow of moisture either remained more or less constant with increase in moisture content or it increased at a slower rate than the increase in moisture content. This may be associated with the fact that at low moisture contents, the water molecules are directly attached to sorption sites in wood. The wood layers near the hot face were desorbing samples and as shown in Table 4, the moisture content corresponding to complete monolayer coverage based on the Hailwood-Horrobin sorption model is about 8.5%. Thus significant increase in the rate of moisture flow with increase in moisture content should not occur until this moisture content level is attained. This seems to be the case here as there appears to be a transition moisture content level where the reduction in the Soret coefficient is suddenly reversed. This occurred at around 8 to 12% MC. Beyond this transition moisture content, the imposed temperature gradient caused substantial moisture flow as to necessitate the establishment of higher relative moisture content gradient to counterbalance thermal diffusion.

The magnitude of the Soret coefficient provides a picture of the rate of thermal diffusion. Compared to the ordinary diffusion coefficient, the thermal diffusion coefficient is smaller by a factor of about  $10^2$ . Assuming a diffusion coefficient at 12% MC of  $1 \times 10^{-6} \frac{\text{cm}^2}{\text{s}}$  for yellow poplar (Comstock, 1963), and combining this with an  $S_T$  of about  $0.04 \frac{1}{\text{K}}$  obtained in this study, the thermal diffusion coefficient is calculated to be approximately  $4 \times 10^{-8} \frac{\text{cm}^2}{\text{s K}}$ . A unit temperature gradient imposed on a yellow poplar sample at 12% MC ( $G_o = 0.47$  or  $G_{12} = 0.45$ ) will thus cause a moisture flux due to thermal diffusion of

$$J_w^T = \frac{(12)(0.45)(1 \frac{\text{g}}{\text{cm}^3})}{100} \left( 4 \times 10^{-8} \frac{\text{cm}^2}{\text{s K}} \right) \left( 1 \frac{\text{K}}{\text{cm}} \right) \quad [118a]$$

$$J_w^T = 2.16 \times 10^{-9} \frac{g}{cm^2 s} \quad [118b]$$

Analyses of variance were also performed at three different locations along the thickness of the material to evaluate the effect of the different experimental variables on the Soret coefficient (Table 6). The results were similar to the ANOVA for the  $\frac{dM}{dT}$  ratio. At  $x=0.75$  of the thickness, no interaction effects were significant, and comparison of the means showed that the average Soret coefficient was highest at the highest initial moisture content level (0.06 1/K), and lowest at the lowest initial moisture content value (0.03 1/K), with  $S_T$  at the 12% MC about midway (0.04 1/K) between these two extremes. With regard to the effect of temperature range, the average  $S_T$  was found to be higher (0.05 1/K) at the (25 to 45°C) range than at the (15 to 35°C) temperature range ( $S_T = 0.04 \frac{1}{K}$ ). When the average  $S_T$  was calculated for the two species, the result was higher for yellow poplar (0.05 1/K) compared to that for hard maple (0.04 1/K). At the other two locations, the average  $S_T$  exhibited the same behavior with changing levels of experimental variable as for  $x=0.75$  of the thickness except for a mild interaction effect at  $x=0.50$  of the thickness. At this location, the graph of average  $S_T$  vs. initial moisture content level for the two species at the (25 to 45°C) temperature range crossed one another, that is, average  $S_T$  was higher for yellow poplar at the two lower levels of moisture content but at the highest level, the average Soret coefficient was higher for hard maple.

The heat of transfer, a quantity which often arises in discussions of the phenomenon of thermal diffusion may also be obtained from the experimental data generated in this study. From equation (104), an expression for  $Q^*$  may be written as

**Table 6. Analyses of variance for the effect of species (SPEC), temperature range (TEMP), and initial moisture content (MC) on the Soret coefficient.**

| Location              | SV           | DF | SS     | F      | PR     |
|-----------------------|--------------|----|--------|--------|--------|
| 0.25 of the thickness | SPEC         | 1  | 0.0006 | 34.64  | 0.0001 |
|                       | TEMP         | 1  | 0.0020 | 119.14 | 0.0001 |
|                       | MC           | 2  | 0.0069 | 209.22 | 0.0001 |
|                       | SPECxTEMP    | 1  | 0.0000 | 0.03   | 0.8710 |
|                       | SPECxMC      | 2  | 0.0001 | 4.37   | 0.0215 |
|                       | TEMPxMC      | 2  | 0.0003 | 10.40  | 0.0004 |
|                       | SPECxTEMPxMC | 2  | 0.0000 | 0.30   | 0.7405 |
| 0.50 of the thickness | SPEC         | 1  | 0.0000 | 16.37  | 0.0003 |
|                       | TEMP         | 1  | 0.0002 | 122.01 | 0.0001 |
|                       | MC           | 2  | 0.0010 | 269.67 | 0.0001 |
|                       | SPECxTEMP    | 1  | 0.0000 | 0.81   | 0.3751 |
|                       | SPECxMC      | 2  | 0.0000 | 3.74   | 0.0354 |
|                       | TEMPxMC      | 2  | 0.0000 | 5.05   | 0.0129 |
|                       | SPECxTEMPxMC | 2  | 0.0000 | 0.92   | 0.4096 |
| 0.75 of the thickness | SPEC         | 1  | 0.0001 | 26.11  | 0.0001 |
|                       | TEMP         | 1  | 0.0001 | 51.17  | 0.0001 |
|                       | MC           | 2  | 0.0031 | 602.19 | 0.0001 |
|                       | SPECxTEMP    | 1  | 0.0000 | 2.56   | 0.1201 |
|                       | SPECxMC      | 2  | 0.0000 | 2.10   | 0.1406 |
|                       | TEMPxMC      | 2  | 0.0000 | 0.66   | 0.5240 |
|                       | SPECxTEMPxMC | 2  | 0.0000 | 1.13   | 0.3376 |

$$Q^* = -\frac{RT^2}{H} \left( \frac{\partial H}{\partial M} \right)_T \left( \frac{dM}{dT} \right)_s \quad [119]$$

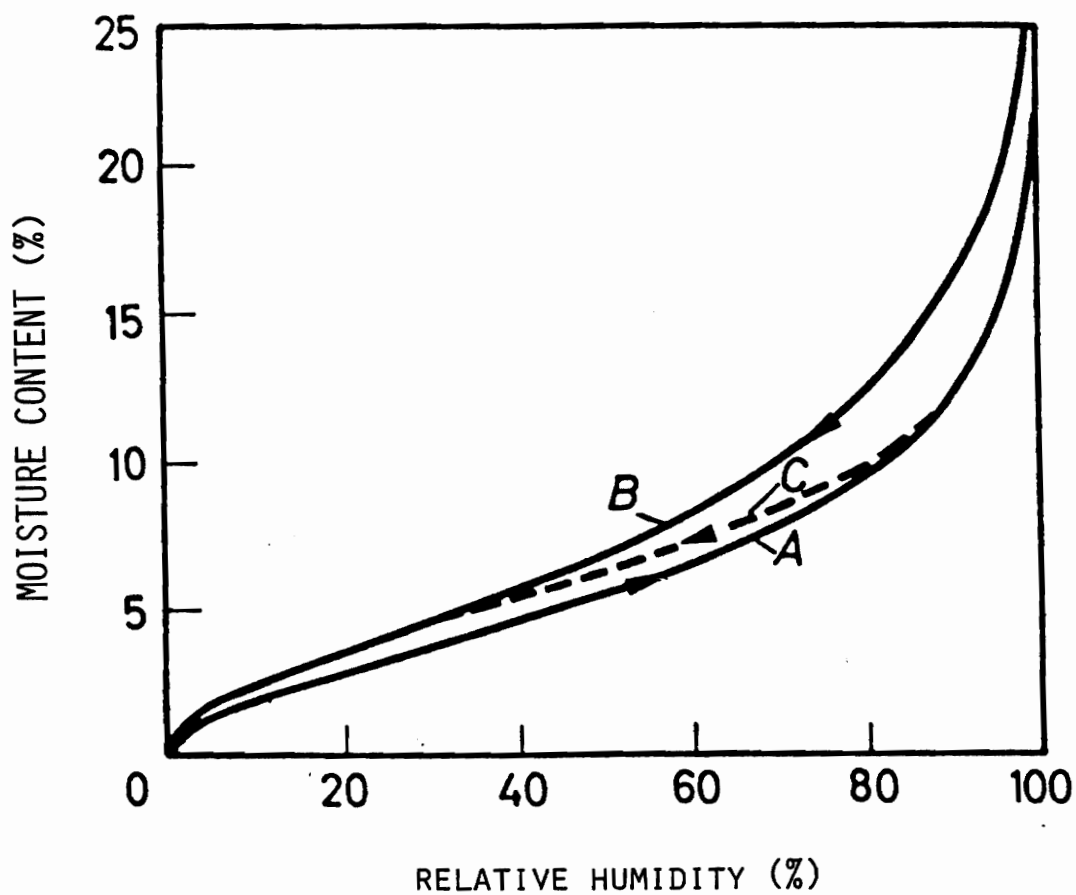
In order to evaluate this equation, information on the effective sorption isotherm must be obtained. The moisture sorption data shown in Figures 10 and 11 were obtained for wood samples undergoing either desorption from the fully swollen condition or for adsorption from the fully dry condition, all at a single temperature of 30°C. The wood samples in the nonisothermal tests were subjected to different moisture and temperature histories depending on their locations in a given assembly, and also on their initial moisture contents, as well as the temperature range. To calculate the heat of transfer and in order to test the various models proposed to explain nonisothermal moisture transport in wood, it is necessary to know the equilibrium relative humidities and temperatures throughout each assembly. The procedure used for estimating the equilibrium relative humidities for each location in an assembly is given below.

When a sample is subjected to a partial sorption cycle, the sorption curves followed by the material differ from the isotherms for the complete cycle. Take, for instance, the hypothetical case of a yellow poplar sample initially at the oven-dry condition and then placed in a chamber set at 30°C. If the relative humidity in the chamber is slowly increased from 0 to 70% at 5% intervals and the equilibrium moisture content is measured at each relative humidity condition, the sample is expected to follow a sorption curve similar to the lower part of the adsorption isotherm in Figure 10. At 70% RH, the piece of wood will at equilibrium have a moisture content of 10.56%. If at this point the relative humidity is decreased to 65% and then further to 60%, the material is now subjected to a desorption process. To obtain the

moisture content of the wood, it is tempting to use the complete desorption curve in Figure 10, which at 60% RH gives an equilibrium moisture content of 11.47%, which is higher than 10.56%. This is apparently a wrong approach for experience dictates that the material should have a moisture content lower than 10.56%.

When a material is subjected to a smaller sorption cycle than the full cycle shown in Figures 10 and 11, studies have shown that the partial isotherms fall within the complete isotherm (Urquhart, 1960). Thus in Figure 22, the dotted curve C demonstrates a typical result for the desorption of a sample which had previously been adsorbing. This means that the complete curves are the limiting boundaries and may be viewed according to Urquhart not as equilibrium loci but as borders which define an equilibrium area. Morton and Hearle (1975) noted that the intermediate curves for cotton are very long, such that if adsorption is started from 10% RH on the desorption curve, the complete adsorption curve will not be joined below 80% RH. In contrast, the intermediate curve for wool is shorter, a change of 18% RH being sufficient to pass between the complete adsorption and the complete desorption isotherms (Speakman and Cooper, 1936). Knight and Pratt (1935) in studying five wood species also observed that the partial sorption curves lie between the complete curves. They concluded, like Urquhart (1960), that the "moisture contents corresponding with given temperatures and humidities can not well be shown by any single line but will lie within a zone."

The sorption isotherms shown in Figures 10 and 11 were adjusted to account for both hysteresis and temperature in the nonisothermal experiments. The hysteresis was accounted for by constructing a composite sorption isotherm intermediate between those for adsorption and desorption. For each assembly, the lowest moisture



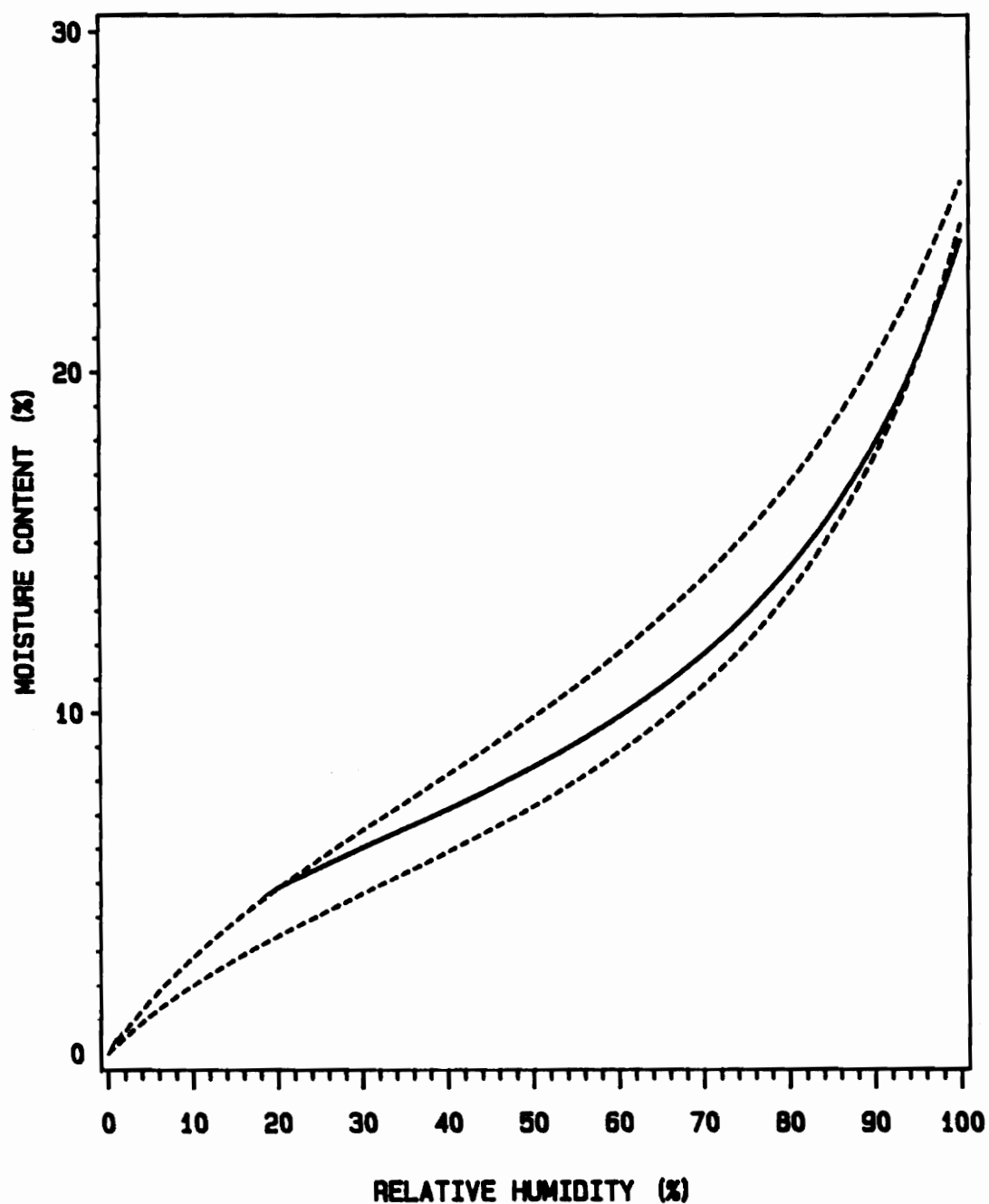
**Figure 22.** Illustration of an intermediate partial isotherm relative to the complete sorption curves: The partial isotherm is denoted as curve C; while the complete adsorption and desorption isotherms are labeled as curves A and D, respectively. (From: Morton and Hearle, 1975)

content (at the hot-plate face) was presumed to lie on the desorption curve, and the highest moisture content (at the cold-plate face) on the adsorption curve. The intermediate curve between these two points was interpolated between the two extreme curves in proportion to their locations in the assembly. Finally, the Hailwood-Horrobin sorption model was fitted to the nine points, including the two extreme points and the seven interpolated points, to obtain an equation for the intermediate curve. Figure 23 shows such interpolated curve fitted between adsorption and desorption isotherms. The Hailwood-Horrobin parameters for all of these curves are tabulated in appendix Table A7.

The above-described procedure adjusted the sorption isotherms for sorption hysteresis at 30°C. It was also necessary to adjust the isotherms for temperature since this varied throughout the wood assembly. No data were obtained in this study on the effect of temperature on moisture sorption. However, studies by other workers have resulted in empirical equations which account for the temperature effect. These are usually given in terms of the differential heat of sorption,  $\Delta H_s$ , defined by equation (4), the Clausius-Clapeyron equation. In this study, it was more convenient to use this equation in the integrated form, since sorption data were based on a single reference temperature, and adjusted to some other temperature. The integrated equation is

$$\Delta H_s = R T_1 T_2 \left[ \frac{\ln\left(\frac{H_2}{H_1}\right)}{T_2 - T_1} \right]_M \quad [120]$$

where  $H_1$  and  $H_2$  are the relative humidities at temperatures  $T_1$  and  $T_2$ , respectively, at a constant moisture content.



**Figure 23. Composite isotherm for a yellow poplar sample with adsorption and desorption zones:** The solid curve represents the composite isotherm; while the discontinuous curves represent the complete adsorption and desorption isotherms.

An equation relating the differential heat of sorption and moisture content at constant temperature was suggested by Skaar (1972) based on an empirical equation applied to textiles by Cooper and Ashpole (1959):

$$\Delta H_s = \Delta H_{so} [\exp(-B_H M)] \quad [121]$$

where  $\Delta H_{so}$  is the value of  $\Delta H_s$  extrapolated to zero moisture content and  $B_H$  is a constant. Skaar (1988) tabulated values of  $\Delta H_{so}$  and  $B_H$  obtained from several sources (Kajita, 1976; Stamm, 1964; Weichert, 1963; Babbitt, 1942; Stamm and Loughborough, 1935). For the data of Stamm and Loughborough, these parameters are given by

$$\Delta H_{so} = 5040 \frac{\text{cal}}{\text{mol}} \quad [122a]$$

$$B_H = 0.14 \quad [122b]$$

Combining equations (120), (121), (122a) and (122b) results in

$$5040 \exp(-0.14M) = \frac{R T_1 T_2 \ln\left(\frac{H_2}{H_1}\right)}{T_2 - T_1} \quad [123]$$

It must be clarified that this equation is obtained with the assumption that  $\Delta H_s$  is independent of temperature. As mentioned by Skaar (1988), this is not entirely correct. The differential heat of sorption should decrease with increasing temperature but within the limited temperature range in this study, the assumption of the constancy of  $\Delta H_s$  with temperature should be valid.

The Hailwood-Horrobin equation (114a) may be solved for  $H$  giving

$$H = \frac{MB - 1 + \sqrt{(1 - MB)^2 + 4CM^2A}}{2CM} \quad [124]$$

Letting this relative humidity expression represent  $H_1$  in equation (123) and then solving for  $H_2$  results in

$$H_2 = \left\{ \frac{MB - 1 + \sqrt{(1 - MB)^2 + 4CM^2A}}{2CM} \right\} \left\{ \exp \left[ \frac{(5040)(T_2 - T_1)(e^{-0.14M})}{(1.987)(T_1)(T_2)} \right] \right\} \quad [125]$$

The sorption data at 30°C may be used as the reference isotherm, thus,  $T_1$  above is equal to  $30 + 273.15 = 303.15\text{K}$  and the coefficients A, B, and C are the coefficients listed in appendix Table A7. This equation may then be used to obtain the relative humidity in equilibrium with moisture content M at temperature  $T_2$ . As an example, the relative humidities at four different temperatures (288.15, 293.15, 298.15 and 308.15°K) for the group consisting of samples H1, C1, F1, E1 are presented in Table 7, and are obtained by combining equation (125) with the parameters in Table A7 for the given group. Similar calculations may be made for the other samples. Notice in Table 7 that, as expected, the relative humidity at a given moisture content increases with increasing temperature.

The curves of  $\frac{dM}{dT}$ , coupled with information on the effective sorption isotherms, were substituted into equation (119) to calculate values of  $Q'$ . These were plotted as functions of wood moisture content M in Figure 24 for three representative samples of yellow poplar subjected to 15°C on one face and 35°C on the other. Each curve corresponds to a given initial moisture content level.

The computed heat of transfer exhibited wide variation across the thickness of the material. As shown in Figure 24, it first decreased with increase in moisture content,

**Table 7. Relative humidities at different temperatures for different equilibrium moisture content levels of yellow poplar samples.**

| Moisture<br>Content | Relative humidity |       |       |        |       |
|---------------------|-------------------|-------|-------|--------|-------|
|                     | 15°C              | 20°C  | 25°C  | 30°C   | 35°C  |
| 00.00               | -                 | -     | -     | -      | -     |
| 1.98                | 3.60              | 4.03  | 4.50  | 5.00   | 5.54  |
| 3.19                | 7.58              | 8.34  | 9.14  | 10.00  | 10.90 |
| 4.08                | 11.74             | 12.77 | 13.86 | 15.00  | 16.19 |
| 4.80                | 16.02             | 17.30 | 18.62 | 20.00  | 21.43 |
| 5.44                | 20.41             | 21.89 | 23.42 | 25.00  | 26.63 |
| 6.04                | 24.90             | 26.55 | 28.25 | 30.00  | 31.79 |
| 6.63                | 29.48             | 31.28 | 33.12 | 35.00  | 36.92 |
| 7.23                | 34.16             | 36.07 | 38.02 | 40.00  | 42.02 |
| 7.85                | 38.94             | 40.93 | 42.95 | 45.00  | 47.07 |
| 8.52                | 43.83             | 45.87 | 47.92 | 50.00  | 52.10 |
| 9.25                | 48.83             | 50.88 | 52.93 | 55.00  | 57.08 |
| 10.05               | 53.95             | 55.96 | 57.98 | 60.00  | 62.02 |
| 10.95               | 59.19             | 61.13 | 63.07 | 65.00  | 66.92 |
| 11.99               | 64.55             | 66.38 | 68.20 | 70.00  | 71.79 |
| 13.19               | 70.04             | 71.71 | 73.36 | 75.00  | 76.62 |
| 14.61               | 75.64             | 77.11 | 78.57 | 80.00  | 81.41 |
| 16.33               | 81.33             | 82.58 | 83.80 | 85.00  | 86.18 |
| 18.46               | 87.10             | 88.09 | 89.06 | 90.00  | 90.92 |
| 21.16               | 92.89             | 93.61 | 94.32 | 85.00  | 95.67 |
| 24.72               | 98.64             | 99.11 | 99.56 | 100.00 | -     |

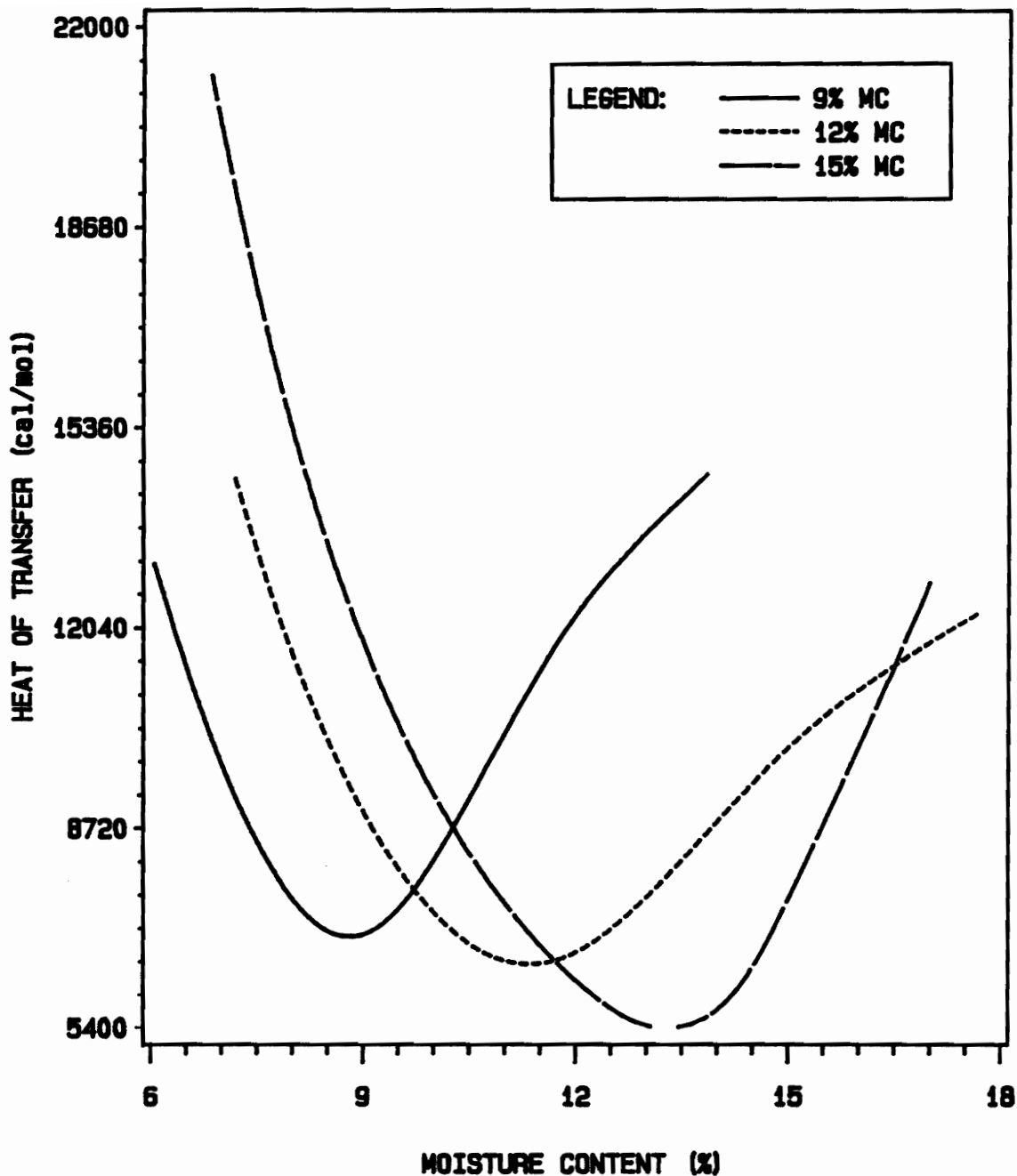


Figure 24. Heat of transfer as a function of moisture content at different locations along the thickness of a nonisothermal steady-state sample.: The graphs are those of yellow poplar samples of different initial moisture contents (9%, 12%, and 15%) subjected to 15 C and 35 C on opposite faces.

reached a minimum at around 9 to 13% MC, and then increased rapidly with increase in moisture content. Excluding the values for the locations in the sample where the moisture contents were outside the range obtained in the sorption studies, the magnitude of  $Q^*$  varied from  $5500 \frac{\text{cal}}{\text{mol}}$  to  $17000 \frac{\text{cal}}{\text{mol}}$ .

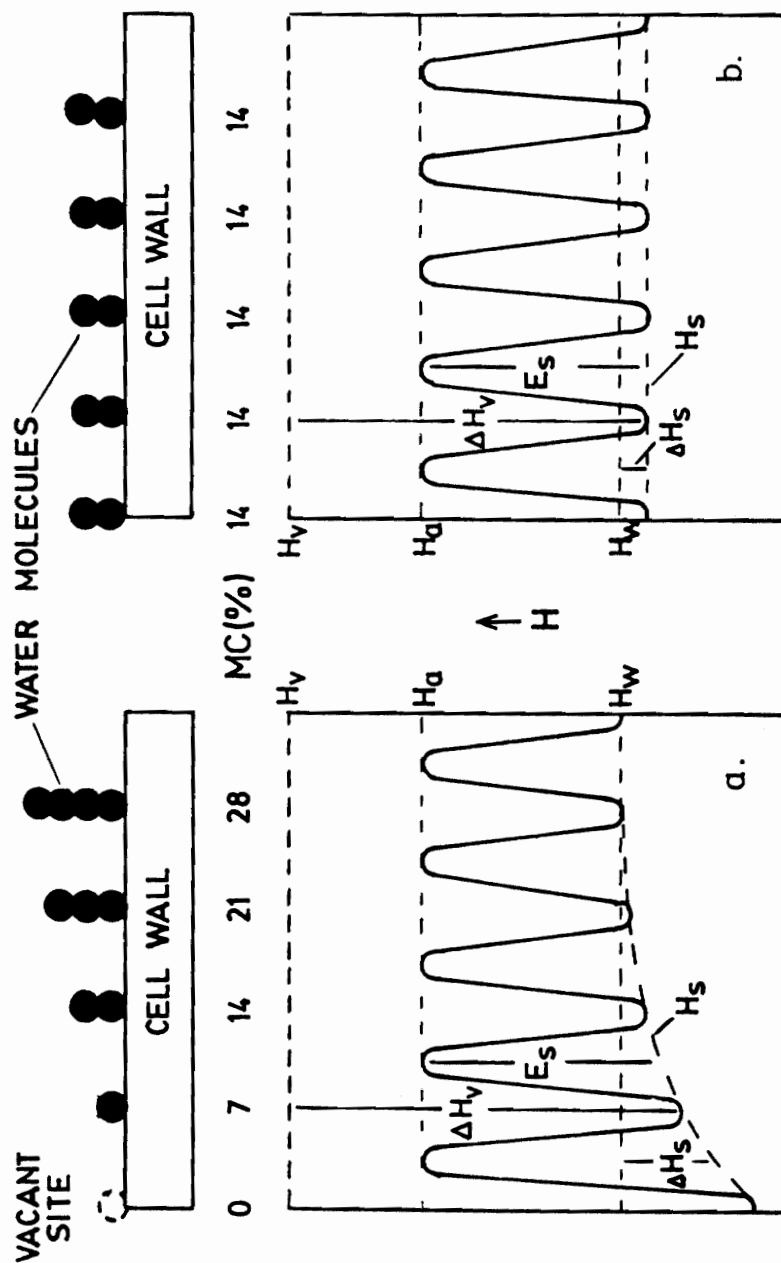
Before discussing the variation of  $Q^*$  across the thickness of the material, a qualitative description of  $Q^*$  will be provided to clarify its meaning (see Katchalsky and Curran, 1965). Referring to Figure 3, consider the system to be isothermal with part 1 separated from part 2 by a 'membrane' that can be penetrated only by molecules of a relatively high energy. In order for molecules to move from one side (say part 1) to the other (say part 2), the energy of these molecules must be greater than the average energy of the molecules on the side from which they come. Thus as the water moves across the 'membrane', it carries a quantity of heat with it. While this transfer makes side 1 cooler, it also makes side 2 warmer. To maintain a condition of uniform temperature, heat equal to the heat of transfer must be added to side 1 and removed from the other side. The nature of the 'membrane' plays a very important role in determining the magnitude of the heat of transfer (Spanner, 1954). The membrane may just act as a sieve where if the openings are coarse, the transfer of water will not alter the temperature of either compartment and no heat of transfer is generated. If the openings are comparable to the intermolecular distance between the water molecules, heat of transfer develops because more faster-moving molecules are able to penetrate the 'membrane'. The membrane may also act as a potential energy barrier to transfer, where in this case the heat of transfer is very nearly equal to the height of the potential energy barrier. For instance, if the 'membrane' is an air space with transport occurring in the vapor phase, the heat of transfer is very nearly the same as the heat of vaporization.

Based on the idea of a potential energy barrier, Skaar and Kuroda (1984) discussed a mechanism for bound water movement under isothermal conditions. In this discussion, they presented energy curves as a function of moisture content with the assumption that the heat of transfer is equal to the activation energy. In constructing Figure 25, they considered that the number of water molecules per sorption site is on the average one for each seven percent moisture content. This is only for convenience since it is not known how many sorption sites there are nor exactly how many molecules are deployed at each sorption site at any given moisture content. Thus for the diagram shown where the first site is empty and the others have 1, 2, 3, and 4 water molecules per sorption site, the moisture distribution is from 0% at the extreme left to 28% at the right. Also included in the diagram are the energy levels of water in the vapor, liquid, and hygroscopic form. For a water molecule at a 14% site to jump to the 7% site, it must have enough energy to overcome the barrier between the two wells. This energy, equal to the activation energy  $E_a (= Q^*)$ , is transferred to the seven percent site during the process. In addition, the molecule transfers its enthalpy  $H_s$  from the 14% site to the 7% site. They interpreted the total energy transferred  $Q^* + H_s$  as the energy of transfer  $U^*$  defined in equation (62). According to the diagram, the same energy barrier  $Q^*$  must be overcome for a water molecule to jump from the 14% site to the 21% site as from the 14% site to the 7% site. However, molecules from the 21% site are also jumping to other sites but the energy barriers are lower, therefore, more molecules per unit time are migrating from the 21% site to the 14% site than in the reverse direction. The same reasoning follows with respect to the 14 and 7% sites so more molecules jump from 14 to 7% sites than the reverse. The process of equilibration continues by activated diffusion until the moisture content is uniform throughout. Thus if each sorption site has 2 water molecules (corresponding to 14% MC), the potential energy wells have the same

energy level with the same height of barrier between any pair of sites. In this case, a given water molecule is as likely to jump in one direction as another. During the process of equilibration, energy and moisture were being transferred from the wetter to the drier portion of the wood. In order to maintain isothermal condition, heat conduction must occur from the drier to the wetter portion of the wood. The temperature gradient established during moisture equilibration is difficult to detect because heat transfer is a lot faster compared to moisture transport (Skaar and Kuroda, 1984).

The variation of the heat of transfer shown in Figure 24 may be explained in terms of the moisture content and temperature dependence of  $Q^*$ . Near the hot face, the moisture content was the main factor which determined its magnitude; while near the cold face, the high heat of transfer means that temperature was controlling its value. If movement of moisture from one sorption site to the other is an activated process, then the heat of transfer should decrease with increase in moisture content. To be able to transfer, a water molecule must break the bond which holds it in the sorption site, overcome the hindrance provided by surrounding water molecules, and open up the cell wall structure. When the moisture content is high, these resistances are diminished so transfer is facilitated and the energy needed for such transfer to occur is reduced.

Similarly, increasing the temperature results in an increase in the number of molecules with sufficient kinetic energy to overcome the potential energy barrier. This results in a reduction in the energy which must be supplied to cause the transfer of water molecules. Thus, in moving from right to left in Figure 24, the heat of transfer decreased because of the increase in temperature. This occurred despite the reduction in moisture content which should cause an increase in the heat of transfer.



**Figure 25.** Hypothetical model showing the variation of the heat of transfer with moisture content: (a) enthalpy levels of water in a sample with a non-uniform moisture distribution; (b) enthalpy levels of water in a sample with uniform moisture distribution. (From: Skaar and Kuroda, 1984).

Eventually, when the force of attraction between the water molecule and the sorption site becomes sufficiently great (as when the moisture content is less than the level corresponding to complete monolayer coverage of sorption sites), the heat of transfer increases, the effect of reduction in moisture content being more pronounced than that due to the increase in temperature.

### 3. Evaluation of the Theoretical Models

To determine the applicability of the different theoretical models in describing nonisothermal moisture movement in wood, the  $\frac{dM}{dT}$  ratio given by equations (104), (105), (106), (107) and (109) were computed. The approach taken to obtain these theoretical values is outlined below:

(a) NET Model (Equation 104)

$$\left( \frac{dM}{dT} \right)_s = - \frac{H Q^*}{R T^2 \left( \frac{\partial H}{\partial M} \right)_T}$$

The temperature  $T$  was taken as the temperature at the different locations along the thickness while a value of  $1.987 \frac{\text{cal}}{\text{mol K}}$  was assigned to the gas constant  $R$ . For the heat of transfer  $Q^*$ , it was assumed that it is equal to the activation energy for the isothermal diffusion of water in wood and thus the expression

$$E_s = (9200 - 70M) \frac{\text{cal}}{\text{mol}} \quad [126]$$

suggested by Skaar and Siau (1981) was used. The relative humidity  $H$  and its partial derivative with respect to moisture content  $\frac{\partial H}{\partial M}$  were determined from equation (125), with the restriction that  $H$  doesn't exceed 100% and  $\frac{\partial H}{\partial M}$  is equal to that at the fiber saturation point for moisture contents beyond the hygroscopic range.

(b) Nelson Model (Equation 105)

$$\left( \frac{dM}{dT} \right)_s = \frac{\Delta H_o + \Delta H_s - C_{pv} T}{B_n T \Delta \mu}$$

The change in the chemical potential of water from the adsorbed state to the liquid state  $\Delta \mu$  and the constant  $B_n$  are parameters introduced by Nelson (1983) in a model for the sorption of water by cellulosic materials. The two-parameter sorption model is given by the expression:

$$\frac{p}{p_o} = \exp \left[ - \frac{\Delta \mu_o}{RT} \exp(B_n m) \right] \quad [127]$$

where  $\Delta \mu_o$  is the change in the chemical potential of water from the adsorbed state to the liquid state extrapolated to zero moisture content.  $\Delta \mu_o$  and  $B_n$  are functions of temperature, thus to derive the temperature-dependent expression for these quantities, the sorption curves obtained earlier through equation (125) were used. Since it was assumed that a unique sorption curve described each group of samples subjected to a given temperature gradient-average moisture content combination in the nonisothermal steady-state experiment, the coefficients  $\Delta \mu_o$  and  $B_n$  were determined for each group.

Using equation (125), the relative humidities at different moisture contents and temperatures were calculated. Five different temperature levels at 5°C intervals were used in these computations. Thus for the samples subjected to the 15 to 35°C gradient, calculations were made at 15, 20, 25, 30 and 35°C; while for those samples exposed to the 25 to 45°C gradient, evaluations were made at 25, 30, 35, 40 and 45°C.

From equation (91), the change in the chemical potential of water from the adsorbed phase to the liquid state is given by:

$$\Delta\mu = -R T \ln\left(\frac{H}{100}\right) \quad [128]$$

Thus by plugging the values of temperature and relative humidities in this equation, the values of  $\Delta\mu$  were obtained. But at a given temperature, the moisture content dependence of  $\Delta\mu$  is given by:

$$\Delta\mu = \Delta\mu_o \exp(B_n m) \quad [129a]$$

or

$$\ln \Delta\mu = A_n + B_n m \quad [129b]$$

where

$$A_n = \ln \Delta\mu_o \quad [129c]$$

After taking the natural logarithm of  $\Delta\mu$ , regression analysis between  $\ln \Delta\mu$  and the fractional moisture content  $M$  at a given temperature may be performed to obtain the values of  $B_n$  and  $(\ln \Delta\mu_o)$  if such a relationship is linear. The results of the regression analyses indicated that the relationship is indeed linear with a minimum  $r^2$  of 0.994 in

all the regression runs. For instance, for the group consisting of samples H1, C1, F1 and E1, the values of  $A_n$  and  $B_n$  at 30°C were 7.8364 and -20.4627, respectively, with an  $r^2$  of 0.998. Substitution of these values in equation (129b) indicates that  $\Delta\mu$  decreases exponentially with increasing moisture content, its value approaching zero as the moisture content of the wood approaches the fiber saturation point. This relationship between  $\Delta\mu$  and moisture content is in agreement with the results of Stamm and Loughborough (1935) and Kelsey and Clarke (1956).

To finally obtain the temperature dependent equations for  $B_n$  and  $\ln \Delta\mu_o$ , a series of regression analyses between  $B_n$  and  $T$ , and between  $\ln \Delta\mu_o$  and  $T$  was again performed for each group of samples resulting in the coefficients listed in appendix Table A8. The relationship between  $B_n$  and temperature  $T$  was linear, the simple linear regression analyses yielding a minimum  $r^2$  of 0.992 in all cases, with the regression analyses being highly significant at the 1% level. On the other hand, a quadratic relationship was obtained between  $\ln \Delta\mu_o$  and  $T$ , the analyses being significant at the 1% level and yielding a minimum of  $r^2$  of 0.987. The quantities  $C_p$  and  $\Delta H_s$  were determined from the following expressions proposed by Nelson (1986b):

$$C_p^v = 0.5[7.8875 + (7.22 + 0.002374 T - 0.000000267 T^2)] \quad [130]$$

$$\Delta H_s = \Delta\mu \left( 1 - m T \frac{dB_n}{dT} - T \frac{d \ln \Delta\mu_o}{dT} \right) \quad [131]$$

with units of  $\frac{\text{cal}}{\text{mol K}}$  and  $\frac{\text{cal}}{\text{mole}}$ , respectively. Values for the heat of vaporization were provided by equation (2) combined with the Kirchoff vapor pressure formula (Skaar, 1988):

$$\ln p_o = 51.29 - \frac{6651}{T} - 4.531 \ln T \quad [132a]$$

or

$$\frac{d(\ln p_o)}{d\left(\frac{1}{T}\right)} = -6651 + 4.531 T \quad [132b]$$

(c) Skaar-Siau Model (Equation 106)

$$\left(\frac{dM}{dT}\right)_s = -\frac{9200 - 70 M}{\frac{R T^2}{M} + 70 T}$$

This equation was evaluated in the same manner as (a) above with the temperatures and moisture contents at different locations directly inserted into the equation.

(d) Siau Model (Equation 107)

$$\left(\frac{dM}{dT}\right)_s = -\frac{H\left(T \frac{d\mu_1^o}{dT} + \Delta H_s + \Delta H_o + E_s + R T \ln \frac{H p_o}{7600}\right)}{R T^2 \left(\frac{\partial H}{\partial M}\right)_T}$$

The quantities  $R$ ,  $H$ ,  $T$ ,  $\frac{\partial H}{\partial M}$ ,  $\Delta H_o$ , and  $E_s$  were obtained as before, while  $p_o$  was calculated from equation (132a) with the resulting value properly converted from mmHg to cmHg. For the differential heat of sorption, a combination of equations (121), (122a), and (122b) was made resulting in

$$\Delta H_s = 5040[\exp(-0.14M)] \quad [133]$$

with units of  $\frac{\text{cal}}{\text{mol}}$ . For  $\frac{d\mu_1^o}{dT}$ , the equation

$$\frac{d\mu_1^0}{dT} = (85.84 - 18 \ln T) \frac{\text{cal}}{\text{mol K}} \quad [134]$$

was employed.

(e) Stanish Model (Equation 109)

$$\left( \frac{dM}{dT} \right)_s = - \frac{H T s_v}{R T^2 \left( \frac{\partial H}{\partial M} \right)_T}$$

The quantities  $R$ ,  $T$ ,  $H$ , and  $\frac{\partial H}{\partial M}$  were obtained as described earlier; while the molar entropy of water vapor  $s_v$  was calculated using equation (98).

The theoretical values of  $\frac{dM}{dT}$  calculated from the above models are presented in Figures 26 to 28 as a function of moisture content at different locations along the thickness of the nonisothermal steady-state sample. Also included in these figures are the experimental values of the  $\frac{dM}{dT}$  ratio. These three figures demonstrate the general pattern of the experimental and theoretical  $\frac{dM}{dT}$  obtained for the 42 samples. To obtain a measure of how well the  $\frac{dM}{dT}$  values computed using the different theoretical models compare with the experimental values, residual analyses were performed. The results of such analyses for the three samples presented in Figures 26 to 28 are summarized in Table 8. In performing these analyses, the  $\frac{dM}{dT}$  values for the locations in the sample where moisture contents were outside the range obtained in the sorption studies were excluded. This was done to minimize error associated with extrapolation of the sorption isotherms beyond the experimental relative humidity range. The occurrence of such error is suggested by Figure 10 where the fitted

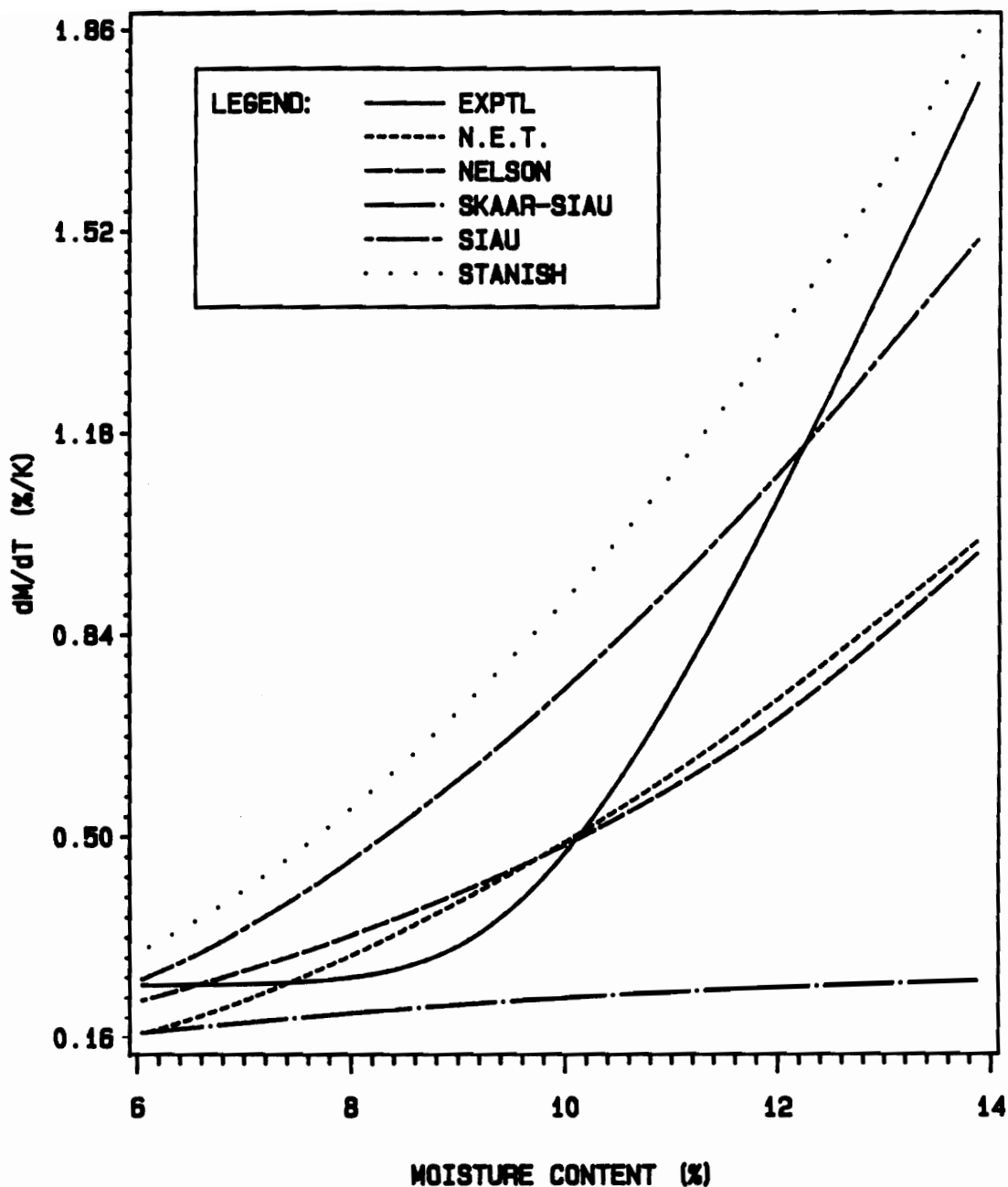


Figure 26. Experimental and theoretical  $dM/dT$  plotted against the MC at different locations along the thickness of a nonisothermal steady-state sample: The yellow poplar sample had an initial moisture content of 9% and was subjected to 15 C and 35 C on opposite faces.

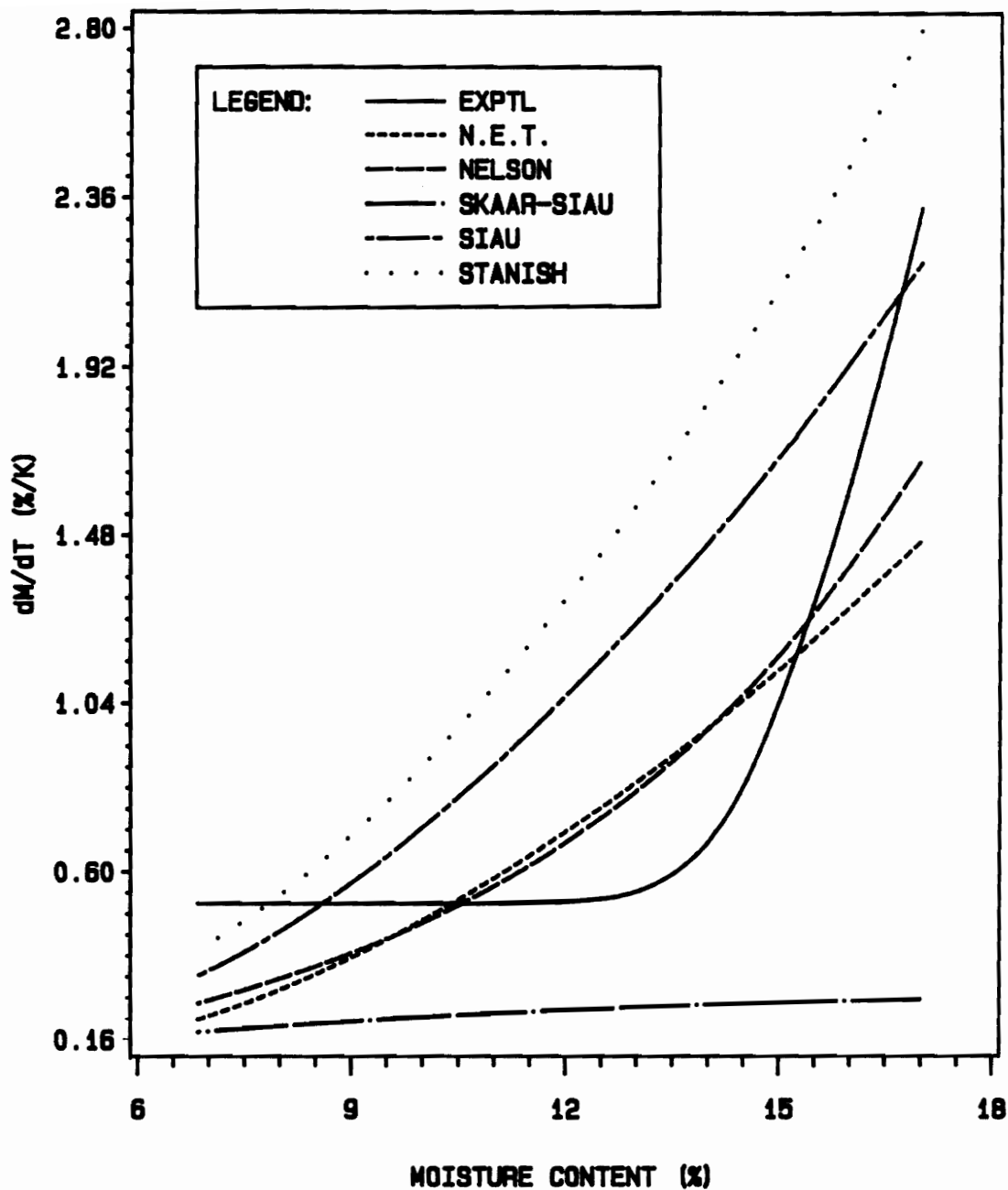


Figure 27. Experimental and theoretical  $dM/dT$  plotted against the MC at different locations along the thickness of a nonisothermal steady-state sample: The yellow poplar sample had an initial moisture content of 12% and was subjected to 15 C and 35 C on opposite faces.

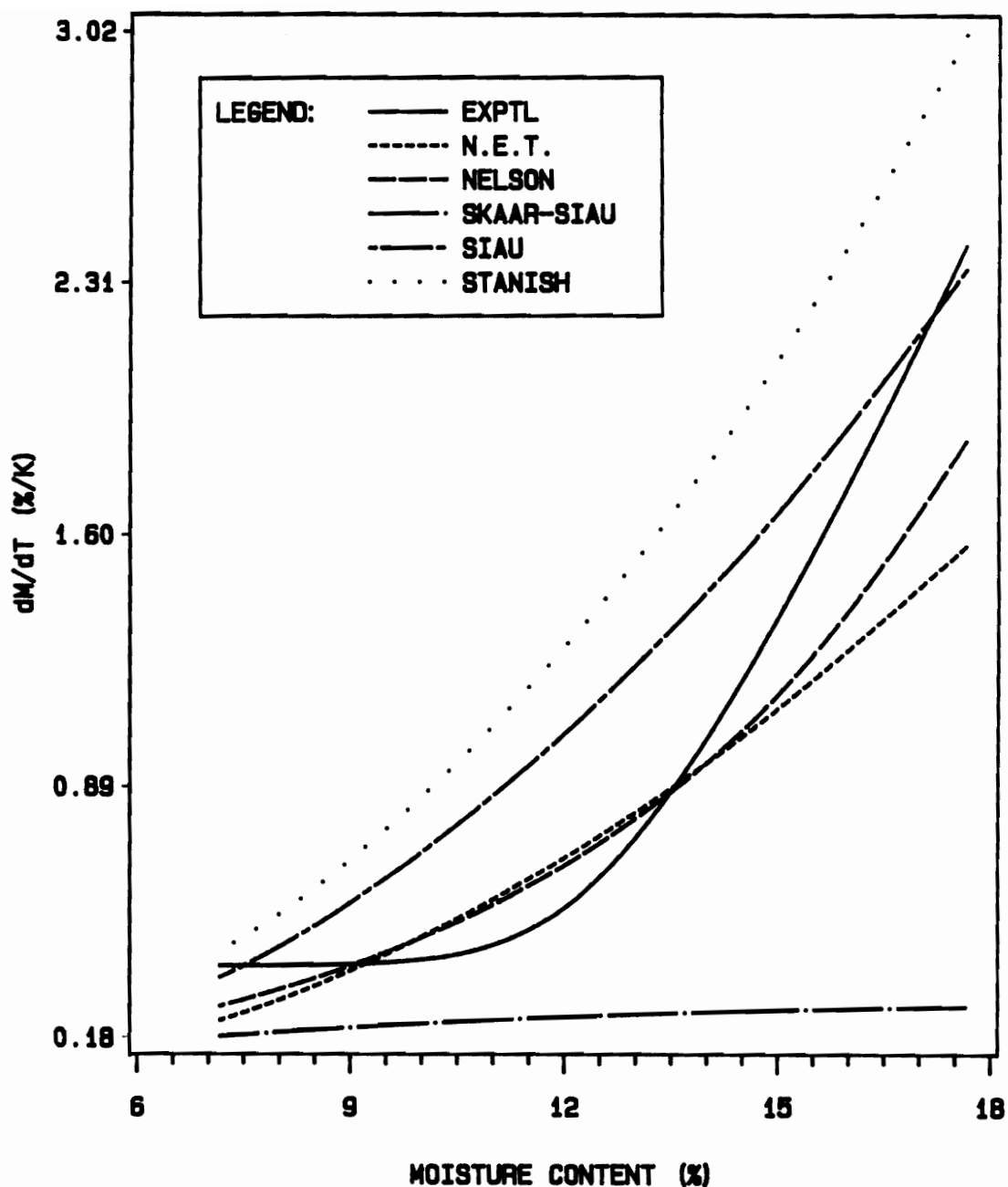


Figure 28. Experimental and theoretical  $dM/dT$  plotted against the MC at different locations along the thickness of a nonisothermal steady-state sample: The yellow poplar sample had an initial moisture content of 15% and was subjected to 15 C and 35 C on opposite faces.

**Table 8.** Mean analyses of the absolute residuals of the theoretical  $dM/dT$  from the experimental  $dM/dT$  for three nonisothermal steady-state samples.

| ID | Model      | Residuals |         |         |                    |
|----|------------|-----------|---------|---------|--------------------|
|    |            | Minimum   | Maximum | Mean    | Standard Deviation |
| A5 | NET        | 0.00229   | 0.77203 | 0.12314 | 0.20515            |
|    | Nelson     | 0.00512   | 0.79234 | 0.13303 | 0.21139            |
|    | Skaar-Siau | 0.05927   | 1.51376 | 0.28003 | 0.41809            |
|    | Siau       | 0.00999   | 0.29193 | 0.17624 | 0.09999            |
|    | Stanish    | 0.05968   | 0.42444 | 0.26634 | 0.12935            |
| H1 | NET        | 0.00626   | 0.84665 | 0.16232 | 0.21904            |
|    | Nelson     | 0.00531   | 0.55012 | 0.12322 | 0.14226            |
|    | Skaar-Siau | 0.17856   | 2.15063 | 0.48287 | 0.57856            |
|    | Siau       | 0.01493   | 0.49397 | 0.27327 | 0.17398            |
|    | Stanish    | 0.04015   | 0.77572 | 0.49218 | 0.25293            |
| B3 | NET        | 0.01443   | 0.86851 | 0.23454 | 0.22297            |
|    | Nelson     | 0.02580   | 0.66142 | 0.20451 | 0.16910            |
|    | Skaar-Siau | 0.28488   | 2.06806 | 0.49513 | 0.51138            |
|    | Siau       | 0.03811   | 0.78037 | 0.37096 | 0.26221            |
|    | Stanish    | 0.04329   | 1.14012 | 0.57295 | 0.39078            |

Hailwood-Horrobin adsorption curve crossed the desorption isotherm at about 98% relative humidity.

The Skaar-Siau activated molecule model underpredicted  $\frac{dM}{dT}$  in all the experimental runs; while the Stanish model overpredicted the ratio. The models which came close to the experimental data were the two NET models and the one proposed by Siau. Based on the results of the residual analyses, the two NET models yielded the least average deviation from the experimental values. These were followed by the Siau model, the Stanish model, and the Skaar-Siau model.

In calculating the  $\frac{dM}{dT}$  ratio by the NET equation (104), the heat of transfer had to be approximated from the activation energy for isothermal diffusion of water in wood. This approach arises from the treatment of moisture transport in biological membranes by Spanner (1954) and which later on was adopted by Briggs (1967) to characterize nonisothermal moisture transport in plant membranes. Consider for instance the system in Figure 3 containing, for simplicity, water only with the two parts separated by a 'membrane'. If a temperature difference is imposed between the two sides, thermodynamic equilibrium is disturbed causing movement of water from one side to the other. As discussed earlier, if the walls of the system are rigid, this flow will build up a pressure difference which eventually causes the flow to stop. If we denote the rate of transfer of water molecule as  $u$ ; then at steady state,  $u_1$  from side 1 will be equal to  $u_2$  from side 2 or  $\Delta u = 0$ . Treating  $u$  as a function of temperature  $T$  and pressure  $P$ , then

$$\Delta u = \frac{\partial u}{\partial T} \Delta T + \frac{\partial u}{\partial P} \Delta P = 0 \quad [135]$$

or by rearranging terms

$$\frac{\Delta P}{\Delta T} = - \frac{\partial u / \partial T}{\partial u / \partial P} = - \frac{\partial \ln u / \partial T}{\partial \ln u / \partial P} \quad [136]$$

If it is assumed that the rate of transfer is proportional to the vapor pressure  $p_{wo}$ , then by a well-known thermodynamic relation,

$$\frac{\partial(\ln u)}{\partial P} = \frac{\partial(\ln p_{wo})}{\partial P} = \frac{V_w}{RT} \quad [137]$$

Combining the last two equations result in

$$\frac{\partial(\ln u)}{\partial T} = - \frac{\Delta P}{\Delta T} \frac{V_w}{RT} \quad [138]$$

From Katchalsky and Curran (1965),  $\left[ \frac{\Delta P}{\Delta T} \right]_{j_w=0} = - \frac{Q^*}{V_w T}$ , thus,

$$\frac{\partial(\ln u)}{\partial T} = \frac{Q^*}{R T^2} \quad [139]$$

This is similar to the semi-empirical Arrhenius equation:

$$\frac{\partial[\ln(\text{rate})]}{\partial T} = \frac{E}{R T^2} \quad [140]$$

which is used to describe the variation of rate processes with temperature. In this equation,  $E$  denotes the activation energy of the process. These last two equations justify the use of the activation energy in place of the heat of transfer in equation (104) for computing  $\frac{dM}{dT}$ . This assumption of equivalence between the activation energy and the heat of transfer was also made by Siau (1980b) when he introduced the non-equilibrium thermodynamics equation for describing nonisothermal moisture movement in wood; and by Skaar and Siau (1981) when they proposed the 'activated

molecule' concept of moisture movement in wood. It must be pointed out, however, that the activation energy expression given by equation (126) was obtained by Skaar and Siau (1981) from Stamm's data on the variation of the conductivity coefficient of the cell wall of Sitka spruce with moisture content (Stamm,1959). The equation incorporates the moisture content dependence of the activation energy but does not include the possible effect of temperature on the heat of transfer as suggested by Figure 24. The ability of equation (104) to predict the magnitude of  $\frac{dM}{dT}$  may further be improved by having a better expression for the activation energy. Better yet is an information on the variation of the heat of transfer with temperature and moisture content.

The good agreement between the experimental  $\frac{dM}{dT}$  values and the quantities obtained using the NET models indicates that nonequilibrium thermodynamics applies to moisture movement in wood. This has been shown by Kawai (1980) for isothermal bound water movement; and by Nelson (1988) for the nonisothermal case. The difference in the  $\frac{dM}{dT}$  value computed using the two approaches based on nonequilibrium thermodynamics may be due mainly to the assumption made in using equation (104) that the heat of transfer is equal to the activation energy. Nelson (1986b) contended that the heat of transfer is greater than the activation energy. Based on the observation that the entropy of water vapor  $s_v$  at the steady state was more or less constant throughout the thickness of the samples in Choong's experiments (Choong,1963), Nelson took the temperature and moisture content dependence of  $s_v$  and came up with the relationship

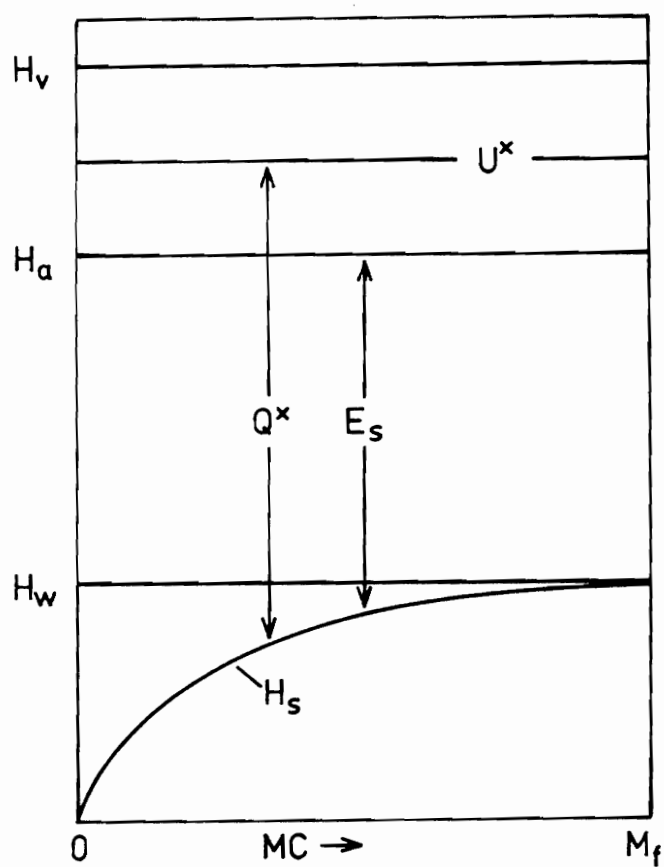
$$Q^* = \Delta H_o + \Delta H_s - C_p^v T \quad [141a]$$

$$Q^* = E_s + \Delta H_o - E_r - \frac{R T}{n} - C_p^v T \quad [141b]$$

where  $E_a$  is the component of activation energy associated with overcoming the attraction between water molecules. He then calculated  $Q^*$  and found out that it exceeded the activation energy by a factor of as much as 1.33. Nelson could not explain this distinction between the two quantities ( $Q^*$  and  $E_a$ ) but hinted that it may be related to the diffusing molecules having an energy in excess of the minimum required for participation in diffusion. He reasoned that more energy is carried by the diffusing molecules than is required for activation of the diffusion process. He therefore proposed in Figure 29 a modification to the enthalpy diagram given by Skaar and Kuroda (1984) in Figure 25. The diagram shows the relationships among the energy of transfer  $U^*$ , heat of transfer  $Q^*$ , activation energy  $E_a$ , and enthalpy of activated molecules  $H_a$ .

To see whether there is a difference in the value of  $Q^*$  and  $E_a$  calculated from equations (141a) and (126), these quantities were calculated for each experimental unit in this study. Also included in the computations were the values of  $(T_s)_v$  from the Stanish model and the magnitude of the expression in (110) from the Siau model. As mentioned earlier, these last two quantities should also approximate the heat of transfer.

Shown in Figures 30 to 32 are the results of the calculations for  $Q^*$  and  $E_a$  from equations (141a) and (126) plotted as a function of moisture content at different locations along the thickness of the material. The information are presented in the same form as Figures 25 and 29, the energy of transfer  $U^*$  being equal to the sum of the enthalpy of sorbed water and the heat of transfer; while the enthalpy of activated water molecules  $H_a$  is equal to the sum of the enthalpy of sorbed water and the activation energy. Two curves for  $U^*$  are included in the figures, one using the  $Q^*$  of



**Figure 29. Nelson's model of the variation of the heat of transfer and activation energy with moisture content:**  $U^x$  denotes the heat of transfer; while  $H_s$ ,  $H_w$ ,  $H_a$ , and  $H_v$  stand for the enthalpies of sorbed water, liquid water, activated water, and water vapor, respectively.

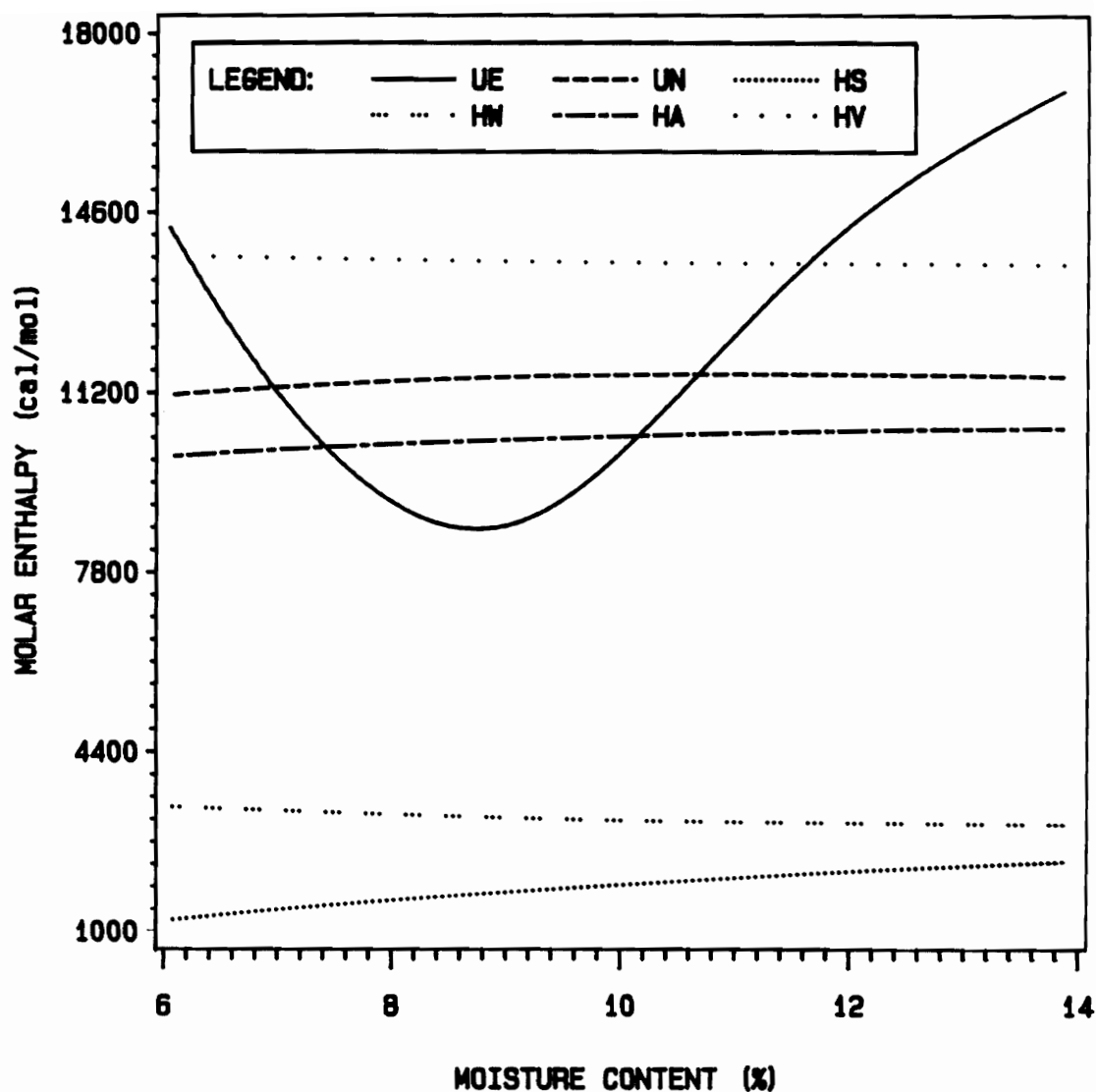


Figure 30. Enthalpies of water graphed against the moisture content at different locations along the thickness of a nonisothermal steady-state sample: UE and UN denote the energy of transfer obtained from the experimental results and from the Nelson model, respectively; while HS, HW,HA, and HV stand for the enthalpies of sorbed water, liquid water, activated water, and water vapor, respectively. The values are those for a yellow poplar sample which had an initial moisture content of 9% and was subjected to 15°C and 35°C on opposite faces.

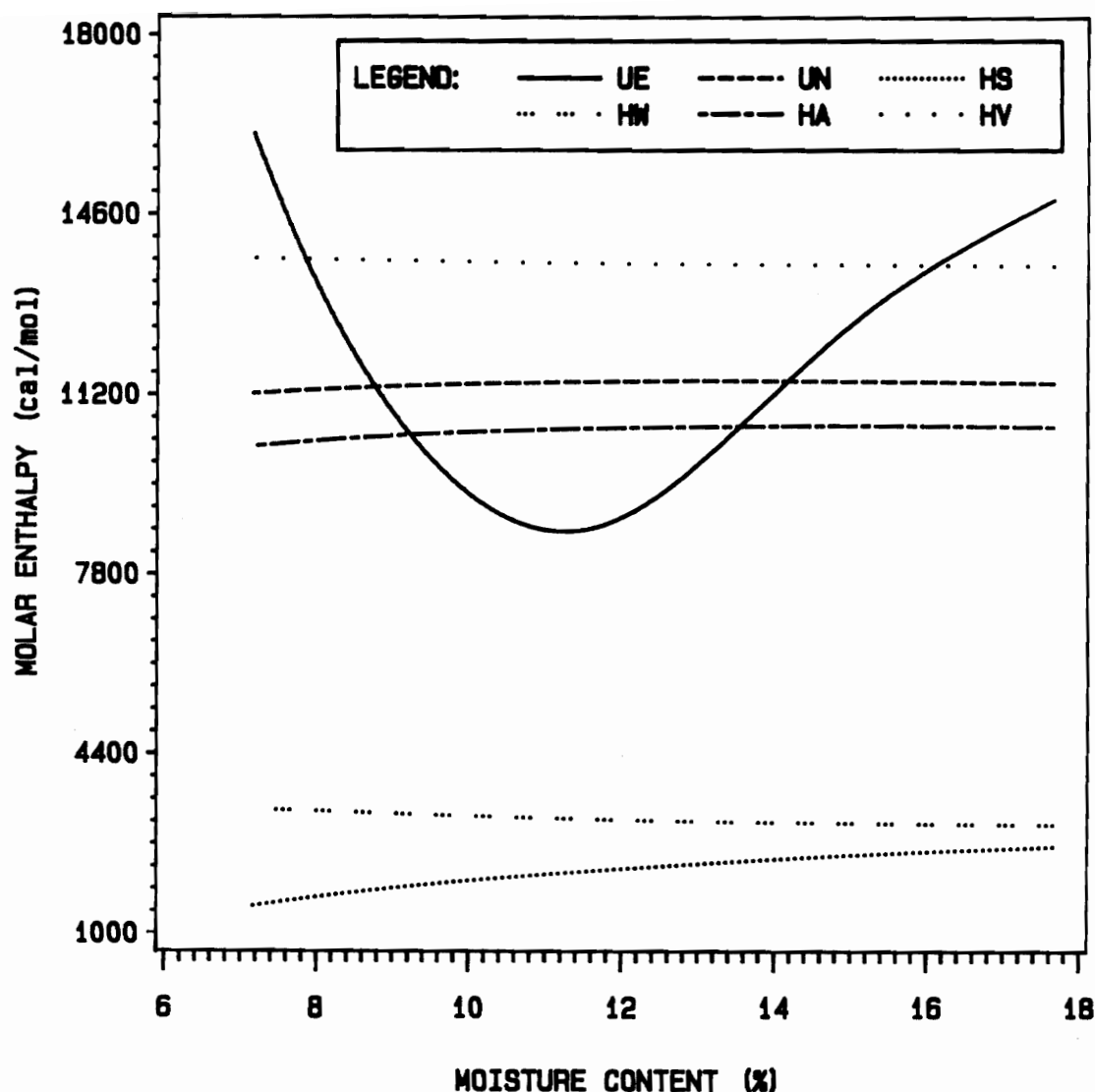
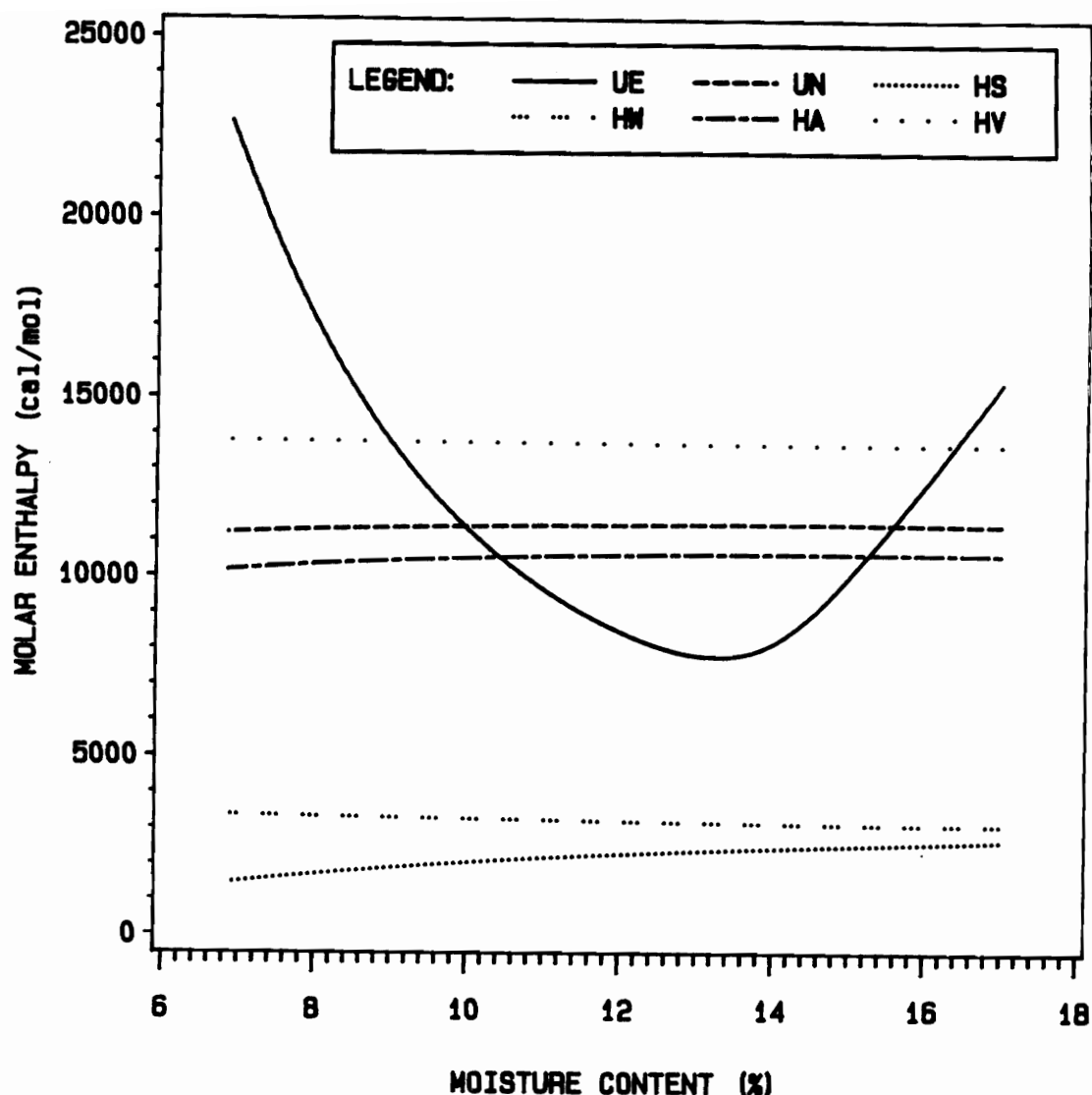


Figure 31. Enthalpies of water graphed against the moisture content at different locations along the thickness of a nonisothermal steady-state sample: UE and UN denote the energy of transfer obtained from the experimental results and from the Nelson model, respectively; while HS, HW, HA, and HV stand for the enthalpies of sorbed water, liquid water, activated water, and water vapor, respectively. The values are those for a yellow poplar sample which had an initial moisture content of 12% and was subjected to 15°C and 35°C on opposite faces.



**Figure 32.** Enthalpies of water graphed against the moisture content at different locations along the thickness of a nonisothermal steady-state sample: UE and UN denote the energy of transfer obtained from the experimental results and from the Nelson model, respectively; while HS, HW, HA, and HV stand for the enthalpies of sorbed water, liquid water, activated water, and water vapor, respectively. The values are those for a yellow poplar sample which had an initial moisture content of 15% and was subjected to 15°C and 35°C on opposite faces.

equation (141a) from the Nelson model, and the other from that of the NET equation (119). The enthalpy of water at a given temperature was calculated using equation (9) which may also be written as

$$H_w = H^o + H_{wm} + \int_{T_m}^T C_{pw} dT \quad [142]$$

where  $H_{wm}$  is the enthalpy of water at the melting point ( $T_m = 273.15\text{K}$ ) and is equal to 2750 cal/mol. Assuming the heat capacity of water is constant between 273.15 K and  $T$ , that is  $C_{pw} = 18 \frac{\text{cal}}{\text{mol K}}$ , then

$$H_w - H^o = 2750 + 18(T - 273.15) \quad [143]$$

The enthalpy of sorbed water was obtained from a combination of equation (8), equation (133), and the result of the above calculation; while the enthalpy of water vapor was calculated from the equation used by Nelson (1986b):

$$H_v = H^o + H_{wm} + \Delta H_{om} + C_p^v(T - 273.15) \quad [144]$$

where  $\Delta H_{om} = 10758 \frac{\text{cal}}{\text{mol}}$  is the heat of vaporization of water at  $T_m$ ; and  $C_p$  the average specific heat between  $T_m$  and  $T$  and is given by

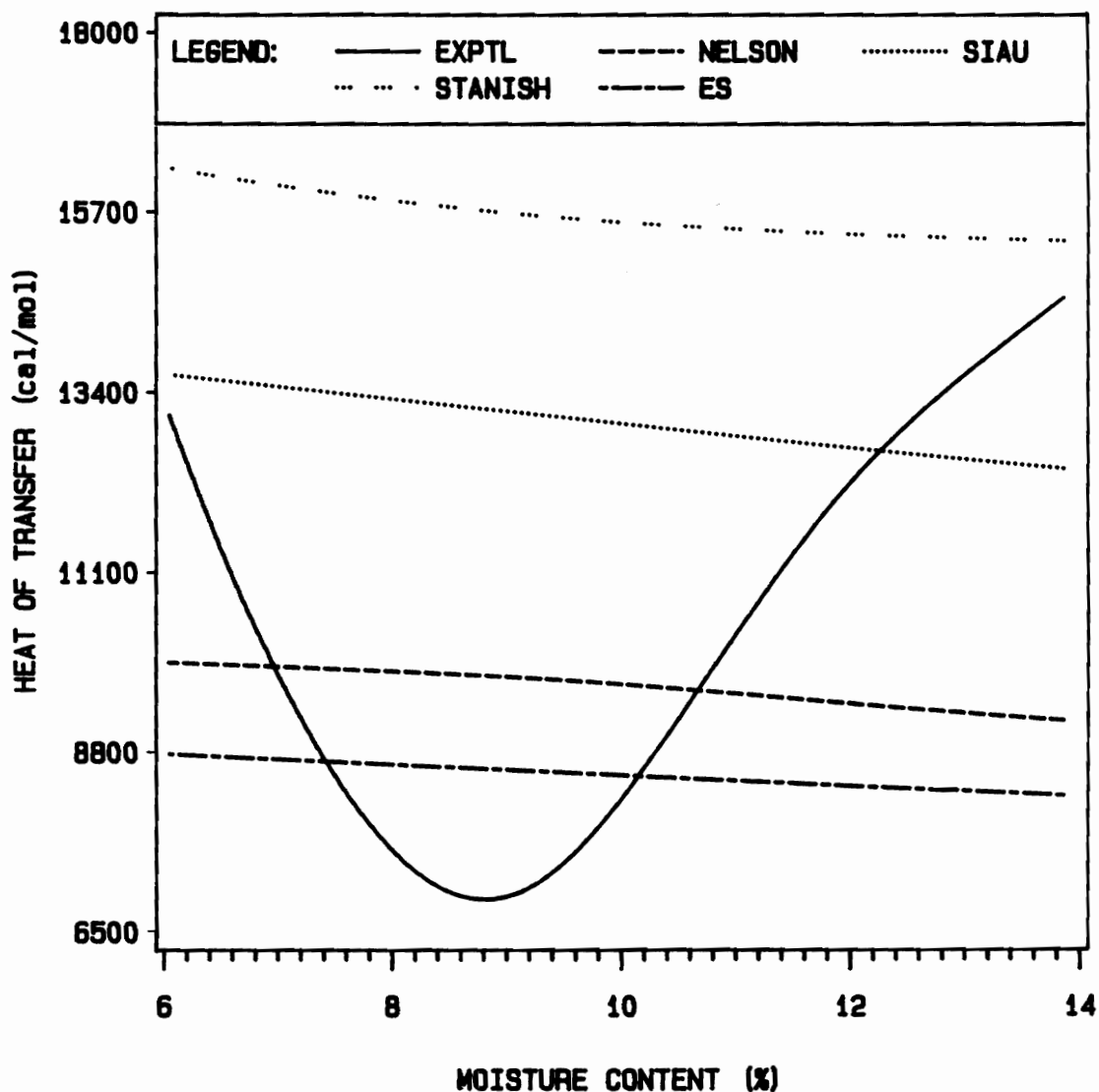
$$C_p^v = 0.5[7.8875 + (7.22 + 0.002374 T - 0.000000267 T^2)] \frac{\text{cal}}{\text{mol K}} \quad [145]$$

Notice in Figures 30 to 32 that the heat of transfer from the Nelson model exceeded the activation energy at all levels of moisture content. When the ratio of these two quantities ( $\frac{Q^*}{E_s}$ ) was taken, the resulting quotient ranged from 1.07 to 1.23, comparable to what Nelson (1986b) obtained from the data of Choong (1963). It is evident

though that the magnitudes of  $Q^*$  from the Nelson model and of  $E_s$  from equation (126) deviate from the experimental  $Q^*$ , a quantity they should approximate. This is better demonstrated in Figures 33 to 35 where they are combined with the  $Q^*$  from the Stanish and the Siau models. The calculated values increased steadily with increase in distance from the cold face with the magnitude varying from 7900 to 8800  $\frac{\text{cal}}{\text{mol}}$  for  $E_s$ , to 15200 to 16500  $\frac{\text{cal}}{\text{mol}}$  for  $Q^*$  computed from the Stanish model. The Nelson and Siau models yielded  $Q^*$  values ranging from 8500 to 9900  $\frac{\text{cal}}{\text{mol}}$ ; and from 11700 to 13600  $\frac{\text{cal}}{\text{mol}}$ , respectively. The monotonic reduction in the calculated heat of transfer with increase in moisture content in Figures 33 to 35 suggest that the theoretical models are more sensitive to moisture content variation than to the effect of temperature. As discussed earlier, the U-shape profile of the experimental heat of transfer was the result of the combined influence of the moisture content and temperature variation across the thickness of the material. The temperature dependence of the heat of transfer is not reflected in the  $Q^*$  calculated from the theoretical models.

#### **4. Miscellaneous Calculations**

From the data generated in these experiments, other quantities of interest may be calculated. For instance, the entropy of sorbed water, liquid water, and water vapor at different locations along the thickness of the material can be easily determined. As mentioned earlier, the basis of Nelson's claim that the heat of transfer is different from the activation energy is the fact that the calculated entropy of water vapor in Choong's experiments was more or less constant across the thickness. To see if this also holds in the experiments performed here,  $s_v$  was obtained for each sample at different locations along the thickness. These, together with the entropy of sorbed



**Figure 33.** Experimental and theoretical heat of transfer graphed against MC at different locations along the thickness of a nonisothermal steady-state sample: The values are those of a yellow poplar sample which had an initial moisture content of 9% and was subjected to 15 C and 35 C on opposite faces. Included in the figure is the activation energy for bound water diffusion, ES.

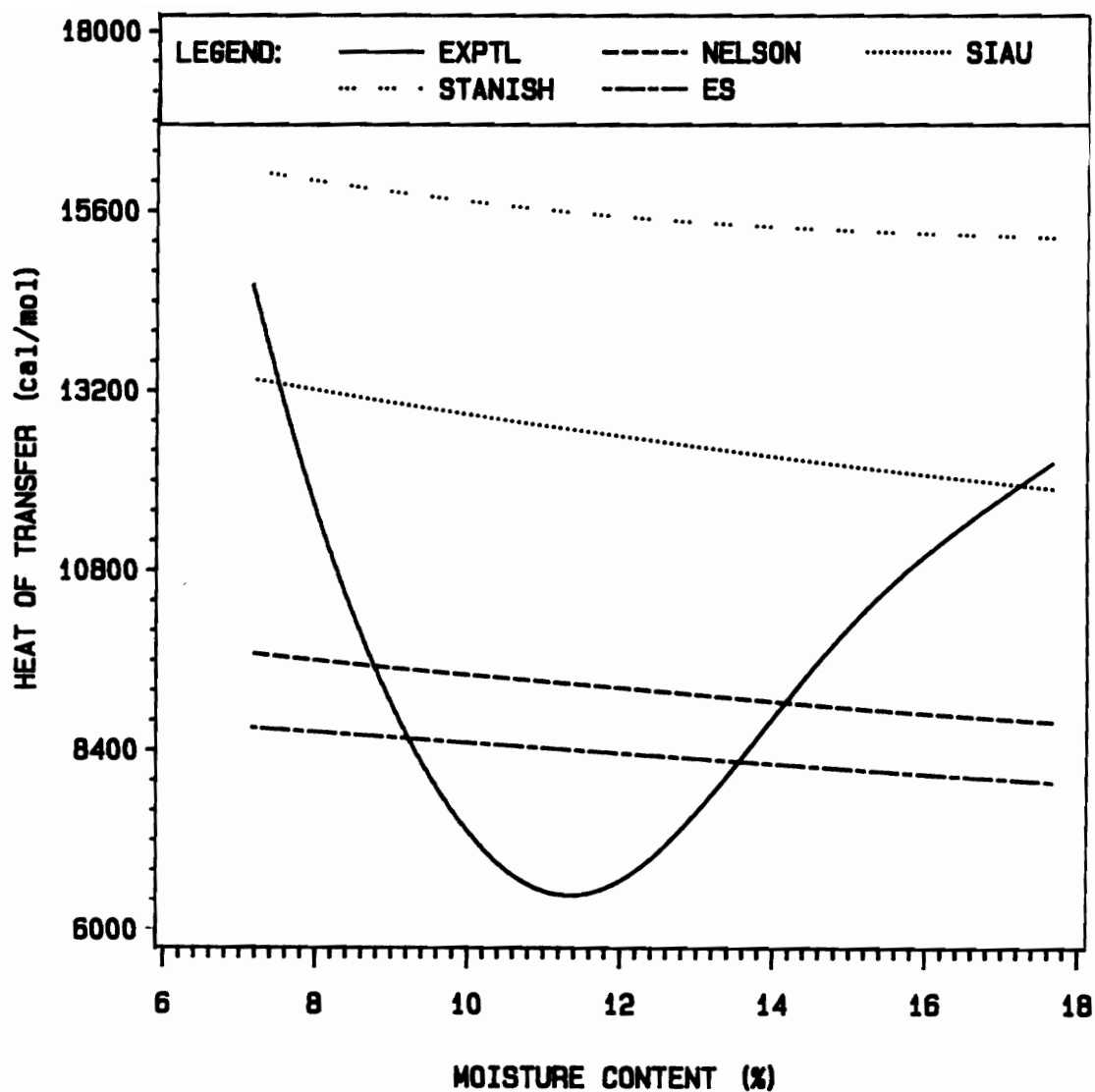


Figure 34. Experimental and theoretical heat of transfer graphed against MC at different locations along the thickness of a nonisothermal steady-state sample: The values are those of a yellow poplar sample which had an initial moisture content of 12% and was subjected to 15 C and 35 C on opposite faces. Included in the figure is the activation energy for bound water diffusion, ES.

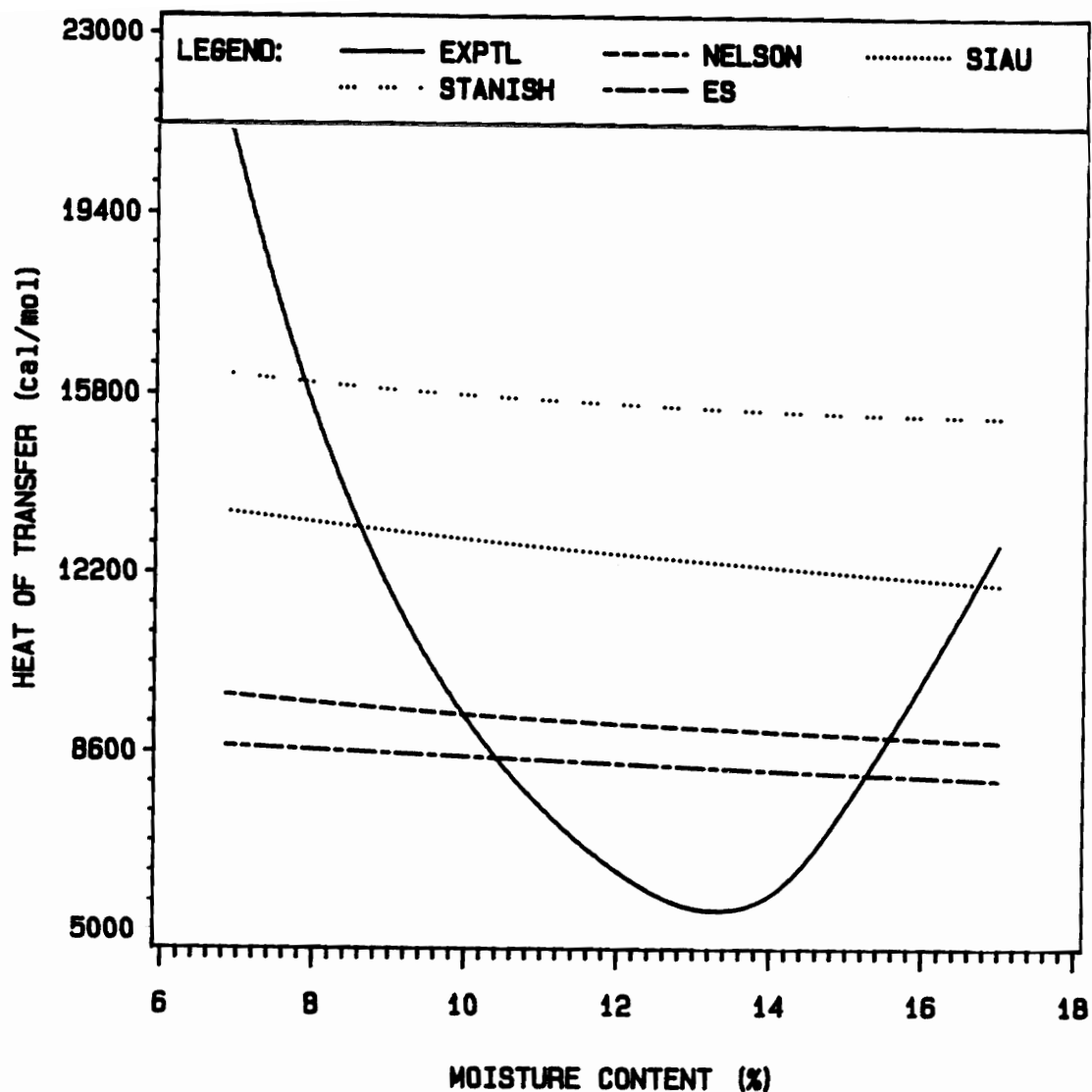


Figure 35. Experimental and theoretical heat of transfer graphed against MC at different locations along the thickness of a nonisothermal steady-state sample: The values are those of a yellow poplar sample which had an initial moisture content of 15% and was subjected to 15 C and 35 C on opposite faces. Included in the figure is the activation energy for bound water diffusion, ES.

water are presented in Figures 36 to 38 for three representative yellow poplar samples. The entropy of water vapor was based on the relationship

$$dS_v = \left[ \frac{\partial S_v}{\partial T} \right]_p dT + \left[ \frac{\partial S}{\partial p} \right]_T dp \quad [146]$$

$$dS_v = C_p \frac{dT}{T} - R \frac{dp}{p} \quad [147]$$

Integration results in the following expression

$$S_v = S_{ref} + C_p \ln \frac{T}{T_{ref}} - R \ln \frac{p}{p_{ref}} \quad [148]$$

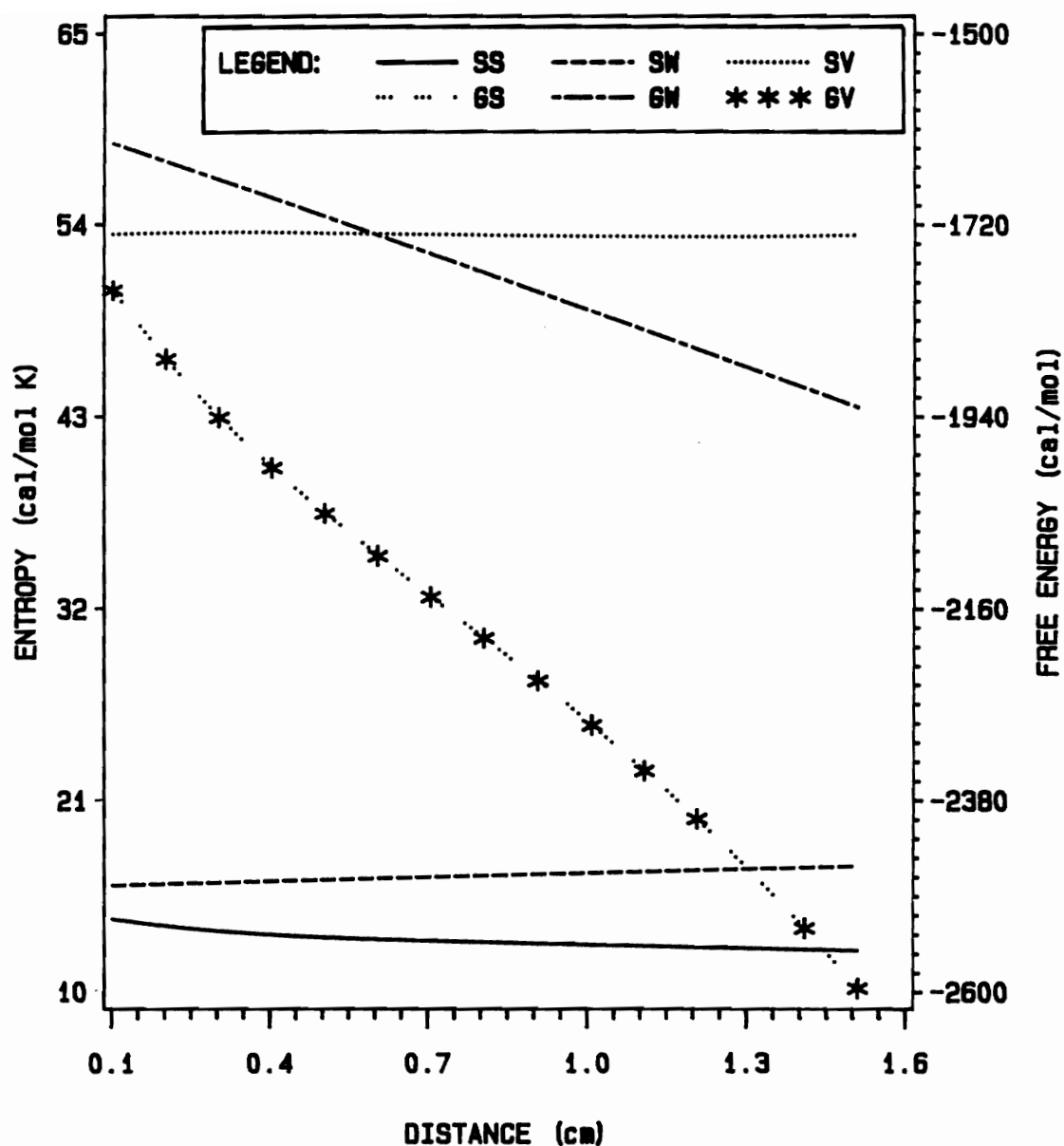
which can be evaluated at any temperature  $T$  and vapor pressure  $p$  based on the following values of  $S_{ref}$  and  $C_p$  at  $T_{ref} = 300K$ ,  $p_{ref} = 760mmhg$  from Eisenberg and Kauzmann (1969):

$$S_{ref} = 45.1492 \frac{\text{cal}}{\text{mol K}} \quad [149]$$

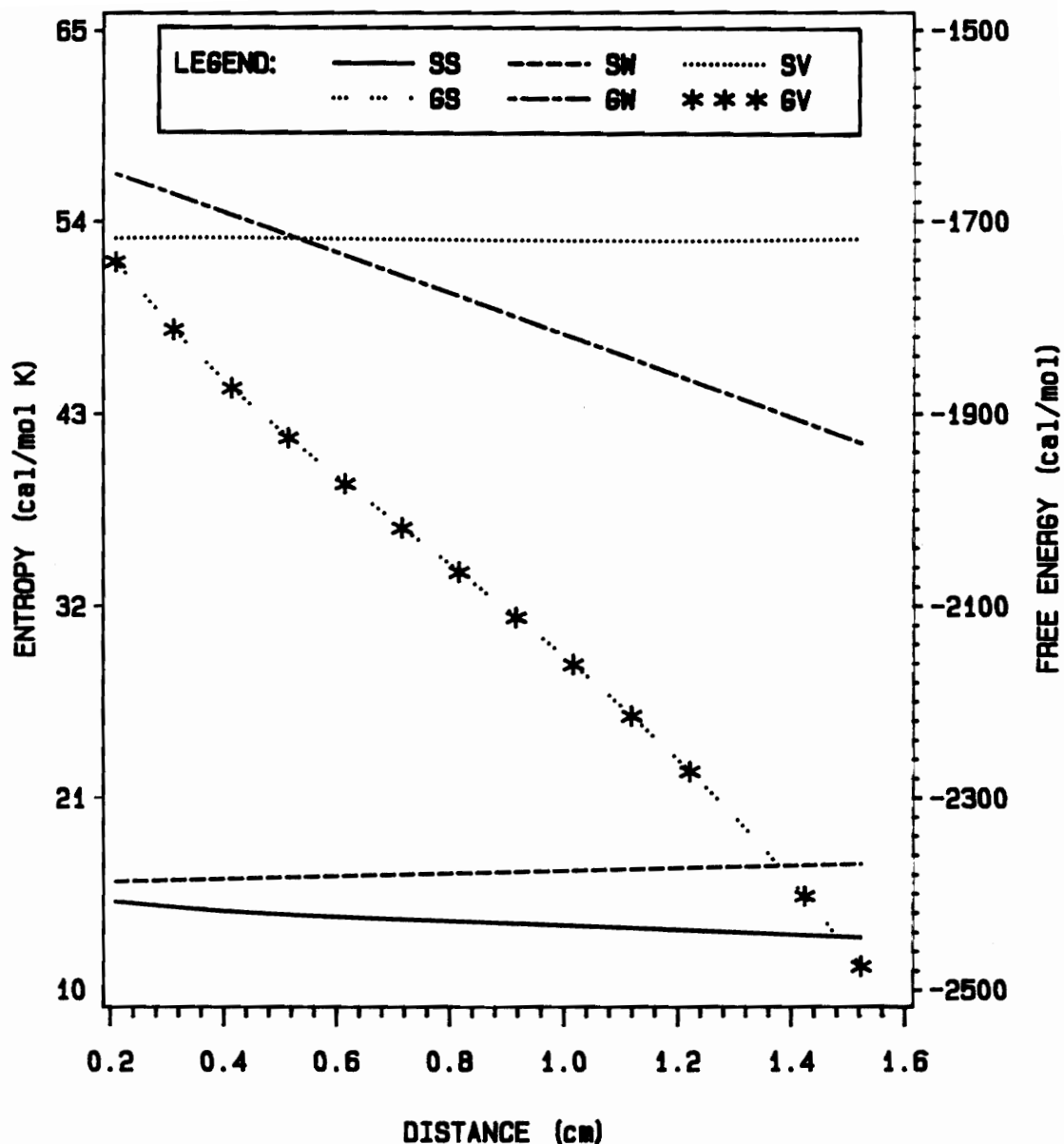
$$C_p = 8.0263 \frac{\text{cal}}{\text{mol K}} \quad [150]$$

The entropy of sorbed water, on the other hand, was determined from equation (11) which may also be written as follows

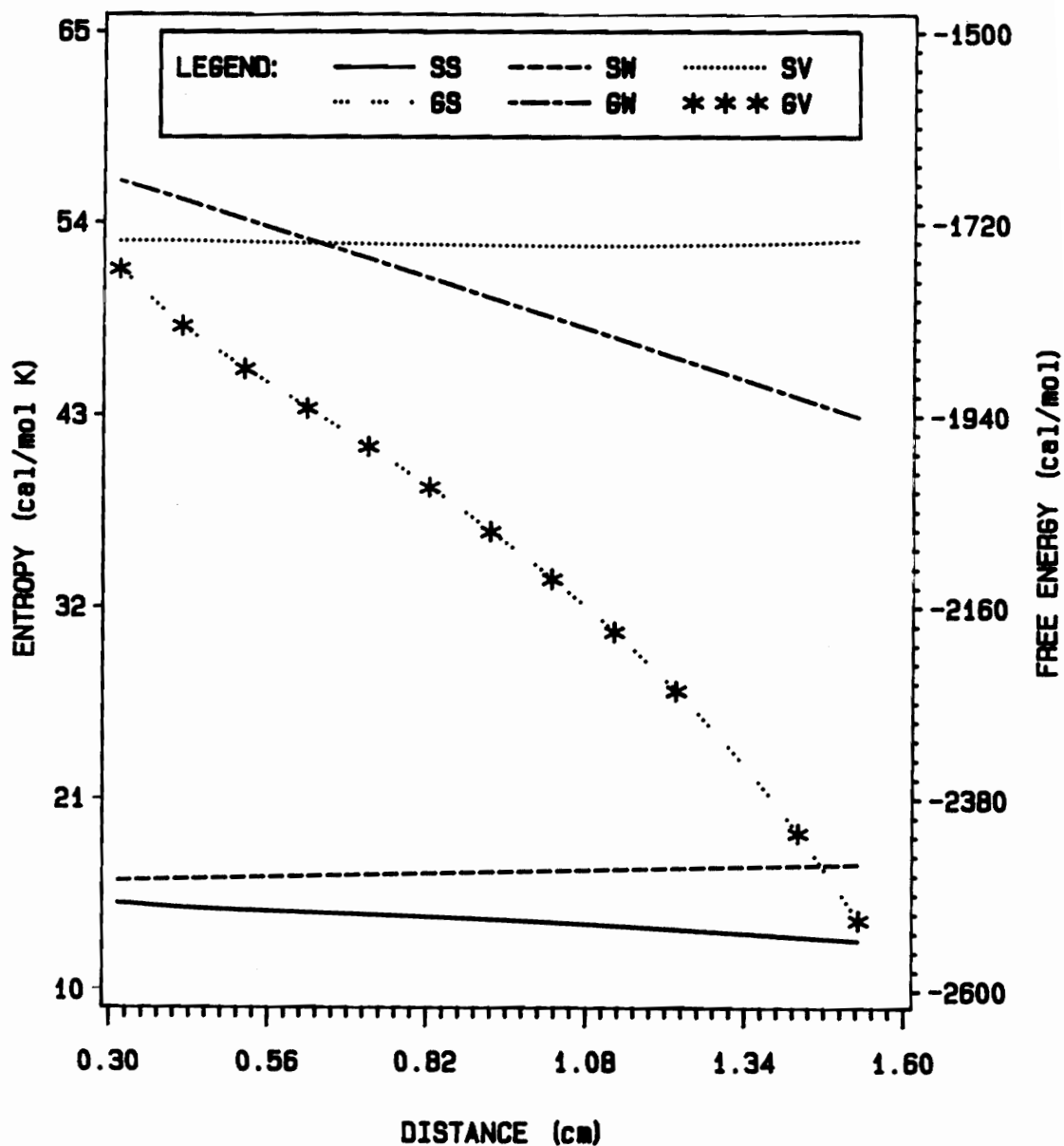
$$S_s = S_{im} + \frac{\Delta H_m}{T_m} - \Delta S_s + \int_{T_m}^T \frac{C_{pw}}{T} dT \quad [151]$$



**Figure 36. Entropy and free energy at different locations along the thickness of a nonisothermal steady-state sample:** The values are those of a yellow poplar sample which had an initial moisture content of 9% and was subjected to 15°C and 35°C on opposite faces. SS, SW, and SV refer to the entropy of sorbed water, liquid water, and water vapor, respectively; while GS, GW, and GV denote the free energy of sorbed water, liquid water, and water vapor, respectively.



**Figure 37. Entropy and free energy at different locations along the thickness of a nonisothermal steady-state sample:** The values are those of a yellow poplar sample which had an initial moisture content of 12% and was subjected to 15°C and 35°C on opposite faces. SS, SW, and SV refer to the entropy of sorbed water, liquid water, and water vapor, respectively; while GS, GW, and GV denote the free energy of sorbed water, liquid water, and water vapor, respectively.



**Figure 38. Entropy and free energy at different locations along the thickness of a nonisothermal steady-state sample:** The values are those of a yellow poplar sample which had an initial moisture content of 15% and was subjected to 15°C and 35°C on opposite faces. SS, SW, and SV refer to the entropy of sorbed water, liquid water, and water vapor, respectively; while GS, GW, and GV denote the free energy of sorbed water, liquid water, and water vapor, respectively.

where  $S_{im} = 9.86 \frac{\text{cal}}{\text{mol K}}$  is the entropy of ice at the melting point, and  $\Delta H_m = 1440 \frac{\text{cal}}{\text{mol K}}$  is the heat of fusion. From equation (5),  $\Delta S_s = \frac{\Delta H_s + RT \ln(p/p_o)}{T}$  thus

$$S_s = 1513 + 18 \ln\left(\frac{T}{273.15}\right) - \frac{\Delta H_s + R T \ln\left(\frac{p}{p_o}\right)}{T} \quad [152]$$

The entropy profiles in Figures 36 to 38 are indeed more or less constant across the thickness supporting Nelson's claim. The way Nelson (1986b) interpreted this is that at the steady state, the constant entropy is a result of the adherence of the system to the minimum entropy production concept of nonequilibrium thermodynamics. A variation in entropy from one point in the system to another would be associated with additional entropy production.

Another thermodynamic variable which can be evaluated from the information generated in this experiment is the molar Gibb's free energy. It is important to be able to compare the free energy of the two forms of water (sorbed water and water vapor) present in wood since a very important assumption of nonequilibrium thermodynamics is that of local equilibrium. At a particular location in the material, the free energy of water vapor must be equal to the free energy of sorbed water. This assumption is also the foundation on which Stanish's equation was built (Stanish, 1986). The graph of the molar Gibb's free energy of water vapor and sorbed water are included in Figures 36 to 38. These values were obtained by difference from the quantities obtained earlier, that is,

$$G_s = H_s - T S_s \quad [153a]$$

and

$$G_v = H_v - T S_v \quad [153b]$$

Examination of Figures 36 to 38 reveal that the molar free energy of the two phases of water present in wood are practically coincident indicating the validity of the assumption of nonequilibrium thermodynamics and of Stanish's supposition. Notice also that in the sample with the highest initial moisture content, the free energy curves of water vapor, liquid water, and sorbed water converged near the cold face where the moisture content of the wood layers exceeded the fiber saturation point, demonstrating equilibrium among the three phases of water present in the wood. Another information which can be gathered from the figures is that at the steady state condition, there exists a gradient in the molar free energy of sorbed water and that this is opposite to that of the temperature gradient. If we take the concentration-dependent component of the chemical potential, that is, if we add to the sorbed water chemical potential gradient the product of the sorbed water entropy and the temperature gradient, this picture suggests that there is a balance in the flow of water due to the thermal gradient and the flow of water due to the concentration-dependent component of the chemical potential as expressed by equation (61a). Thus the flow of water is shown to be the result of the action of two forces which at the steady state must balance each other. This is in contrast to Bramhall's hypothesis (Bramhall, 1979) that the flow of water is proportional to only one driving force and that this driving force is the vapor pressure. To show that the single-force, vapor-pressure-driven flow idea doesn't hold for the nonisothermal case, the vapor pressure  $p$  at different locations across the thickness of the material were calculated in all the samples studied here. Included in these computations was the spreading pressure  $\phi$ , another driving force suggested for moisture movement in wood. These quantities were obtained using the following equations:

$$p = \frac{H}{100} p_o \quad [154a]$$

$$\phi = -\frac{\Delta\mu_o}{B_n M \Sigma} [1 + (B_n m - 1) \exp(B_n m)] \quad [154b]$$

where  $p_o$  is the saturated vapor pressure obtained from equation (157);  $\Sigma = 260 \frac{m^2}{g}$  is the internal contact area per unit mass of adsorbent;  $M = 18 \frac{g}{mol}$  is the molecular weight of water; and  $B_n$  and  $\Delta\mu_o$  are the Nelson sorption parameters obtained from Table A8.

The results of these calculations are presented in Figures 39 to 41 for three representative samples. It is apparent that the vapor pressure and spreading pressure at the steady state were variable across the thickness of the material proving that other forces were opposing them to keep a balance of flow in both directions of increasing and decreasing distance from the cold face.

A moisture flux equation was derived earlier where a new transfer quantity  $Q_2$  was defined. The quantity  $Q_2$  deserves consideration because of the simplicity of the flux equation (equation 72) and the fact that the parameter can be easily determined from a simple experiment like the nonisothermal steady state studies performed here. The only information needed to evaluate it are the final temperature and moisture content profiles in a closed nonisothermal system which has attained steady state. The magnitude of this parameter was calculated for each sample used in this study, with its variation across the thickness of the material demonstrated in Figure 42. These profiles were obtained using only one working equation since the functions which described the variation of temperature and moisture content with distance from the cold face had the same form in all samples. The equation is given by

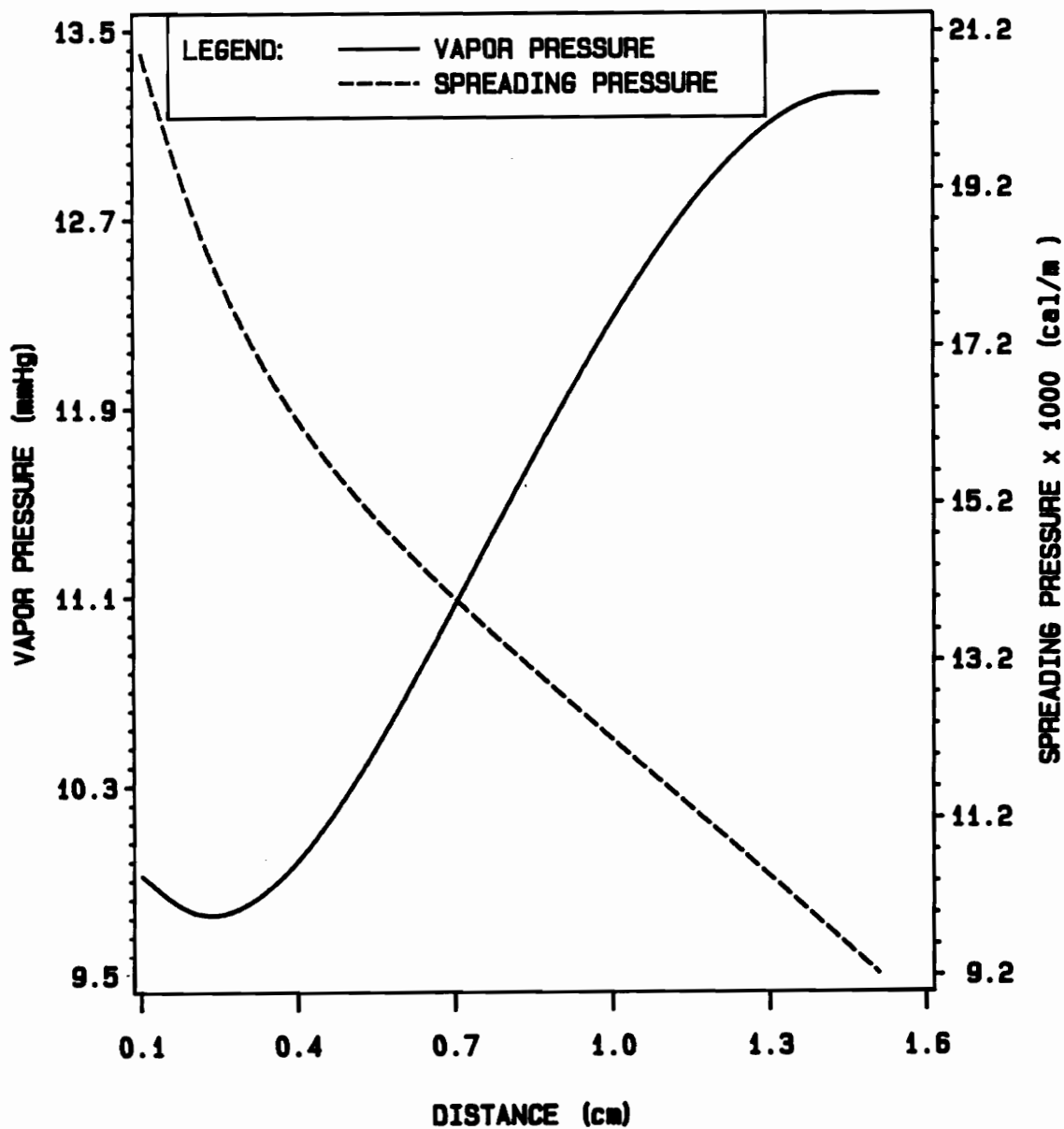
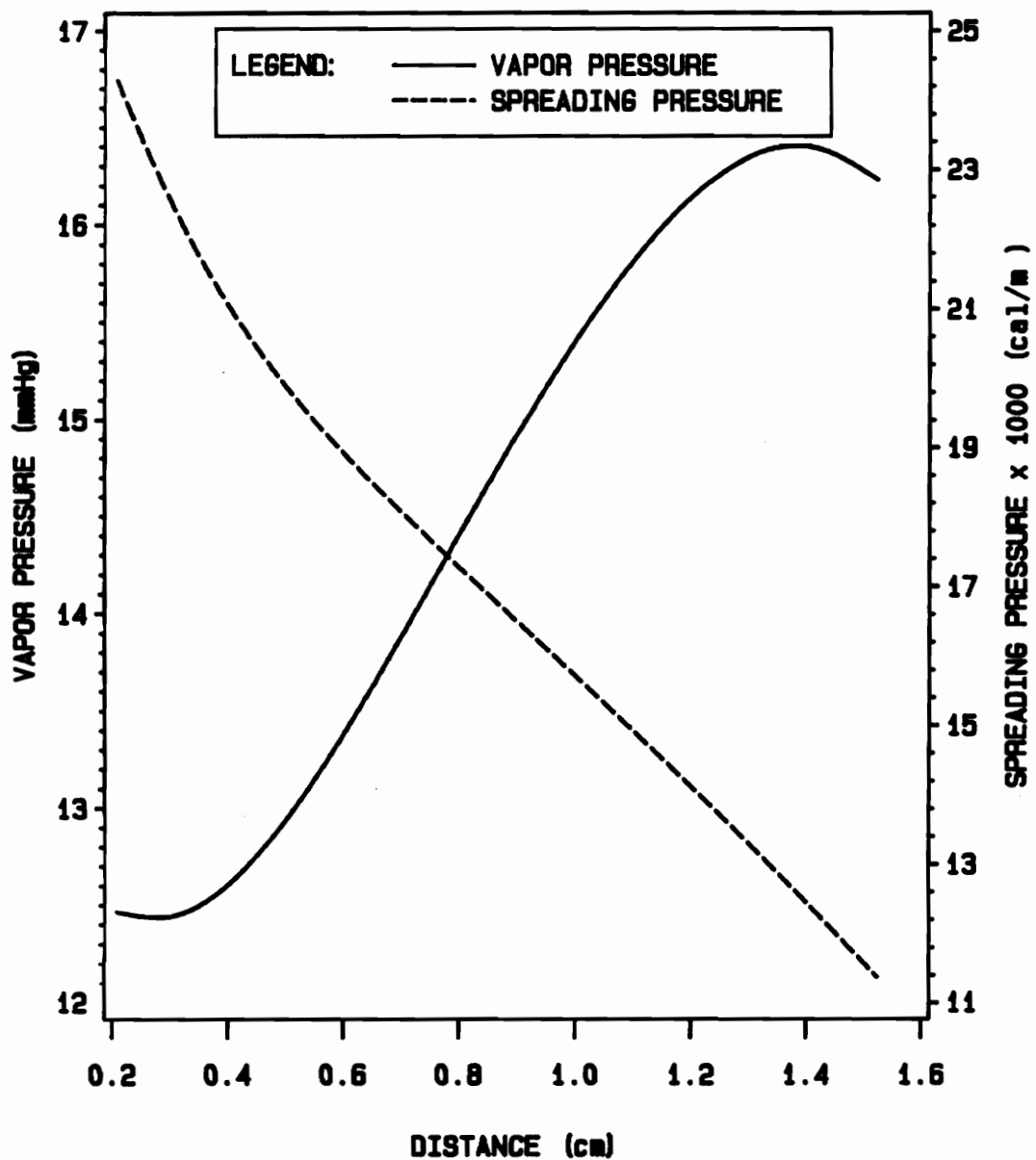
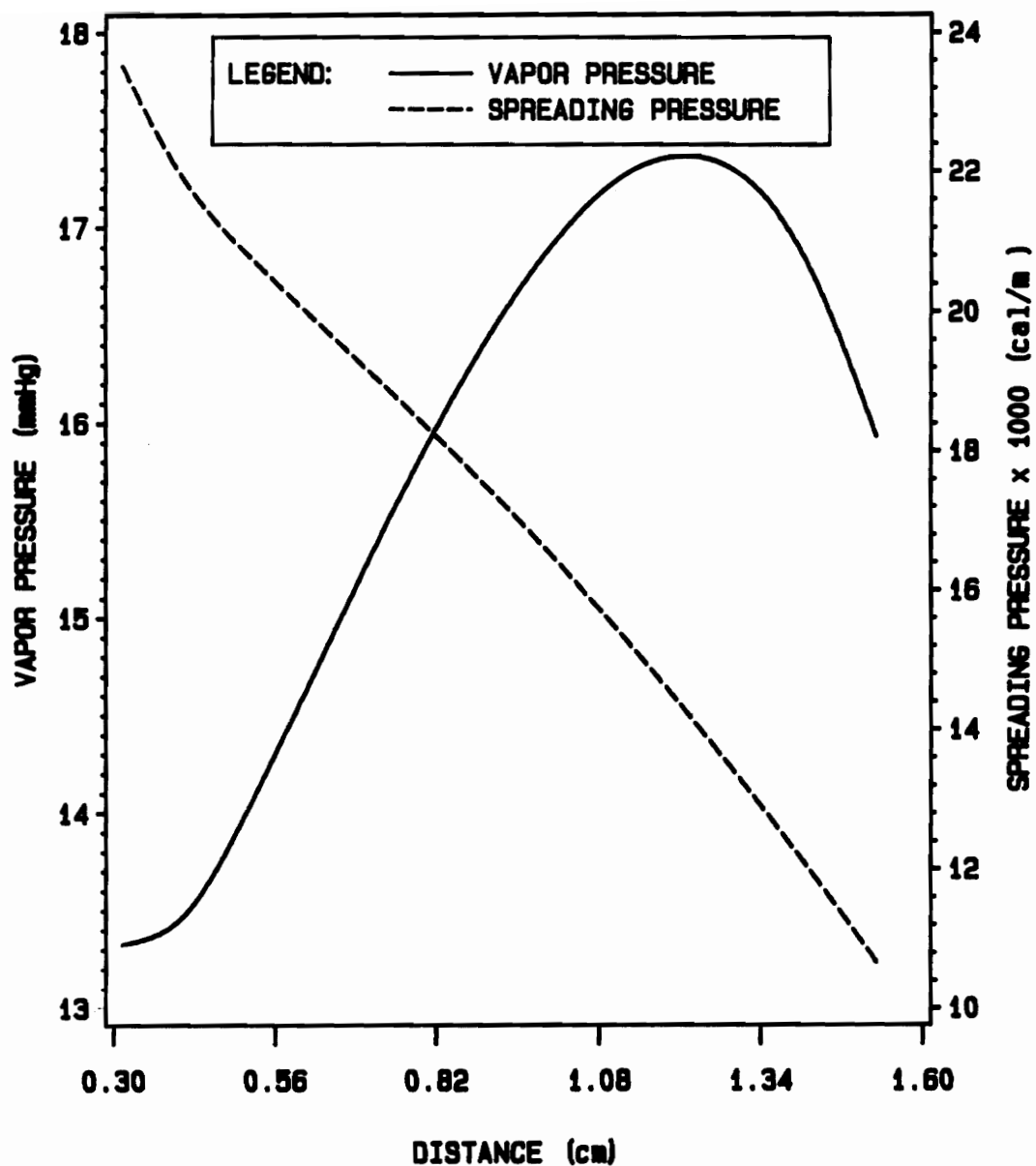


Figure 39. Vapor pressure and spreading pressure at different locations along the thickness of a nonisothermal steady-state sample: The values are those of a yellow poplar sample which had an initial moisture content of 9% and was subjected to 15 C and 35 C on opposite faces.



**Figure 40.** Vapor pressure and spreading pressure at different locations along the thickness of a nonisothermal steady-state sample: The values are those of a yellow poplar sample which had an initial moisture content of 12% and was subjected to 15 C and 35 C on opposite faces.



**Figure 41.** Vapor pressure and spreading pressure at different locations along the thickness of a nonisothermal steady-state sample: The values are those of a yellow poplar sample which had an initial moisture content of 15% and was subjected to 15 C and 35 C on opposite faces.

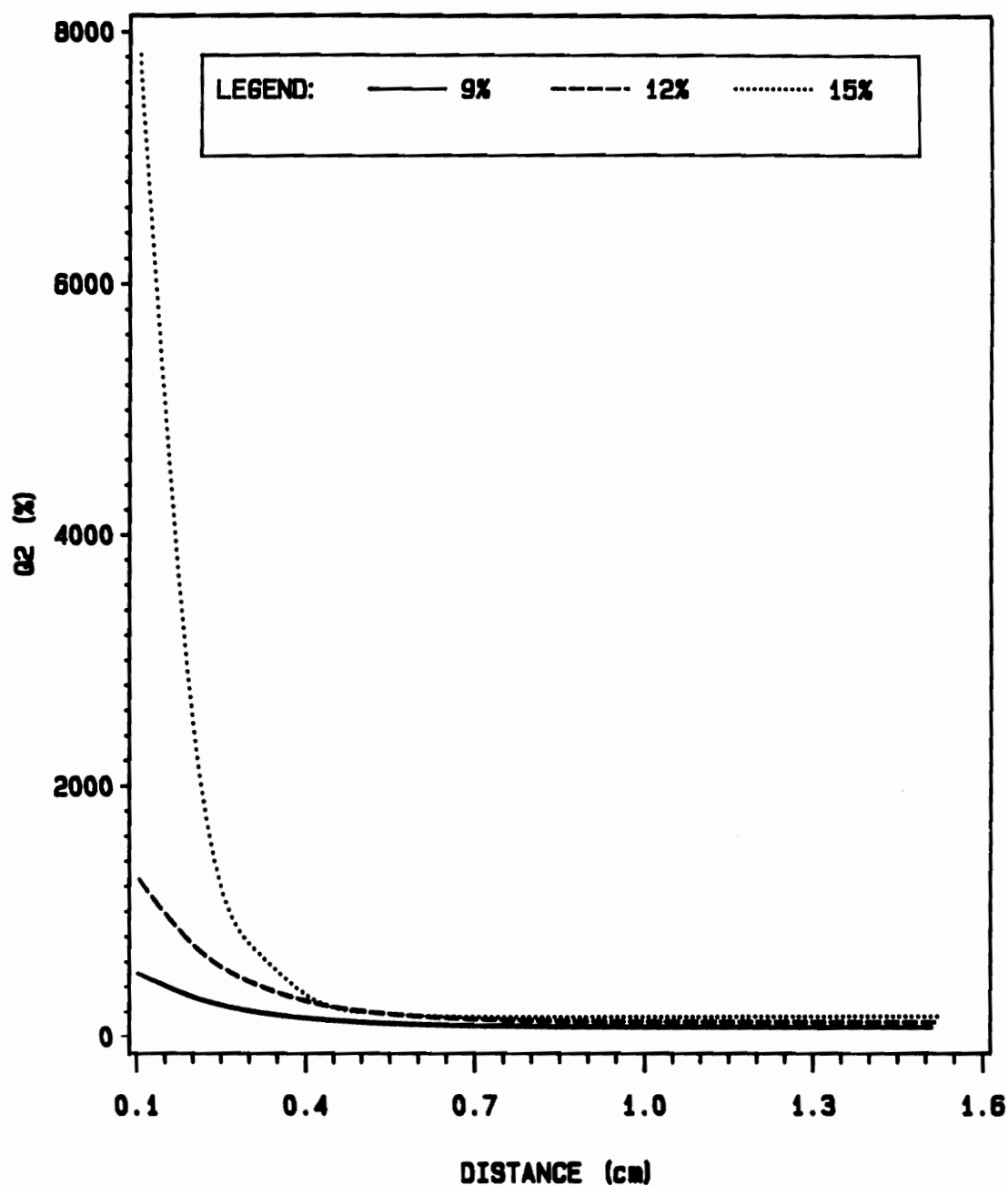


Figure 42. Transfer quantity  $Q_2$  at different locations along the thickness for three nonisothermal steady-state samples: The values are those of yellow poplar samples whose opposite faces were subjected to 15 C and 35 C.

$$Q_2 = - \frac{(A_T + B_T x)(B_M - C_M D_M \exp(-D_M x))}{B_T} \quad [155]$$

where  $x$  is the distance from the cold face; and  $A_T$ ,  $B_T$ ,  $B_M$ ,  $C_M$ , and  $D_M$  are the coefficients in Table A6. The shape of the resulting curves were about the same for all samples where it initially decreased with distance from the cold face and then remained more or less constant for about the remaining half of the thickness. Analyses of variance were also performed to test the effect of the different experimental variables on the magnitude of  $Q_2$ . This was done at three different locations of 0.25, 0.50, and 0.75 of the thickness. For  $x=0.25$  and 0.50 of the thickness, interaction effects were significant, meaning no statements can be made regarding the main factors. For  $x=0.75$  of the thickness, no such interaction effects were observed, thus, it is instructive to first take a look at  $Q_2$  at this last location. Mean analyses showed that this quantity increased with increase in both the temperature and moisture content, and that it was higher for hard maple than for yellow poplar. When the same mean comparisons were performed at the first two locations, disregarding the effect of the highest moisture content level which was mainly responsible for the interaction effects, the same pattern of increasing mean value of  $Q_2$  with temperature and moisture content were observed. With regard to the species effect, the same observation as for  $x=0.75$  of the thickness was noted for location  $x=0.50$  of the thickness but for the first location, it was found out that  $Q_2$  was higher for yellow poplar. The picture all these analyses paint is that  $Q_2$  is a complicated quantity. If only it were constant then it would have been a very useful parameter in modelling nonisothermal moisture movement in wood. The simplicity of equation (72) is, therefore, very misleading. Its usefulness is contingent on finding a quantity which can approximate  $Q_2$  (as activation energy is to the heat of transfer, for instance). But the fact that no physical interpre-

tation could yet be accorded  $Q_2$  makes finding such an alternative entity difficult. One option is of course to study  $Q_2$  in detail, investigate its dependence on factors like moisture content, temperature, density, etc. but with the already complex behavior of  $K_M$  (which also appears in equation 72), we could not afford to include another network to an already difficult maze.

### ***5. Assumptions in the Derivation of the NET Equations***

Although the nonequilibrium thermodynamics approach has been shown to model nonisothermal moisture movement in wood quite well, it is necessary to consider the conditions under which it applies. Some of these assumptions which have to be met are inherent in the general theory of nonequilibrium thermodynamics while some are simplifications which were made in finally arriving at equations (61a) and (61b). These are enumerated as follows:

- (1). The system should not be far from equilibrium.
- (2). The flow must be adequately described by linear equations.
- (3). The phenomenological coefficients must be symmetric.
- (4). No chemical reaction must take place in the material where flow is occurring.
- (5). The system must be maintained at a constant total pressure.
- (6). The flow must be slow so that viscous forces can be neglected.

(7). Water must be the only substance that flows, that is, there is no flow of solutes or minerals in the material.

(8). All energy flows must be accounted for.

## Summary and Conclusions

The primary purpose of this study was to measure experimentally the uniaxial (tangential direction) equilibrium moisture profiles in moisture-sealed wood samples subjected to constant but different temperatures  $T$  on opposite faces, and to compare these profiles with those predicted by each of several theoretical models. Each test assembly consisted of eight end-matched wood laminae, each 0.2 cm thick, for a total thickness of 1.6 cm in the tangential direction. Opposite faces of each moisture-sealed assembly were exposed continuously for approximately five weeks to different but constant temperatures until the original uniform moisture content  $M$  redistributed itself to a new constant but non-uniform moisture profile. At moisture equilibrium, the individual wood laminae were removed from the assembly and their moisture contents measured gravimetrically. Both temperature,  $T$  vs  $x$ , and moisture profiles,  $M$  vs  $x$ , where  $x$  is the distance from the cold face were plotted for each test. The experimental variables considered were wood species (yellow poplar and hard maple), initial moisture content (9%, 12%, and 15%), and temperature range (15°C to 35°C, and 25°C to 45°C). Each condition was replicated 3 or 4 times, giving a total number of 44 different tests.

Evaluation of the different theoretical models required sorption isotherm and heat of sorption data; and in some cases, the activation energy for moisture transport through wood. Adsorption and desorption isotherm data were obtained at 30°C for both species. Heat of sorption and moisture transport activation energy data used in testing the models were taken from the literature.

## **A. Moisture Sorption**

The nonlinear regression analyses of the moisture content - relative humidity data showed that the Hailwood-Horrobin model gives a good fit to the sorption data. Absolute deviations of less than 0.60% MC were obtained for all adsorption and desorption curves for both yellow poplar and hard maple, thus, reflecting the theory's ability to reasonably describe the sorption process for wood.

Comparison of the sorption curves of the two species used in this study showed that hard maple was more hygroscopic than yellow poplar but the difference was very small, the maximum difference being no greater than 0.5% MC at any given relative humidity.

The Hailwood-Horrobin parameters obtained in this study compare reasonably well with those obtained by other investigators. The generally observed lowering of the equilibrium moisture content at a given relative humidity on adsorption relative to that on desorption was also apparent in this study. The adsorption-to-desorption moisture content ratio ranged from 0.71 to 0.85, which is in accord with those reported by other investigators.

## B. Nonisothermal Steady-state Experiments

At the steady state, a moisture content profile opposite to the temperature gradient was established. The temperature gradient  $\frac{dT}{dx}$  was constant in all cases, with the moisture content profile increasing almost exponentially with decreasing temperature. The absolute magnitude of the calculated ratio  $\frac{dM}{dT}$  was found to vary with initial moisture content, temperature range, and species. The Soret coefficient, defined as  $-\left(\frac{1}{M}\right)\left(\frac{dM}{dT}\right)$ , was also calculated and was found to vary with the above variables as the  $\frac{dM}{dT}$  ratio. These two quantities always increased with wood moisture content. They were also slightly higher at the higher temperature range. There was only a small difference between species, with yellow poplar giving somewhat higher mean values. The Soret coefficient was generally in the range of 0.03 to 0.05 per degree Kelvin, except for the extremely high moisture contents near and above fiber saturation, where the calculated values approached 0.5 per degree Kelvin.

The moisture content dependence of the  $\frac{dM}{dT}$  ratio and of the Soret coefficient was explained in terms of the increased mobility of sorbed water with an increase in the polymolecularity with which it is held in the sorption sites; and also in terms of the swelling of the wood structure which reduces restriction to movement. The effect of temperature was explained in terms of the increase with temperature of the number of water molecules having enough energy to overcome the potential energy barrier which keeps them bound to a particular site in wood.

Comparison of the  $\frac{dM}{dT}$  values computed using the different theoretical models with the experimental results showed that the two models based on the principles of

nonequilibrium thermodynamics (NET) describe nonisothermal flow of water in wood quite well. In the order of increasing deviation from the experimental results, the two NET equations were followed by those proposed by Siau (1984), Stanish (1986), and Skaar and Siau (1981). The Skaar-Siau equation underpredicted  $\frac{dM}{dT}$  at all values of  $x$  in all experimental runs; while the Stanish model generally overpredicted the ratio.

The difference in the predicted  $\frac{dM}{dT}$  values of the two NET models was attributed to the assumption made in the general model that the heat of transfer is equal to the activation energy. Calculations showed that a difference existed between these two quantities with the heat of transfer calculated from the Nelson-modification of the NET model exceeding the computed activation energy by a factor of 1.07 to 1.23.

The heat of transfer was also computed using the two NET models as well as those of Stanish and Siau. Values ranged from 5500 to 17000  $\frac{\text{cal}}{\text{mol}}$  for the general NET model and from 8100 to 9900  $\frac{\text{cal}}{\text{mol}}$  based on the Nelson model. The corresponding values for the Stanish model range from 15200 to 16500; while those of the Siau model varied between 11700 to 13600  $\frac{\text{cal}}{\text{mol}}$ .

From the data generated in these experiments, other quantities of interest were calculated. It was found out for instance that at the steady state, the vapor pressure was not constant across the thickness of the material demonstrating that the single-force, vapor-pressure-driven flow idea doesn't hold for the nonisothermal moisture movement in wood. The spreading pressure, another driving force suggested for moisture transport in wood, was also found to vary with location in the material at the steady state.

The chemical potential of water vapor and sorbed water were found to be nearly equal at all points in the material indicating local equilibrium; while the entropies of the two phases of water present in wood were more or less constant across the thickness of the sample.

A transfer quantity  $Q_2$  was also evaluated but its variability across the thickness of the sample and the lack of physical interpretation limits its usefulness in quantifying nonisothermal moisture movement in wood.

Although the research described above is primarily a fundamental study of wood moisture relations, it has certain important practical applications. One of these is related to the accumulation of high moisture content regions in the outer walls of heated wood structures subjected to winter conditions. Such moisture accumulation, combined with a favorable temperature, makes the wood structure susceptible to deterioration by biological organisms. A second application is in the development of moisture gradients and the associated longitudinal shrinkage differentials in wood trusses, caused by temperature gradients. A third potential application is the development of temperature gradients in lumber while drying. These generally oppose the moisture gradient, causing some reduction in drying rate.

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## Appendix A. Equations of Change

### 1. Equation of Continuity

The equation of continuity is developed by writing a mass balance over a volume element through which a fluid is flowing (Bird et al, 1960). Consider for instance the volume element  $(\Delta x \Delta y \Delta z)$  in Figure 43. If no chemical reaction is taking place, the rate of mass accumulation is equal to the difference in the rate of mass moving into the volume element and the rate of mass moving out of the volume element. Referring to the pair of faces perpendicular to the  $x$  axis, the rate of mass in through the face at  $x$  is  $(\rho \vec{v}_x)|_x \Delta y \Delta z$ , while the rate of mass out through the face at  $(x + \Delta x)$  is  $(\rho \vec{v}_x)|_{x+\Delta x} \Delta y \Delta z$  where  $\rho$  is the density of the fluid,  $\vec{v}_x$  is the  $x$  component of the fluid velocity vector. Similar expressions may be written for the other two pairs of faces to obtain the following mass balance considering that the rate of mass accumulation is  $(\Delta x \Delta y \Delta z) \left( \frac{\partial \rho}{\partial t} \right)$ :

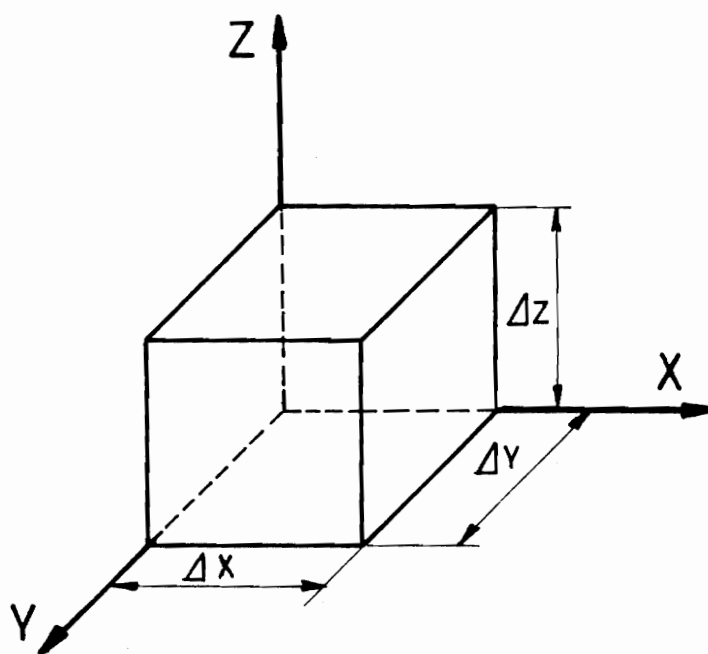


Figure 43. Volume-element fixed in space through which a fluid is flowing.

$$\Delta x \Delta y \Delta z \frac{\partial \rho}{\partial t} = \Delta y \Delta z [(\rho \vec{v}_x)|_x - (\rho \vec{v}_x)|_{x+\Delta x}] + \Delta x \Delta z [(\rho \vec{v}_y)|_y - (\rho \vec{v}_y)|_{y+\Delta y}] + \Delta x \Delta y [(\rho \vec{v}_z)|_z - (\rho \vec{v}_z)|_{z+\Delta z}] \quad [156]$$

By dividing both sides of the equation by  $(\Delta x \Delta y \Delta z)$  and taking the limits as these dimensions approach zero, we get

$$\frac{\partial \rho}{\partial t} = - \left( \frac{\partial \rho \vec{v}_x}{\partial x} + \frac{\partial \rho \vec{v}_y}{\partial y} + \frac{\partial \rho \vec{v}_z}{\partial z} \right) \quad [157]$$

Or in vector symbolism

$$\frac{\partial \rho}{\partial t} = - (\nabla \cdot \rho \vec{v}) \quad [158]$$

For a multicomponent system, the equation of continuity for component  $i$  can be written as:

$$\frac{\partial \rho_i}{\partial t} = (\nabla \cdot \rho_i \vec{v}_i) \quad [159]$$

where  $\rho_i$  is the mass of component  $i$  in a unit bulk volume, and  $\vec{v}_i$  is the velocity of  $i$ . In terms of the substantial time derivative, the equation of continuity for component  $i$  can be expressed as

$$\frac{d\rho_i}{dt} = - \rho_i \nabla \cdot \vec{v} - \nabla \cdot \vec{J}_i \quad [160]$$

where  $\vec{J}_i = \rho_i(\vec{v}_i - \vec{v})$  is the flux of component  $i$  with respect to the barycentric motion. If the mass fraction is employed, equation (160) becomes

$$\rho \frac{dC_i}{dt} = -\nabla \cdot \vec{J}_i \quad [161]$$

## 2. Equation of Energy

For the equation of energy, we start as before with a stationary volume element ( $\Delta x \Delta y \Delta z$ ) of a pure fluid and write the law of conservation of energy for this volume element at any given time. the rate of energy accumulation is equal to the sum of the net rate of energy input by convection, the net rate of heat addition by conduction, and the net rate of work done on the element by the surroundings. The individual terms in the energy equation are given as follows (Bird et al, 1960):

(a) rate of energy accumulation

$$\Delta x \Delta y \Delta z \left[ \frac{\partial}{\partial t} \left( \rho u + \frac{1}{2} \rho \vec{v}^2 \right) \right] \quad [162]$$

where  $u$  is the specific internal energy and  $(\frac{1}{2} \vec{v}^2)$  is the specific kinetic energy.

(b) net rate of energy input by convection

$$\begin{aligned} \Delta y \Delta z \left[ \vec{v}_x \left( \rho u + \frac{1}{2} \rho \vec{v}^2 \right) \Big|_x - \vec{v}_x \left( \rho u + \frac{1}{2} \rho \vec{v}^2 \right) \Big|_{x+\Delta x} \right] \\ + \Delta x \Delta z \left[ \vec{v}_y \left( \rho u + \frac{1}{2} \rho \vec{v}^2 \right) \Big|_y - \vec{v}_y \left( \rho u + \frac{1}{2} \rho \vec{v}^2 \right) \Big|_{y+\Delta y} \right] \\ + \Delta x \Delta y \left[ \vec{v}_z \left( \rho u + \frac{1}{2} \rho \vec{v}^2 \right) \Big|_z - \vec{v}_z \left( \rho u + \frac{1}{2} \rho \vec{v}^2 \right) \Big|_{z+\Delta z} \right] \end{aligned} \quad [163]$$

(c) net rate of heat addition by conduction

$$\Delta y \Delta z [\vec{J}_{qx}|_x - \vec{J}_{qx}|_{x+\Delta x}] + \Delta x \Delta z [\vec{J}_{qy}|_y - \vec{J}_{qy}|_{y+\Delta y}] + \Delta x \Delta y [\vec{J}_{qz}|_z - \vec{J}_{qz}|_{z+\Delta z}] \quad [164]$$

where  $\vec{J}_{qx}$ ,  $\vec{J}_{qy}$ ,  $\vec{J}_{qz}$  are the x, y, and z components of the heat flux vector  $\vec{J}_q$ .

(d) net rate of work done against volume forces

$$- \rho \Delta x \Delta y \Delta z (\vec{v}_x g_x + \vec{v}_y g_y + \vec{v}_z g_z) \quad [165]$$

where  $g_x$ ,  $g_y$ , and  $g_z$  are the 3 components of the gravitational force per unit mass  $g$ .

(e) net rate of work against static pressure at the six faces:

$$\Delta y \Delta z [(P\vec{v}_x)|_{x+\Delta x} - (P\vec{v}_x)|_x] + \Delta x \Delta z [(P\vec{v}_y)|_{y+\Delta y} - (P\vec{v}_y)|_y] + \Delta x \Delta y [(P\vec{v}_z)|_{z+\Delta z} - (P\vec{v}_z)|_z] \quad [166]$$

where  $P$  is pressure.

(f) net rate of work against viscous forces:

$$\Delta y \Delta z [(\tau_{xx}\vec{v}_x + \tau_{xy}\vec{v}_y + \tau_{xz}\vec{v}_z)|_{x+\Delta x} - (\tau_{xx}\vec{v}_x + \tau_{xy}\vec{v}_y + \tau_{xz}\vec{v}_z)|_x] + \Delta x \Delta z [(\tau_{yx}\vec{v}_x + \tau_{yy}\vec{v}_y + \tau_{yz}\vec{v}_z)|_{y+\Delta y} - (\tau_{yx}\vec{v}_x + \tau_{yy}\vec{v}_y + \tau_{yz}\vec{v}_z)|_y] + \Delta x \Delta y [(\tau_{zx}\vec{v}_x + \tau_{zy}\vec{v}_y + \tau_{zz}\vec{v}_z)|_{z+\Delta z} - (\tau_{zx}\vec{v}_x + \tau_{zy}\vec{v}_y + \tau_{zz}\vec{v}_z)|_z] \quad [167]$$

where  $\tau_{ij}$  are the normal stresses if  $i=j$  and the tangential or shear stresses if  $i \neq j$ .

The above expressions may then be combined to obtain an equation for the conservation of energy. Dividing the equation by  $\Delta x \Delta y \Delta z$  and taking the limits as these dimensions approach zero results in the following form of the equation of energy:

$$\begin{aligned} \frac{\partial}{\partial t} \left[ \rho \left( u + \frac{1}{2} \vec{v}^2 \right) \right] = & \left[ \nabla \cdot \rho \vec{v} \left( u + \frac{1}{2} \vec{v}^2 \right) \right] - (\nabla \cdot \vec{J}_q) \\ & - (\nabla \cdot P \vec{v}) - [\nabla \cdot (\tau \cdot \vec{v})] + \rho (\vec{v} \cdot \vec{g}) \end{aligned} \quad [168]$$

For a multicomponent system, the equation of energy takes the following form:

$$\begin{aligned} \frac{\partial}{\partial t} \left[ \rho \left( u + \frac{1}{2} \vec{v}^2 \right) \right] = & \left[ \nabla \cdot \rho \vec{v} \left( u + \frac{1}{2} \vec{v}^2 \right) \right] - (\nabla \cdot \vec{J}_q) \\ & - (\nabla \cdot P \vec{v}) - [\nabla \cdot (\tau \cdot \vec{v})] + \sum_{i=1}^n F_i \cdot \vec{J}_i \end{aligned} \quad [169]$$

Equation (169) differs from the energy equation for a pure fluid only in the last term which takes into account the fact that each component may be acted on by different external force per unit mass  $F_i$ . By subtracting the kinetic energy component, equation (169) reduces to (Yao, 1981):

$$\frac{\partial \rho u}{\partial t} = - \nabla \cdot \rho u \vec{v} - \nabla \cdot \vec{J}_q - \nabla \cdot P \vec{v} - \nabla \cdot (\tau \cdot \vec{v}) + \sum_{i=1}^n F_i \cdot \vec{J}_i \quad [170]$$

In terms of the substantial time derivative, equation (170) may be written as

$$\rho \frac{du}{dt} = -\nabla \cdot \vec{J}_q - P \nabla \cdot \vec{v} - \tau : \nabla \vec{v} + \sum_{i=1}^n F_i \cdot \vec{J}_i \quad [171]$$

where  $(:)$  represents double dot product.

# Appendix B. Appendix Tables

**Table A1. Moisture content of yellow poplar adsorption samples at different relative humidities at a dry bulb temperature of 30 C.**

| Relative Humidity (%) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------------------|----------------------|---------------|-------------------|
| 28.0                  | 4.52                 | 4.34812       | 0.17188           |
|                       | 4.52                 | 4.34812       | 0.17188           |
|                       | 4.41                 | 4.34812       | 0.06188           |
|                       | 4.41                 | 4.34812       | 0.06188           |
|                       | 4.49                 | 4.34812       | 0.14188           |
|                       | 4.26                 | 4.34812       | -0.08812          |
|                       | 4.43                 | 4.34812       | 0.08188           |
|                       | 4.42                 | 4.34812       | 0.07188           |
|                       | 4.32                 | 4.34812       | -0.02812          |
|                       | 4.51                 | 4.34812       | 0.16188           |
|                       | 4.47                 | 4.34812       | 0.12188           |
|                       | 4.50                 | 4.34812       | 0.15188           |
|                       | 4.46                 | 4.34812       | 0.11188           |
|                       | 4.43                 | 4.34812       | 0.08188           |
|                       | 4.49                 | 4.34812       | 0.14188           |
|                       | 4.42                 | 4.34812       | 0.07188           |
|                       | 4.42                 | 4.34812       | 0.07188           |
|                       | 4.41                 | 4.34812       | 0.06188           |
| 41.2                  | 5.85                 | 5.88264       | -0.03264          |
|                       | 5.89                 | 5.88264       | 0.00736           |
|                       | 5.59                 | 5.88264       | -0.29264          |
|                       | 5.51                 | 5.88264       | -0.37264          |
|                       | 5.62                 | 5.88264       | -0.26264          |
|                       | 5.46                 | 5.88264       | -0.42264          |
|                       | 5.61                 | 5.88264       | -0.27264          |
|                       | 5.71                 | 5.88264       | -0.17264          |
|                       | 5.68                 | 5.88264       | -0.20264          |
|                       | 5.94                 | 5.88264       | 0.05736           |
|                       | 5.87                 | 5.88264       | -0.01264          |
|                       | 5.91                 | 5.88264       | 0.02736           |
|                       | 5.82                 | 5.88264       | -0.06264          |
|                       | 5.72                 | 5.88264       | -0.16264          |
|                       | 5.86                 | 5.88264       | -0.02264          |
|                       | 5.56                 | 5.88264       | -0.32264          |
|                       | 5.56                 | 5.88264       | -0.32264          |
|                       | 5.63                 | 5.88264       | -0.25264          |

| Relative Humidity (%) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------------------|----------------------|---------------|-------------------|
| 61.8                  | 9.10                 | 8.87916       | 0.22084           |
|                       | 9.13                 | 8.87916       | 0.25084           |
|                       | 8.98                 | 8.87916       | 0.10084           |
|                       | 8.87                 | 8.87916       | -0.00916          |
|                       | 8.94                 | 8.87916       | 0.06084           |
|                       | 8.89                 | 8.87916       | 0.01084           |
|                       | 8.88                 | 8.87916       | 0.00084           |
|                       | 8.92                 | 8.87916       | 0.04084           |
|                       | 8.83                 | 8.87916       | -0.04916          |
|                       | 9.18                 | 8.87916       | 0.30084           |
|                       | 9.01                 | 8.87916       | 0.13084           |
|                       | 9.09                 | 8.87916       | 0.21084           |
|                       | 8.97                 | 8.87916       | 0.09084           |
|                       | 9.00                 | 8.87916       | 0.12084           |
|                       | 9.09                 | 8.87916       | 0.21084           |
|                       | 8.89                 | 8.87916       | 0.01084           |
|                       | 8.89                 | 8.87916       | 0.01084           |
|                       | 9.05                 | 8.87916       | 0.17084           |
| 66.5                  | 10.06                | 9.7903        | 0.26966           |
|                       | 9.98                 | 9.7903        | 0.18966           |
|                       | 9.75                 | 9.7903        | -0.04034          |
|                       | 9.56                 | 9.7903        | -0.23034          |
|                       | 9.63                 | 9.7903        | -0.16034          |
|                       | 9.52                 | 9.7903        | -0.27034          |
|                       | 9.68                 | 9.7903        | -0.11034          |
|                       | 9.74                 | 9.7903        | -0.05034          |
|                       | 9.65                 | 9.7903        | -0.14034          |
|                       | 10.06                | 9.7903        | 0.26966           |
|                       | 10.28                | 9.7903        | 0.48966           |
|                       | 10.08                | 9.7903        | 0.28966           |
|                       | 9.94                 | 9.7903        | 0.14966           |
|                       | 9.98                 | 9.7903        | 0.18966           |
|                       | 10.02                | 9.7903        | 0.22966           |
|                       | 9.64                 | 9.7903        | -0.15034          |
|                       | 9.64                 | 9.7903        | -0.15034          |
|                       | 9.68                 | 9.7903        | -0.11034          |

| Relative Humidity (%) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------------------|----------------------|---------------|-------------------|
| 76.6                  | 12.56                | 12.2881       | 0.27191           |
|                       | 12.50                | 12.2881       | 0.21191           |
|                       | 12.25                | 12.2881       | -0.03809          |
|                       | 11.90                | 12.2881       | -0.38809          |
|                       | 11.90                | 12.2881       | -0.38809          |
|                       | 11.70                | 12.2881       | -0.58809          |
|                       | 12.09                | 12.2881       | -0.19809          |
|                       | 11.97                | 12.2881       | -0.31809          |
|                       | 11.91                | 12.2881       | -0.37809          |
|                       | 12.56                | 12.2881       | 0.27191           |
|                       | 12.66                | 12.2881       | 0.37191           |
|                       | 12.53                | 12.2881       | 0.24191           |
|                       | 12.44                | 12.2881       | 0.15191           |
|                       | 12.50                | 12.2881       | 0.21191           |
|                       | 12.59                | 12.2881       | 0.30191           |
|                       | 11.83                | 12.2881       | -0.45809          |
|                       | 11.86                | 12.2881       | -0.42809          |
|                       | 12.04                | 12.2881       | -0.24809          |
| 83.8                  | 14.97                | 14.7793       | 0.19073           |
|                       | 14.94                | 14.7793       | 0.16073           |
|                       | 14.75                | 14.7793       | -0.02927          |
|                       | 14.36                | 14.7793       | -0.41927          |
|                       | 14.47                | 14.7793       | -0.30927          |
|                       | 14.42                | 14.7793       | -0.35927          |
|                       | 14.66                | 14.7793       | -0.11927          |
|                       | 14.68                | 14.7793       | -0.09927          |
|                       | 14.53                | 14.7793       | -0.24927          |
|                       | 15.36                | 14.7793       | 0.58073           |
|                       | 15.24                | 14.7793       | 0.46073           |
|                       | 15.02                | 14.7793       | 0.24073           |
|                       | 15.14                | 14.7793       | 0.36073           |
|                       | 14.98                | 14.7793       | 0.20073           |
|                       | 15.02                | 14.7793       | 0.24073           |
|                       | 14.64                | 14.7793       | -0.13927          |
|                       | 14.55                | 14.7793       | -0.22927          |
|                       | 14.64                | 14.7793       | -0.13927          |

**Table A2. Moisture content of yellow poplar desorption samples at different relative humidities at a dry bulb temperature of 30 C.**

| Relative Humidity (%) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------------------|----------------------|---------------|-------------------|
| 33.6                  | 6.96                 | 6.9823        | -0.02233          |
|                       | 7.11                 | 6.9823        | 0.12767           |
|                       | 6.87                 | 6.9823        | -0.11233          |
|                       | 6.97                 | 6.9823        | 0.01233           |
|                       | 7.11                 | 6.9823        | 0.12767           |
|                       | 6.91                 | 6.9823        | -0.07233          |
|                       | 6.91                 | 6.9823        | -0.07233          |
|                       | 6.88                 | 6.9823        | -0.10233          |
|                       | 6.96                 | 6.9823        | -0.02233          |
|                       | 7.15                 | 6.9823        | 0.16767           |
|                       | 7.06                 | 6.9823        | 0.07767           |
|                       | 6.87                 | 6.9823        | -0.11233          |
|                       | 6.91                 | 6.9823        | -0.07233          |
|                       | 6.94                 | 6.9823        | -0.04233          |
| 40.5                  | 8.10                 | 8.0760        | 0.02403           |
|                       | 8.32                 | 8.0760        | 0.24403           |
|                       | 7.94                 | 8.0760        | -0.13597          |
|                       | 8.05                 | 8.0760        | -0.02597          |
|                       | 8.20                 | 8.0760        | 0.12403           |
|                       | 7.97                 | 8.0760        | -0.10597          |
|                       | 8.10                 | 8.0760        | 0.02403           |
|                       | 8.20                 | 8.0760        | 0.12403           |
|                       | 8.16                 | 8.0760        | 0.08403           |
|                       | 8.33                 | 8.0760        | 0.25403           |
|                       | 8.18                 | 8.0760        | 0.10403           |
|                       | 8.01                 | 8.0760        | -0.06597          |
|                       | 8.18                 | 8.0760        | 0.10403           |
|                       | 8.07                 | 8.0760        | -0.00597          |

| Relative Humidity (%) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------------------|----------------------|---------------|-------------------|
| 61.8                  | 11.47                | 11.8342       | -0.36423          |
|                       | 11.55                | 11.8342       | -0.28423          |
|                       | 11.50                | 11.8342       | -0.33423          |
|                       | 11.54                | 11.8342       | -0.29423          |
|                       | 11.55                | 11.8342       | -0.28423          |
|                       | 11.50                | 11.8342       | -0.33423          |
|                       | 11.54                | 11.8342       | -0.29423          |
|                       | 11.57                | 11.8342       | -0.26423          |
|                       | 11.59                | 11.8342       | -0.24423          |
|                       | 11.87                | 11.8342       | 0.03577           |
|                       | 11.75                | 11.8342       | -0.08423          |
|                       | 11.50                | 11.8342       | -0.33423          |
|                       | 11.54                | 11.8342       | -0.29423          |
|                       | 11.59                | 11.8342       | -0.24423          |
| 68.0                  | 13.50                | 13.1689       | 0.33105           |
|                       | 13.68                | 13.1689       | 0.51105           |
|                       | 13.37                | 13.1689       | 0.20105           |
|                       | 13.40                | 13.1689       | 0.23105           |
|                       | 13.31                | 13.1689       | 0.14105           |
|                       | 13.21                | 13.1689       | 0.04105           |
|                       | 13.31                | 13.1689       | 0.14105           |
|                       | 13.41                | 13.1689       | 0.24105           |
|                       | 13.65                | 13.1689       | 0.48105           |
|                       | 13.55                | 13.1689       | 0.38105           |
|                       | 13.42                | 13.1689       | 0.25105           |
|                       | 13.43                | 13.1689       | 0.26105           |
|                       | 13.48                | 13.1689       | 0.31105           |
| 82                    | 17.20                | 16.9612       | 0.23877           |
|                       | 17.20                | 16.9612       | 0.23877           |
|                       | 16.99                | 16.9612       | 0.02877           |
|                       | 16.81                | 16.9612       | -0.15123          |
|                       | 16.81                | 16.9612       | -0.15123          |
|                       | 16.68                | 16.9612       | -0.28123          |
|                       | 16.56                | 16.9612       | -0.40123          |
|                       | 16.67                | 16.9612       | -0.29123          |
|                       | 17.15                | 16.9612       | 0.18877           |
|                       | 17.29                | 16.9612       | 0.32877           |
|                       | 17.11                | 16.9612       | 0.14877           |
|                       | 16.83                | 16.9612       | -0.13123          |
|                       | 16.84                | 16.9612       | -0.12123          |
|                       | 16.81                | 16.9612       | -0.15123          |

**Table A3. Moisture content of hard maple adsorption samples at different relative humidities at a dry bulb temperature of 30 C.**

| Relative Humidity (%) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------------------|----------------------|---------------|-------------------|
| 28.0                  | 4.52                 | 4.4384        | 0.08164           |
|                       | 4.53                 | 4.4384        | 0.09164           |
|                       | 4.52                 | 4.4384        | 0.08164           |
|                       | 4.42                 | 4.4384        | -0.01836          |
|                       | 4.41                 | 4.4384        | -0.02836          |
|                       | 4.46                 | 4.4384        | 0.02164           |
|                       | 4.52                 | 4.4384        | 0.08164           |
|                       | 4.46                 | 4.4384        | 0.02164           |
|                       | 4.32                 | 4.4384        | -0.11836          |
|                       | 4.59                 | 4.4384        | 0.15164           |
|                       | 4.58                 | 4.4384        | 0.14164           |
|                       | 4.46                 | 4.4384        | 0.02164           |
| 41.2                  | 6.07                 | 6.0680        | 0.00199           |
|                       | 6.05                 | 6.0680        | -0.01801          |
|                       | 6.03                 | 6.0680        | -0.03801          |
|                       | 5.97                 | 6.0680        | -0.09801          |
|                       | 5.93                 | 6.0680        | -0.13801          |
|                       | 6.02                 | 6.0680        | -0.04801          |
|                       | 5.85                 | 6.0680        | -0.21801          |
|                       | 6.09                 | 6.0680        | 0.02199           |
|                       | 5.78                 | 6.0680        | -0.28801          |
|                       | 6.07                 | 6.0680        | 0.00199           |
|                       | 6.00                 | 6.0680        | -0.06801          |
|                       | 5.92                 | 6.0680        | -0.14801          |
| 61.8                  | 9.26                 | 9.1599        | 0.10014           |
|                       | 9.32                 | 9.1599        | 0.16014           |
|                       | 9.21                 | 9.1599        | 0.05014           |
|                       | 9.18                 | 9.1599        | 0.02014           |
|                       | 9.15                 | 9.1599        | -0.00986          |
|                       | 9.16                 | 9.1599        | 0.00014           |
|                       | 9.25                 | 9.1599        | 0.09014           |
|                       | 9.18                 | 9.1599        | 0.02014           |
|                       | 9.03                 | 9.1599        | -0.12986          |
|                       | 9.27                 | 9.1599        | 0.11014           |
|                       | 9.24                 | 9.1599        | 0.08014           |
|                       | 9.18                 | 9.1599        | 0.02014           |

| Relative Humidity (%) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------------------|----------------------|---------------|-------------------|
| 66.5                  | 10.22                | 10.0734       | 0.14655           |
|                       | 10.19                | 10.0734       | 0.11655           |
|                       | 10.15                | 10.0734       | 0.07655           |
|                       | 10.13                | 10.0734       | 0.05655           |
|                       | 10.15                | 10.0734       | 0.07655           |
|                       | 10.04                | 10.0734       | -0.03345          |
|                       | 10.21                | 10.0734       | 0.13655           |
|                       | 10.12                | 10.0734       | 0.04655           |
|                       | 9.92                 | 10.0734       | -0.15345          |
|                       | 10.12                | 10.0734       | 0.04655           |
|                       | 10.16                | 10.0734       | 0.08655           |
|                       | 10.07                | 10.0734       | -0.00345          |
| 76.6                  | 12.60                | 12.5187       | 0.08132           |
|                       | 12.55                | 12.5187       | 0.03132           |
|                       | 12.56                | 12.5187       | 0.04132           |
|                       | 12.38                | 12.5187       | -0.13868          |
|                       | 12.53                | 12.5187       | 0.01132           |
|                       | 12.45                | 12.5187       | -0.06868          |
|                       | 12.40                | 12.5187       | -0.11868          |
|                       | 12.39                | 12.5187       | -0.12868          |
|                       | 12.16                | 12.5187       | -0.35868          |
|                       | 12.49                | 12.5187       | -0.02868          |
|                       | 12.50                | 12.5187       | -0.01868          |
|                       | 12.37                | 12.5187       | -0.14868          |
| 83.8                  | 15.02                | 14.8771       | 0.14287           |
|                       | 15.12                | 14.8771       | 0.24287           |
|                       | 15.13                | 14.8771       | 0.25287           |
|                       | 14.82                | 14.8771       | -0.05713          |
|                       | 14.90                | 14.8771       | 0.02287           |
|                       | 14.76                | 14.8771       | -0.11713          |
|                       | 14.76                | 14.8771       | -0.11713          |
|                       | 14.88                | 14.8771       | 0.00287           |
|                       | 14.64                | 14.8771       | -0.23713          |
|                       | 14.93                | 14.8771       | 0.05287           |
|                       | 14.92                | 14.8771       | 0.04287           |
|                       | 14.90                | 14.8771       | 0.02287           |

**Table A4. Moisture content of hard maple desorption samples at different relative humidities at a dry bulb temperature of 30 C.**

| Relative Humidity (%) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------------------|----------------------|---------------|-------------------|
| 33.6                  | 7.21                 | 7.1377        | 0.07229           |
|                       | 7.15                 | 7.1377        | 0.01229           |
|                       | 7.06                 | 7.1377        | -0.07771          |
|                       | 7.10                 | 7.1377        | -0.03771          |
|                       | 7.22                 | 7.1377        | 0.08229           |
|                       | 7.10                 | 7.1377        | -0.03771          |
|                       | 7.14                 | 7.1377        | 0.00229           |
|                       | 7.05                 | 7.1377        | -0.08771          |
| 40.5                  | 8.35                 | 8.2652        | 0.08483           |
|                       | 8.34                 | 8.2652        | 0.07483           |
|                       | 8.18                 | 8.2652        | -0.08517          |
|                       | 8.20                 | 8.2652        | -0.06517          |
|                       | 8.39                 | 8.2652        | 0.12483           |
|                       | 8.28                 | 8.2652        | 0.01483           |
|                       | 8.31                 | 8.2652        | 0.04483           |
|                       | 8.41                 | 8.2652        | 0.14483           |
| 61.8                  | 12.02                | 12.1384       | -0.11839          |
|                       | 11.99                | 12.1384       | -0.14839          |
|                       | 11.82                | 12.1384       | -0.31839          |
|                       | 11.84                | 12.1384       | -0.29839          |
|                       | 12.00                | 12.1384       | -0.13839          |
|                       | 12.08                | 12.1384       | -0.05839          |
|                       | 11.89                | 12.1384       | -0.24839          |
|                       | 11.89                | 12.1384       | -0.24839          |
| 68.0                  | 13.82                | 13.5125       | 0.30748           |
|                       | 13.79                | 13.5125       | 0.27748           |
|                       | 13.54                | 13.5125       | 0.02748           |
|                       | 13.64                | 13.5125       | 0.12748           |
|                       | 13.66                | 13.5125       | 0.14748           |
|                       | 13.64                | 13.5125       | 0.12748           |
|                       | 13.64                | 13.5125       | 0.12748           |
|                       | 13.90                | 13.5125       | 0.38748           |
| 82.0                  | 17.50                | 17.4124       | 0.08761           |
|                       | 17.45                | 17.4124       | 0.03761           |
|                       | 17.34                | 17.4124       | -0.07239          |
|                       | 17.35                | 17.4124       | -0.06239          |
|                       | 17.43                | 17.4124       | 0.01761           |
|                       | 17.40                | 17.4124       | -0.01239          |
|                       | 17.20                | 17.4124       | -0.21239          |
|                       | 17.41                | 17.4124       | -0.00239          |

Table A5. Moisture contents and temperatures at various distances from the cold face of nonisothermal steady-state samples.

| Sample ID | Thermo-couple Location (cm) | Temperature (K) | $\hat{T}$ (K) | $T - \hat{T}$ (K) | Moisture Content Location (cm) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------|-----------------------------|-----------------|---------------|-------------------|--------------------------------|----------------------|---------------|-------------------|
| A5        | 1.61036                     | 308.22          | 308.249       | -0.02908          | 1.51003                        | 6.01                 | 6.0418        | -0.03176          |
|           | 1.40970                     | 305.65          | 305.657       | -0.00736          |                                |                      |               |                   |
|           | 1.20650                     | 303.13          | 303.033       | 0.09717           | 1.10744                        | 7.31                 | 7.3339        | -0.02385          |
|           | 1.00838                     | 300.58          | 300.474       | 0.10609           | 0.90678                        | 8.14                 | 7.9937        | 0.14626           |
|           | 0.80518                     | 297.84          | 297.849       | -0.00938          | 0.70485                        | 8.70                 | 8.7035        | -0.00346          |
|           | 0.60452                     | 295.20          | 295.258       | -0.05766          | 0.50419                        | 9.40                 | 9.5576        | -0.15758          |
|           | 0.40386                     | 292.45          | 292.666       | -0.21593          | 0.30353                        | 10.98                | 10.8984       | 0.08164           |
|           | 0.20320                     | 289.89          | 290.074       | -0.18421          | 0.10160                        | 13.85                | 13.8612       | -0.01124          |
|           | 0.00000                     | 287.75          | 287.450       | 0.30032           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| B4        | 1.61036                     | 308.59          | 308.432       | 0.15774           | 1.51130                        | 5.88                 | 5.9413        | -0.06129          |
|           | 1.41224                     | 306.03          | 305.864       | 0.16553           |                                |                      |               |                   |
|           | 1.23698                     | 303.38          | 303.593       | -0.21297          | 1.11125                        | 7.20                 | 7.1230        | 0.07703           |
|           | 1.00838                     | 300.67          | 300.630       | 0.03986           | 0.90805                        | 7.82                 | 7.7411        | 0.07886           |
|           | 0.80772                     | 297.94          | 298.029       | -0.08944          | 0.70866                        | 8.37                 | 8.3973        | -0.02730          |
|           | 0.60960                     | 295.29          | 295.462       | -0.17166          | 0.50927                        | 9.08                 | 9.2125        | -0.13253          |
|           | 0.40894                     | 292.60          | 292.861       | -0.26095          | 0.30734                        | 10.64                | 10.5640       | 0.07604           |
|           | 0.20574                     | 290.32          | 290.227       | 0.09267           | 0.10287                        | 13.69                | 13.7008       | -0.01081          |
|           | 0.00000                     | 287.84          | 287.561       | 0.27922           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| C4        | 1.62814                     | 308.61          | 308.342       | 0.26768           | 1.52908                        | 5.99                 | 6.0471        | -0.05706          |
|           | 1.43002                     | 305.90          | 305.825       | 0.07458           |                                |                      |               |                   |
|           | 1.22936                     | 303.08          | 303.276       | -0.19625          | 1.12903                        | 7.27                 | 7.2230        | 0.04704           |
|           | 1.02870                     | 300.37          | 300.727       | -0.35708          | 0.92710                        | 7.96                 | 7.8320        | 0.12799           |
|           | 0.82550                     | 298.19          | 298.146       | 0.04435           | 0.72263                        | 8.43                 | 8.4923        | -0.06228          |
|           | 0.61976                     | 295.59          | 295.532       | 0.05806           | 0.51689                        | 9.18                 | 9.2988        | -0.11879          |
|           | 0.41402                     | 292.92          | 292.918       | 0.00176           | 0.31115                        | 10.64                | 10.5660       | 0.07401           |
|           | 0.20828                     | 290.27          | 290.305       | -0.03453          | 0.10414                        | 13.34                | 13.3509       | -0.01090          |
|           | 0.00000                     | 287.80          | 287.659       | 0.14144           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |

| Sample ID | Thermo-couple Location (cm) | Temperature (K) | $\hat{T}$ (K) | $T - \hat{T}$ (K) | Moisture Content Location (cm) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------|-----------------------------|-----------------|---------------|-------------------|--------------------------------|----------------------|---------------|-------------------|
| A7        | 1.60782                     | 307.83          | 307.751       | 0.07928           | 1.51130                        | 6.22                 | 6.2757        | -0.05571          |
|           | 1.41478                     | 305.25          | 305.340       | -0.09038          |                                |                      |               |                   |
|           | 1.21920                     | 302.76          | 302.898       | -0.13832          | 1.11887                        | 7.52                 | 7.4559        | 0.06407           |
|           | 1.01854                     | 300.54          | 300.393       | 0.14717           | 0.91821                        | 8.16                 | 8.0812        | 0.07885           |
|           | 0.81788                     | 297.92          | 297.887       | 0.03266           | 0.71628                        | 8.75                 | 8.7674        | -0.01738          |
|           | 0.61468                     | 295.34          | 295.350       | -0.01013          | 0.51181                        | 9.50                 | 9.6396        | -0.13957          |
|           | 0.40894                     | 292.80          | 292.781       | 0.01879           | 0.30734                        | 11.14                | 11.0578       | 0.08224           |
|           | 0.20574                     | 290.20          | 290.244       | -0.04401          | 0.10287                        | 14.14                | 14.1525       | 0.01250           |
|           | 0.00000                     | 287.68          | 287.675       | 0.00491           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| H1        | 1.62306                     | 308.31          | 308.302       | 0.00773           | 1.52400                        | 7.06                 | 7.1563        | -0.09629          |
|           | 1.42494                     | 305.85          | 305.771       | 0.07933           |                                |                      |               |                   |
|           | 1.22174                     | 303.28          | 303.174       | 0.10585           | 1.11887                        | 9.20                 | 9.1450        | 0.05501           |
|           | 1.01600                     | 300.52          | 300.545       | -0.02517          | 0.91567                        | 10.38                | 10.1691       | 0.21086           |
|           | 0.81534                     | 297.88          | 297.981       | -0.10111          | 0.71501                        | 11.27                | 11.2643       | 0.00572           |
|           | 0.61468                     | 295.34          | 295.417       | -0.07705          | 0.51435                        | 12.36                | 12.6605       | -0.30045          |
|           | 0.41402                     | 292.68          | 292.853       | -0.17299          | 0.31115                        | 15.33                | 15.1873       | 0.14269           |
|           | 0.20828                     | 290.09          | 290.224       | -0.13401          | 0.10414                        | 21.99                | 22.0075       | -0.01753          |
|           | 0.00000                     | 287.88          | 287.563       | 0.31742           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| C1        | 1.67386                     | 308.27          | 308.484       | -0.21407          | 1.55067                        | 7.03                 | 7.0943        | -0.06428          |
|           | 1.42748                     | 305.75          | 305.369       | 0.38068           |                                |                      |               |                   |
|           | 1.23190                     | 302.93          | 302.897       | 0.03321           | 1.13030                        | 9.24                 | 9.1914        | 0.04856           |
|           | 1.02870                     | 300.31          | 300.328       | -0.01792          | 0.92964                        | 10.31                | 10.2117       | 0.09833           |
|           | 0.83058                     | 297.84          | 297.823       | 0.01672           | 0.72644                        | 11.36                | 11.3158       | 0.04420           |
|           | 0.62230                     | 295.03          | 295.190       | -0.16020          | 0.51943                        | 12.55                | 12.7476       | -0.19759          |
|           | 0.41656                     | 292.33          | 292.589       | -0.25922          | 0.31242                        | 15.57                | 15.4906       | 0.07935           |
|           | 0.20828                     | 289.89          | 289.956       | -0.06614          | 0.10414                        | 23.90                | 23.9086       | -0.00858          |
|           | 0.00000                     | 287.61          | 287.323       | 0.28695           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |

| Sample ID | Thermo-couple Location (cm) | Temperature (K) | $\hat{T}$ (K) | $T - \hat{T}$ (K) | Moisture Content Location (cm) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------|-----------------------------|-----------------|---------------|-------------------|--------------------------------|----------------------|---------------|-------------------|
| F1        | 1.65100                     | 307.80          | 307.640       | 0.16050           | 1.55067                        | 7.59                 | 7.6850        | -0.09501          |
|           | 1.45034                     | 305.09          | 305.227       | -0.13686          |                                |                      |               |                   |
|           | 1.25222                     | 302.78          | 302.845       | -0.06476          | 1.15189                        | 9.66                 | 9.5504        | 0.10956           |
|           | 1.05156                     | 300.44          | 300.432       | 0.00788           | 0.94742                        | 10.70                | 10.5418       | 0.15824           |
|           | 0.84328                     | 298.03          | 297.928       | 0.10214           | 0.74041                        | 11.54                | 11.6412       | -0.10123          |
|           | 0.63754                     | 295.41          | 295.454       | -0.04414          | 0.53467                        | 12.87                | 13.0323       | -0.16232          |
|           | 0.43180                     | 292.92          | 292.980       | -0.06043          | 0.32639                        | 15.50                | 15.3939       | 0.10611           |
|           | 0.22098                     | 290.33          | 290.446       | -0.11563          | 0.11049                        | 21.08                | 21.0954       | -0.01536          |
|           | 0.00000                     | 287.94          | 287.789       | 0.15133           |                                |                      |               |                   |
| E1        | 1.65354                     | 308.39          | 308.314       | 0.07636           | 1.55321                        | 7.32                 | 7.3964        | -0.07643          |
|           | 1.45288                     | 305.88          | 305.825       | 0.05518           |                                |                      |               |                   |
|           | 1.24968                     | 303.31          | 303.304       | 0.00551           | 1.14808                        | 9.44                 | 9.3862        | 0.05382           |
|           | 1.04648                     | 300.82          | 300.784       | 0.03583           | 0.94488                        | 10.54                | 10.4083       | 0.13168           |
|           | 0.84328                     | 298.23          | 298.264       | -0.03385          | 0.74041                        | 11.56                | 11.5076       | 0.05237           |
|           | 0.63754                     | 295.56          | 295.712       | -0.15202          | 0.53340                        | 12.59                | 12.8644       | -0.27437          |
|           | 0.42926                     | 292.92          | 293.129       | -0.20868          | 0.32385                        | 15.22                | 15.0908       | 0.12918           |
|           | 0.21844                     | 290.35          | 290.514       | -0.16385          | 0.10922                        | 20.46                | 20.4763       | -0.01627          |
|           | 0.00000                     | 288.19          | 287.804       | 0.38550           |                                |                      |               |                   |
| B3        | 1.62560                     | 309.00          | 308.951       | 1.52654           | 7.18                           | 6.8379               | 0.34206       |                   |
|           | 1.42748                     | 306.43          | 306.324       |                   |                                |                      |               |                   |
|           | 1.22682                     | 303.81          | 303.663       | 1.12522           | 9.22                           | 9.5776               | -0.35761      |                   |
|           | 1.02362                     | 300.87          | 300.968       | 0.92329           | 10.62                          | 10.9568              | -0.33676      |                   |
|           | 0.82296                     | 298.03          | 298.307       | 0.72263           | 12.32                          | 12.3355              | -0.01550      |                   |
|           | 0.62230                     | 295.60          | 295.646       | 0.51943           | 14.27                          | 13.8453              | 0.42470       |                   |
|           | 0.41656                     | 292.81          | 292.918       | 0.31369           | 16.93                          | 16.9889              | -0.05889      |                   |
|           | 0.21082                     | 290.14          | 290.190       | 0.10541           | 43.89                          | 43.8880              | 0.00199       |                   |
|           | 0.00000                     | 287.67          | 287.394       |                   |                                |                      |               |                   |

| Sample ID | Thermo-couple Location (cm) | Temperature (K) | $\hat{T}$ (K) | $T - \hat{T}$ (K) | Moisture Content Location (cm) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------|-----------------------------|-----------------|---------------|-------------------|--------------------------------|----------------------|---------------|-------------------|
| H2        | 1.62560                     | 307.72          | 307.617       | 0.10304           | 1.52908                        | 7.60                 | 7.3171        | 0.28290           |
|           | 1.43256                     | 305.40          | 305.218       | 0.18239           |                                |                      |               | -0.23280          |
|           | 1.23698                     | 302.90          | 302.787       | 0.11331           | 1.13792                        | 9.67                 | 9.9028        | -0.34133          |
|           | 0.03886                     | 300.19          | 300.324       | -0.13420          | 0.93853                        | 10.88                | 11.2213       | -0.05323          |
|           | 0.83820                     | 297.82          | 297.830       | -0.01014          | 0.73660                        | 12.51                | 12.5632       | 0.39340           |
|           | 0.63500                     | 294.88          | 295.305       | -0.42450          | 0.52832                        | 14.44                | 14.0466       | -0.05055          |
|           | 0.42164                     | 292.46          | 292.653       | -0.19259          | 0.31877                        | 17.00                | 17.0505       | 0.00162           |
|           | 0.21590                     | 289.77          | 290.095       | -0.32538          | 0.10795                        | 43.44                | 43.4384       |                   |
|           | 0.00000                     | 288.10          | 287.412       | 0.68810           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| A6        | 1.61036                     | 318.38          | 318.140       | 0.23959           | 1.51384                        | 5.76                 | 5.7767        | -0.01670          |
|           | 1.41732                     | 315.68          | 315.624       | 0.05568           |                                |                      |               | -0.00598          |
|           | 1.21412                     | 312.94          | 312.976       | -0.03580          | 1.11379                        | 7.15                 | 7.1560        | 0.08739           |
|           | 1.01346                     | 310.27          | 310.360       | -0.09039          | 0.91694                        | 7.97                 | 7.8826        | -0.04025          |
|           | 0.82042                     | 307.69          | 307.844       | -0.15430          | 0.71755                        | 8.67                 | 8.7103        | -0.06738          |
|           | 0.61468                     | 304.98          | 305.163       | -0.18268          | 0.51054                        | 9.73                 | 9.7974        | 0.05340           |
|           | 0.40640                     | 302.27          | 302.448       | -0.17795          | 0.30226                        | 11.50                | 11.4466       | -0.01046          |
|           | 0.19812                     | 299.64          | 299.733       | -0.09322          | 0.09906                        | 14.32                | 14.3305       |                   |
|           | 0.00000                     | 297.59          | 297.151       | 0.43908           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| B5        | 1.46812                     | 317.70          | 317.489       | 0.21121           | 1.37541                        | 5.82                 | 5.8263        | -0.00630          |
|           | 1.28270                     | 315.00          | 314.978       | 0.02160           |                                |                      |               | -0.00388          |
|           | 1.09982                     | 312.47          | 312.502       | -0.03240          | 1.00838                        | 7.03                 | 7.0339        | 0.03640           |
|           | 0.91694                     | 309.98          | 310.026       | -0.04641          | 0.82677                        | 7.74                 | 7.7036        | -0.01022          |
|           | 0.73660                     | 307.51          | 307.585       | -0.07479          | 0.64643                        | 8.48                 | 8.4902        | -0.04103          |
|           | c.55626                     | 304.94          | 305.143       | -0.20318          | 0.46482                        | 9.50                 | 9.5410        | 0.03122           |
|           | 0.37338                     | 302.33          | 302.667       | -0.33719          | 0.28067                        | 11.20                | 11.1688       | -0.00617          |
|           | 0.18796                     | 300.34          | 300.157       | 0.18320           | 0.09398                        | 14.05                | 14.0562       |                   |
|           | 0.00000                     | 297.89          | 297.612       | 0.27798           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |

| Sample ID | Thermo-couple Location (cm) | Temperature (K) | $\hat{T}$ (K) | $T - \hat{T}$ (K) | Moisture Content Location (cm) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------|-----------------------------|-----------------|---------------|-------------------|--------------------------------|----------------------|---------------|-------------------|
| E3        | 1.63830                     | 317.59          | 317.279       | 0.31104           | 1.53670                        | 6.14                 | 6.1943        | -0.05434          |
|           | 1.43510                     | 314.93          | 314.882       | 0.04772           |                                |                      |               |                   |
|           | 1.23444                     | 312.28          | 312.516       | -0.23555          | 1.13284                        | 7.49                 | 7.3686        | 0.12135           |
|           | 1.03124                     | 309.69          | 310.119       | -0.42886          | 0.93091                        | 8.00                 | 7.9924        | 0.00762           |
|           | 0.83058                     | 307.77          | 307.752       | 0.01787           | 0.72644                        | 8.62                 | 8.6989        | -0.07889          |
|           | 0.62230                     | 305.47          | 305.296       | 0.17447           | 0.52070                        | 9.56                 | 9.5956        | -0.03561          |
|           | 0.41910                     | 302.95          | 302.899       | 0.05116           | 0.31496                        | 11.00                | 10.9495       | 0.05051           |
|           | 0.21082                     | 300.49          | 300.442       | 0.04777           | 0.10541                        | 13.48                | 13.4907       | -0.01065          |
|           | 0.00000                     | 297.97          | 297.956       | 0.01433           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| C5        | 1.61798                     | 318.82          | 318.677       | 0.14303           | 1.51892                        | 5.68                 | 5.6855        | -0.00549          |
|           | 1.41986                     | 316.10          | 316.048       | 0.05181           |                                |                      |               |                   |
|           | 1.21920                     | 313.20          | 313.386       | -0.18571          | 1.12014                        | 6.90                 | 6.9006        | -0.00062          |
|           | 1.02108                     | 310.87          | 310.757       | 0.11307           | 0.92202                        | 7.61                 | 7.5805        | 0.02947           |
|           | 0.82296                     | 308.16          | 308.128       | 0.03186           | 0.72644                        | 8.36                 | 8.3773        | -0.01729          |
|           | 0.62992                     | 305.37          | 305.567       | -0.19677          | 0.52959                        | 9.42                 | 9.4417        | -0.02169          |
|           | 0.42926                     | 302.75          | 302.904       | -0.15428          | 0.32639                        | 11.14                | 11.1206       | 0.01943           |
|           | 0.22352                     | 300.04          | 300.174       | -0.13439          | 0.11176                        | 14.27                | 14.2738       | -0.00380          |
|           | 0.00000                     | 297.54          | 297.209       | 0.33141           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| B1        | 1.50622                     | 317.74          | 317.686       | 0.05397           | 1.41224                        | 6.92                 | 6.9003        | 0.01972           |
|           | 1.31826                     | 315.27          | 315.183       | 0.08711           |                                |                      |               |                   |
|           | 1.13284                     | 312.76          | 312.714       | 0.04643           | 1.04013                        | 8.78                 | 8.8230        | -0.04304          |
|           | 0.94742                     | 310.17          | 310.244       | -0.07425          | 0.85471                        | 9.80                 | 9.8229        | -0.02286          |
|           | 0.76200                     | 307.70          | 307.775       | -0.07494          | 0.66929                        | 11.02                | 10.9360       | 0.08398           |
|           | 0.57658                     | 305.27          | 305.306       | -0.03562          | 0.48387                        | 12.36                | 12.4060       | -0.04604          |
|           | 0.39116                     | 302.64          | 302.836       | -0.19630          | 0.29591                        | 15.06                | 15.0513       | 0.00869           |
|           | 0.20066                     | 300.18          | 300.299       | -0.11933          | 0.10033                        | 21.82                | 21.8204       | -0.00044          |
|           | 0.00000                     | 297.94          | 297.627       | 0.31300           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |

| Sample ID | Thermo-couple Location (cm) | Temperature (K) | $\hat{T}$ (K) | $T - \hat{T}$ (K) | Moisture Content Location (cm) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------|-----------------------------|-----------------|---------------|-------------------|--------------------------------|----------------------|---------------|-------------------|
| A2        | 1.64846                     | 318.77          | 318.579       | 0.19081           | 1.54686                        | 6.71                 | 6.7344        | -0.02442          |
|           | 1.44526                     | 315.95          | 316.007       | -0.05703          |                                |                      |               |                   |
|           | 1.23952                     | 313.44          | 313.403       | 0.03727           | 1.13792                        | 8.88                 | 8.8714        | 0.00856           |
|           | 1.03632                     | 310.69          | 310.831       | -0.14057          | 0.93599                        | 10.01                | 9.9564        | 0.05364           |
|           | 0.83566                     | 308.20          | 308.291       | -0.09057          | 0.73025                        | 11.18                | 11.1593       | 0.02066           |
|           | 0.62484                     | 305.66          | 305.622       | 0.03804           | 0.52324                        | 12.64                | 12.7364       | -0.09639          |
|           | 0.42164                     | 303.02          | 303.050       | -0.02981          | 0.31877                        | 15.67                | 15.6270       | 0.04299           |
|           | 0.21590                     | 300.13          | 300.446       | -0.31550          | 0.10795                        | 23.80                | 23.8051       | -0.00506          |
|           | 0.00000                     | 298.08          | 297.713       | 0.36741           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| E2        | 1.64084                     | 317.18          | 316.980       | 0.19968           | 1.54178                        | 7.11                 | 7.1222        | -0.01218          |
|           | 1.44272                     | 314.70          | 314.678       | 0.02157           |                                |                      |               |                   |
|           | 1.23952                     | 312.16          | 312.318       | -0.15752          | 1.13792                        | 9.15                 | 9.1637        | -0.01374          |
|           | 1.03632                     | 309.71          | 309.957       | -0.24661          | 0.93345                        | 10.31                | 10.2408       | 0.06921           |
|           | 0.83058                     | 307.67          | 307.566       | 0.10382           | 0.72898                        | 11.42                | 11.4329       | -0.01287          |
|           | 0.62738                     | 305.26          | 305.205       | 0.05473           | 0.52451                        | 12.92                | 12.9786       | -0.05855          |
|           | 0.42164                     | 302.78          | 302.815       | -0.03484          | 0.31750                        | 15.69                | 15.6572       | 0.03283           |
|           | 0.21336                     | 300.33          | 300.395       | -0.06491          | 0.10668                        | 21.99                | 21.9947       | -0.00467          |
|           | 0.00000                     | 298.04          | 297.916       | 0.12405           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| A1        | 1.62560                     | 317.42          | 317.289       | 0.13139           | 1.52527                        | 7.0                  | 6.9973        | 0.02270           |
|           | 1.42494                     | 314.91          | 314.877       | 0.03304           |                                |                      |               |                   |
|           | 1.22174                     | 312.21          | 312.435       | -0.22477          | 1.12014                        | 8.9                  | 8.9850        | -0.06499          |
|           | 1.01854                     | 310.19          | 309.993       | 0.19741           | 0.91821                        | 10.0                 | 10.0241       | 0.00589           |
|           | 0.81788                     | 307.62          | 307.581       | 0.03906           | 0.72136                        | 11.2                 | 11.1588       | 0.08120           |
|           | 0.62484                     | 305.04          | 305.261       | -0.22086          | 0.52324                        | 12.6                 | 12.6674       | -0.05741          |
|           | 0.42164                     | 302.70          | 302.819       | -0.11868          | 0.31750                        | 15.4                 | 15.4263       | 0.01368           |
|           | 0.21336                     | 300.17          | 300.315       | -0.14544          | 0.10668                        | 22.2                 | 22.2211       | -0.00107          |
|           | 0.00000                     | 298.06          | 297.751       | 0.30885           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |

| Sample ID | Thermo-couple Location (cm) | Temperature (K) | $\hat{T}$ (K) | $T - \hat{T}$ (K) | Moisture Content Location (cm) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------|-----------------------------|-----------------|---------------|-------------------|--------------------------------|----------------------|---------------|-------------------|
| B2        | 1.57734                     | 317.27          | 317.058       | 0.21191           | 1.47574                        | 7.04                 | 6.7671        | 0.27293           |
|           | 1.37414                     | 314.43          | 314.516       | -0.08619          |                                |                      |               | -0.31381          |
|           | 1.17602                     | 312.14          | 312.038       | 0.10216           | 1.07823                        | 9.02                 | 9.3338        | -0.29386          |
|           | 0.98044                     | 309.41          | 309.591       | -0.18126          | 0.88519                        | 10.29                | 10.5839       | 0.06306           |
|           | 0.78994                     | 307.20          | 307.208       | -0.00823          | 0.69596                        | 11.90                | 11.8369       | 0.34533           |
|           | 0.60198                     | 304.79          | 304.857       | -0.06697          | 0.50927                        | 13.64                | 13.2947       | -0.07726          |
|           | 0.41656                     | 302.45          | 302.537       | -0.08749          | 0.31623                        | 16.67                | 16.7473       | 0.00361           |
|           | 0.21590                     | 299.68          | 300.027       | -0.34736          | 0.10795                        | 41.20                | 41.1964       |                   |
|           | 0.00000                     | 297.79          | 297.327       | 0.46341           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| A4        | 1.64338                     | 318.26          | 317.969       | 0.29129           | 1.54305                        | 7.05                 | 6.7453        | 0.30473           |
|           | 1.44272                     | 315.60          | 315.486       | 0.11434           |                                |                      |               | -0.32375          |
|           | 1.24206                     | 313.18          | 313.003       | 0.17739           | 1.14300                        | 9.06                 | 9.3838        | -0.29951          |
|           | 1.04394                     | 310.21          | 310.551       | -0.34099          | 0.94234                        | 10.41                | 10.7095       | 0.00155           |
|           | 0.84074                     | 307.57          | 308.037       | -0.46651          | 0.73406                        | 12.11                | 12.1084       | 0.39000           |
|           | 0.62738                     | 305.33          | 305.396       | -0.06631          | 0.52578                        | 14.13                | 13.7400       | -0.07654          |
|           | 0.42418                     | 302.75          | 302.882       | -0.13183          | 0.32004                        | 17.56                | 17.6365       | 0.00352           |
|           | 0.21590                     | 300.22          | 300.304       | -0.08449          | 0.10795                        | 46.16                | 46.1565       |                   |
|           | 0.00000                     | 298.14          | 297.633       | 0.50715           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| C3        | 1.62560                     | 318.37          | 318.478       | -0.10841          | 1.52654                        | 7.13                 | 6.8141        | 0.31590           |
|           | 1.42748                     | 315.80          | 315.892       | -0.09166          |                                |                      |               | -0.32200          |
|           | 1.22936                     | 313.53          | 313.305       | 0.22508           | 1.12903                        | 8.97                 | 9.2920        | -0.30222          |
|           | 1.02870                     | 310.81          | 310.685       | 0.12499           | 0.92710                        | 10.25                | 10.5522       | -0.06603          |
|           | 0.82550                     | 308.10          | 308.032       | 0.06807           | 0.72390                        | 11.77                | 11.8360       | 0.44786           |
|           | 0.62230                     | 305.43          | 305.379       | 0.05114           | 0.52070                        | 13.74                | 13.2921       | -0.07667          |
|           | 0.41910                     | 302.77          | 302.726       | 0.04421           | 0.31623                        | 16.61                | 16.6867       | 0.00315           |
|           | 0.21336                     | 299.08          | 300.040       | -0.95956          | 0.10668                        | 43.28                | 43.2769       |                   |
|           | 0.00000                     | 297.90          | 297.254       | 0.64617           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |

| Sample ID | Thermo-couple Location (cm) | Temperature (K) | $\hat{T}$ (K) | $T - \hat{T}$ (K) | Moisture Content Location (cm) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------|-----------------------------|-----------------|---------------|-------------------|--------------------------------|----------------------|---------------|-------------------|
| J1        | 1.65608                     | 317.88          | 317.733       | 0.14687           | 1.55702                        | 7.43                 | 7.2300        | 0.19996           |
|           | 1.45796                     | 315.54          | 315.343       | 0.19716           |                                |                      |               |                   |
|           | 1.25984                     | 313.01          | 312.953       | 0.05745           | 1.15951                        | 9.70                 | 9.8973        | -0.19725          |
|           | 1.05918                     | 310.42          | 310.532       | -0.11161          | 0.95504                        | 11.04                | 11.2737       | -0.23373          |
|           | 0.85090                     | 307.79          | 308.019       | -0.22874          | 0.74803                        | 12.72                | 12.7008       | 0.01916           |
|           | 0.64516                     | 305.27          | 305.537       | -0.26652          | 0.53848                        | 14.69                | 14.4165       | 0.27346           |
|           | 0.43180                     | 302.74          | 302.962       | -0.22236          | 0.32766                        | 18.29                | 18.3553       | -0.06534          |
|           | 0.22352                     | 300.35          | 300.449       | -0.09949          | 0.11176                        | 41.54                | 41.5363       |                   |
|           | 0.00000                     | 298.28          | 297.753       | 0.52725           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| X1        | 1.77800                     | 308.15          | 307.968       | 0.18198           | 1.66878                        | 6.97                 | 7.0359        | -0.06586          |
|           | 1.55956                     | 305.85          | 305.687       | 0.16334           |                                |                      |               |                   |
|           | 1.34112                     | 303.36          | 303.405       | -0.04530          | 1.23444                        | 8.26                 | 8.1555        | 0.10450           |
|           | 1.12776                     | 301.01          | 301.177       | -0.16699          | 1.01600                        | 8.76                 | 8.7247        | 0.03530           |
|           | 0.90424                     | 298.62          | 298.843       | -0.22258          | 0.79248                        | 9.31                 | 9.3269        | -0.01685          |
|           | 0.68072                     | 296.23          | 296.508       | -0.27816          | 0.56769                        | 9.90                 | 10.0050       | -0.10499          |
|           | 0.45466                     | 294.21          | 294.147       | 0.06278           | 0.34163                        | 11.01                | 10.9549       | 0.05507           |
|           | 0.22860                     | 291.93          | 291.786       | 0.14373           | 0.11430                        | 12.90                | 12.9072       | -0.00717          |
|           | 0.00000                     | 289.56          | 289.399       | 0.16120           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| Z1        | 1.76276                     | 308.11          | 307.824       | 0.28597           | 1.65100                        | 6.69                 | 6.7331        | -0.04309          |
|           | 1.53924                     | 305.49          | 305.461       | 0.02882           |                                |                      |               |                   |
|           | 1.32842                     | 303.17          | 303.233       | -0.06259          | 1.21666                        | 7.93                 | 7.8857        | 0.04434           |
|           | 1.10490                     | 300.66          | 300.870       | -0.20974          | 0.99441                        | 8.57                 | 8.4860        | 0.08401           |
|           | 0.88392                     | 298.20          | 298.534       | -0.33374          | 0.77343                        | 9.06                 | 9.1130        | -0.05296          |
|           | 0.66294                     | 296.24          | 296.198       | 0.04226           | 0.55372                        | 9.76                 | 9.8337        | -0.07374          |
|           | 0.44450                     | 293.94          | 293.889       | 0.05140           | 0.33401                        | 10.92                | 10.8714       | 0.04863           |
|           | 0.22352                     | 291.60          | 291.553       | 0.04740           | 0.11176                        | 12.97                | 12.9772       | -0.00719          |
|           | 0.00000                     | 289.34          | 289.190       | 0.15025           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |

| Sample ID | Thermo-couple Location (cm) | Temperature (K) | $\hat{T}$ (K) | $T - \hat{T}$ (K) | Moisture Content Location (cm) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------|-----------------------------|-----------------|---------------|-------------------|--------------------------------|----------------------|---------------|-------------------|
| X3        | 1.80594                     | 308.27          | 308.144       | 0.12638           | 1.69291                        | 7.18                 | 7.2473        | -0.06726          |
|           | 1.57988                     | 305.60          | 305.731       | -0.13130          |                                |                      |               |                   |
|           | 1.35636                     | 303.36          | 303.346       | 0.01392           | 1.24460                        | 8.47                 | 8.3474        | 0.12263           |
|           | 1.13284                     | 300.92          | 300.961       | -0.04086          | 1.01981                        | 8.96                 | 8.9196        | 0.04044           |
|           | 0.90678                     | 298.55          | 298.549       | 0.00146           | 0.79375                        | 9.48                 | 9.5423        | -0.06234          |
|           | 0.68072                     | 296.14          | 296.136       | 0.00379           | 0.56642                        | 10.20                | 10.2987       | -0.09869          |
|           | 0.45212                     | 293.67          | 293.697       | -0.02679          | 0.33909                        | 11.49                | 11.4103       | 0.07967           |
|           | 0.22606                     | 291.35          | 291.284       | 0.06554           | 0.11303                        | 13.46                | 13.4745       | -0.01445          |
|           | 0.00000                     | 288.86          | 288.872       | -0.01214          |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| Y1        | 1.76276                     | 308.63          | 308.735       | -0.10457          | 1.65481                        | 6.91                 | 7.0066        | -0.09657          |
|           | 1.54686                     | 306.39          | 306.293       | 0.09683           |                                |                      |               |                   |
|           | 1.35382                     | 304.11          | 304.110       | -0.00028          | 1.24079                        | 8.28                 | 8.1212        | 0.15877           |
|           | 1.12776                     | 301.58          | 301.554       | 0.02601           | 1.01473                        | 8.81                 | 8.7462        | 0.06383           |
|           | 0.90170                     | 299.02          | 298.998       | 0.02230           | 0.78867                        | 9.34                 | 9.4141        | -0.07409          |
|           | 0.67564                     | 296.45          | 296.441       | 0.00859           | 0.56515                        | 10.07                | 10.2012       | -0.13118          |
|           | 0.45466                     | 293.87          | 293.943       | -0.07257          | 0.34417                        | 11.45                | 11.3470       | 0.10298           |
|           | 0.23114                     | 291.47          | 291.415       | 0.05500           | 0.11557                        | 13.67                | 13.6851       | -0.01511          |
|           | 0.00000                     | 288.77          | 288.801       | -0.03127          |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| W3        | 1.68910                     | 307.65          | 307.193       | 0.45678           | 1.58623                        | 8.03                 | 8.1303        | -0.10035          |
|           | 1.48336                     | 304.96          | 304.851       | 0.10948           |                                |                      |               |                   |
|           | 1.26746                     | 302.32          | 302.392       | -0.07213          | 1.17348                        | 10.12                | 10.0173       | 0.10265           |
|           | 1.07950                     | 299.92          | 300.252       | -0.33189          | 0.96774                        | 11.11                | 10.9814       | 0.12856           |
|           | 0.85598                     | 297.49          | 297.707       | -0.21673          | 0.75311                        | 12.09                | 12.0590       | 0.03098           |
|           | 0.65024                     | 295.10          | 295.364       | -0.26403          | 0.53594                        | 13.12                | 13.4023       | -0.28234          |
|           | 0.42164                     | 292.38          | 292.761       | -0.38103          | 0.31623                        | 15.80                | 15.6596       | 0.14037           |
|           | 0.21082                     | 290.52          | 290.360       | 0.15952           | 0.10541                        | 20.71                | 20.7299       | -0.01987          |
|           | 0.00000                     | 288.50          | 287.960       | 0.54006           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |

| Sample ID | Thermo-couple Location (cm) | Temperature (K) | $\hat{T}$ (K) | $T - \hat{T}$ (K) | Moisture Content Location (cm) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------|-----------------------------|-----------------|---------------|-------------------|--------------------------------|----------------------|---------------|-------------------|
| X7        | 1.76022                     | 308.19          | 307.835       | 0.35517           | 1.64973                        | 7.91                 | 7.9877        | -0.07770          |
|           | 1.53924                     | 305.45          | 305.392       | 0.05831           |                                |                      |               |                   |
|           | 1.31318                     | 302.89          | 302.892       | -0.00238          | 1.19888                        | 10.08                | 10.0227       | 0.05729           |
|           | 1.08458                     | 300.17          | 300.365       | -0.19500          | 0.97536                        | 11.19                | 11.0413       | 0.14874           |
|           | 0.86614                     | 297.70          | 297.950       | -0.24994          | 0.75311                        | 12.08                | 12.0949       | -0.01492          |
|           | 0.64008                     | 295.00          | 295.451       | -0.45063          | 0.53721                        | 13.11                | 13.2990       | -0.18901          |
|           | 0.43434                     | 293.07          | 293.176       | -0.10598          | 0.33528                        | 15.21                | 15.1258       | 0.08419           |
|           | 0.23622                     | 291.20          | 290.986       | 0.21442           | 0.11811                        | 20.40                | 20.4086       | -0.00858          |
|           | 0.00000                     | 288.75          | 288.374       | 0.37605           |                                |                      |               |                   |
| X9        | 1.81102                     | 307.76          | 307.851       | -0.09131          | 1.70561                        | 7.91                 | 7.9950        | -0.08499          |
|           | 1.60020                     | 305.12          | 305.610       | -0.48990          |                                |                      |               |                   |
|           | 1.36144                     | 303.14          | 303.071       | 0.06856           | 1.24714                        | 10.12                | 10.0238       | 0.09622           |
|           | 1.13284                     | 300.95          | 300.641       | 0.30901           | 1.01727                        | 11.15                | 11.0506       | 0.09940           |
|           | 0.90170                     | 298.63          | 298.184       | 0.44646           | 0.79121                        | 12.10                | 12.0968       | 0.00321           |
|           | 0.68072                     | 296.02          | 295.834       | 0.18589           | 0.56896                        | 13.09                | 13.2746       | -0.18458          |
|           | 0.45720                     | 293.49          | 293.458       | 0.03233           | 0.34417                        | 15.18                | 15.1006       | 0.07941           |
|           | 0.23114                     | 290.89          | 291.054       | -0.16423          | 0.11557                        | 19.74                | 19.7487       | -0.00867          |
|           | 0.00000                     | 288.30          | 288.597       | -0.29678          |                                |                      |               |                   |
| X5        | 1.81356                     | 308.35          | 307.921       | 0.42861           | 1.70434                        | 8.31                 | 8.2592        | 0.05085           |
|           | 1.59512                     | 305.57          | 305.440       | 0.12997           |                                |                      |               |                   |
|           | 1.37160                     | 302.76          | 302.901       | -0.14097          | 1.25857                        | 10.76                | 10.8675       | -0.10753          |
|           | 1.14554                     | 300.25          | 300.333       | -0.08306          | 1.03251                        | 12.17                | 12.2133       | -0.04333          |
|           | 0.91948                     | 297.54          | 297.765       | -0.22514          | 0.81026                        | 13.78                | 13.6141       | 0.16590           |
|           | 0.70104                     | 294.95          | 295.284       | -0.33378          | 0.58420                        | 15.27                | 15.3471       | -0.07712          |
|           | 0.46736                     | 292.21          | 292.629       | -0.41931          | 0.34925                        | 18.48                | 18.4682       | 0.01180           |
|           | 0.23114                     | 289.69          | 289.946       | -0.25598          | 0.11557                        | 27.02                | 27.0205       | -0.00055          |
|           | 0.00000                     | 288.22          | 287.320       | 0.89964           |                                |                      |               |                   |

| Sample ID | Thermo-couple Location (cm) | Temperature (K) | $\hat{T}$ (K) | $T - \hat{T}$ (K) | Moisture Content Location (cm) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------|-----------------------------|-----------------|---------------|-------------------|--------------------------------|----------------------|---------------|-------------------|
| Z4        | 1.78816                     | 308.20          | 307.787       | 0.41317           | 1.67640                        | 8.66                 | 8.6303        | 0.02971           |
|           | 1.56464                     | 305.56          | 305.314       | 0.24650           |                                |                      |               |                   |
|           | 1.36652                     | 302.99          | 303.121       | -0.13124          | 1.25476                        | 11.16                | 11.2436       | -0.08364          |
|           | 1.14300                     | 300.34          | 300.648       | -0.30791          | 1.03124                        | 12.64                | 12.6398       | 0.00015           |
|           | 0.91948                     | 297.61          | 298.175       | -0.56458          | 0.80772                        | 14.21                | 14.0865       | 0.12350           |
|           | 0.69596                     | 295.66          | 295.701       | -0.04126          | 0.58547                        | 15.69                | 15.7786       | -0.08862          |
|           | 0.47498                     | 293.17          | 293.256       | -0.08604          | 0.35941                        | 18.85                | 18.8297       | 0.02028           |
|           | 0.24384                     | 290.68          | 290.698       | -0.01839          | 0.12192                        | 29.79                | 29.7914       | -0.00138          |
|           | 0.00000                     | 288.49          | 288.000       | 0.48978           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| W2        | 1.85166                     | 308.59          | 308.100       | 0.48961           | 1.73863                        | 8.39                 | 8.3131        | 0.07688           |
|           | 1.62560                     | 305.60          | 305.580       | 0.01959           |                                |                      |               |                   |
|           | 1.39700                     | 302.81          | 303.032       | -0.22211          | 1.28270                        | 10.96                | 11.1111       | -0.15114          |
|           | 1.16840                     | 300.04          | 300.484       | -0.44381          | 1.05410                        | 12.47                | 12.5235       | -0.05349          |
|           | 0.93980                     | 297.97          | 297.936       | 0.03449           | 0.82550                        | 14.16                | 13.9794       | 0.18063           |
|           | 0.71120                     | 295.33          | 295.387       | -0.05722          | 0.59436                        | 15.62                | 15.6775       | -0.05746          |
|           | 0.47752                     | 292.60          | 292.782       | -0.18229          | 0.35941                        | 18.62                | 18.6155       | 0.00453           |
|           | 0.24130                     | 290.09          | 290.149       | -0.05905          | 0.12065                        | 28.28                | 28.2799       | 0.00006           |
|           | 0.00000                     | 287.88          | 287.459       | 0.42082           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| X2        | 1.75260                     | 317.91          | 317.815       | 0.09466           | 1.64465                        | 6.62                 | 6.6509        | -0.03091          |
|           | 1.53670                     | 315.59          | 315.545       | 0.04517           |                                |                      |               |                   |
|           | 1.31826                     | 313.21          | 313.248       | -0.03760          | 1.20650                        | 7.97                 | 7.9122        | 0.05776           |
|           | 1.09474                     | 310.75          | 310.897       | -0.14695          | 0.98171                        | 8.60                 | 8.5872        | 0.01279           |
|           | 0.86868                     | 308.48          | 308.520       | -0.03959          | 0.75565                        | 9.31                 | 9.3279        | -0.01792          |
|           | 0.64262                     | 305.99          | 306.142       | -0.15223          | 0.53213                        | 10.16                | 10.2193       | -0.05930          |
|           | 0.42164                     | 304.03          | 303.818       | 0.21171           | 0.31242                        | 11.54                | 11.4931       | 0.04690           |
|           | 0.20320                     | 301.61          | 301.521       | 0.08894           | 0.10160                        | 13.64                | 13.6493       | -0.00930          |
|           | 0.00000                     | 299.32          | 299.384       | -0.06411          |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |

| Sample ID | Thermo-couple Location (cm) | Temperature (K) | $\hat{T}$ (K) | $T - \hat{T}$ (K) | Moisture Content Location (cm) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------|-----------------------------|-----------------|---------------|-------------------|--------------------------------|----------------------|---------------|-------------------|
| Z2        | 1.65862                     | 318.09          | 317.913       | 0.17738           | 1.55575                        | 6.55                 | 6.5728        | -0.02279          |
|           | 1.45288                     | 315.65          | 315.580       | 0.06994           |                                |                      |               |                   |
|           | 1.23952                     | 313.13          | 313.161       | -0.03112          | 1.13538                        | 7.91                 | 7.8652        | 0.04480           |
|           | 1.03124                     | 310.58          | 310.800       | -0.21976          | 0.92964                        | 8.55                 | 8.5404        | 0.00955           |
|           | 0.82804                     | 308.25          | 308.496       | -0.24600          | 0.72898                        | 9.27                 | 9.2702        | -0.00020          |
|           | 0.62992                     | 306.25          | 306.250       | 0.00016           | 0.53213                        | 10.05                | 10.1308       | -0.08079          |
|           | 0.43434                     | 304.19          | 304.032       | 0.15753           | 0.33147                        | 11.38                | 11.3192       | 0.06080           |
|           | 0.22860                     | 301.72          | 301.700       | 0.02009           | 0.11430                        | 13.36                | 13.3714       | -0.01137          |
|           | 0.00000                     | 299.18          | 299.108       | 0.07182           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| X4        | 1.75006                     | 317.63          | 317.484       | 0.14580           | 1.64719                        | 6.60                 | 6.6161        | -0.01606          |
|           | 1.54432                     | 315.13          | 315.254       | -0.12432          |                                |                      |               |                   |
|           | 1.32842                     | 312.90          | 312.914       | -0.01433          | 1.21666                        | 7.86                 | 7.8434        | 0.01656           |
|           | 1.10490                     | 310.46          | 310.492       | -0.03175          | 0.99314                        | 8.56                 | 8.5246        | 0.03541           |
|           | 0.88138                     | 308.06          | 308.069       | -0.00917          | 0.77089                        | 9.27                 | 9.2782        | -0.00823          |
|           | 0.66040                     | 305.64          | 305.674       | -0.03412          | 0.55118                        | 10.11                | 10.1825       | -0.07253          |
|           | 0.44196                     | 303.37          | 303.307       | 0.06341           | 0.33274                        | 11.47                | 11.4137       | 0.05634           |
|           | 0.22352                     | 300.91          | 300.939       | -0.02907          | 0.11176                        | 13.36                | 13.3715       | -0.01149          |
|           | 0.00000                     | 298.55          | 298.516       | 0.03351           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| W1        | 1.60274                     | 318.25          | 318.146       | 0.10365           | 1.50495                        | 6.61                 | 6.6370        | -0.02699          |
|           | 1.40716                     | 315.97          | 315.843       | 0.12656           |                                |                      |               |                   |
|           | 1.20396                     | 313.45          | 313.451       | -0.00081          | 1.09728                        | 8.01                 | 7.9752        | 0.03476           |
|           | 0.99060                     | 310.77          | 310.939       | -0.16854          | 0.89154                        | 8.75                 | 8.6899        | 0.06007           |
|           | 0.79248                     | 308.47          | 308.606       | -0.13573          | 0.69342                        | 9.40                 | 9.4413        | -0.04126          |
|           | 0.59436                     | 306.17          | 306.273       | -0.10291          | 0.49784                        | 10.22                | 10.3086       | -0.08857          |
|           | 0.40132                     | 303.93          | 304.000       | -0.06991          | 0.29210                        | 11.58                | 11.5005       | 0.07948           |
|           | 0.18288                     | 301.54          | 301.428       | 0.11217           | 0.09144                        | 13.22                | 13.2375       | -0.01750          |
|           | 0.00000                     | 299.41          | 299.274       | 0.13554           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |

| Sample ID | Thermo-couple Location (cm) | Temperature (K) | $\hat{T}$ (K) | $T - \hat{T}$ (K) | Moisture Content Location (cm) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------|-----------------------------|-----------------|---------------|-------------------|--------------------------------|----------------------|---------------|-------------------|
| W4        | 1.70942                     | 318.63          | 318.806       | -0.17560          | 1.60147                        | 7.32                 | 7.3114        | 0.00864           |
|           | 1.49352                     | 316.45          | 316.185       | 0.26522           |                                |                      |               |                   |
|           | 1.28270                     | 313.69          | 313.626       | 0.06438           | 1.17094                        | 9.40                 | 9.4147        | -0.01473          |
|           | 1.05918                     | 310.97          | 310.912       | 0.05770           | 0.95377                        | 10.49                | 10.5181       | -0.02811          |
|           | 0.84836                     | 308.37          | 308.353       | 0.01685           | 0.74549                        | 11.75                | 11.6856       | 0.06442           |
|           | 0.64262                     | 305.64          | 305.856       | -0.21566          | 0.53467                        | 13.17                | 13.2086       | -0.03856          |
|           | 0.42672                     | 303.01          | 303.235       | -0.22484          | 0.31750                        | 15.92                | 15.9108       | 0.00916           |
|           | 0.20828                     | 300.49          | 300.583       | -0.09319          | 0.10414                        | 22.12                | 22.1208       | -0.00081          |
|           | 0.00000                     | 298.36          | 298.055       | 0.30513           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| Y2        | 1.78054                     | 318.22          | 317.812       | 0.40807           | 1.67640                        | 7.63                 | 7.7126        | -0.08258          |
|           | 1.57226                     | 315.59          | 315.502       | 0.08800           |                                |                      |               |                   |
|           | 1.35128                     | 312.92          | 313.051       | -0.13122          | 1.23952                        | 9.88                 | 9.7721        | 0.10791           |
|           | 1.12776                     | 310.36          | 310.572       | -0.21227          | 1.01600                        | 10.93                | 10.8530       | 0.07704           |
|           | 0.90424                     | 307.91          | 308.093       | -0.18332          | 0.79248                        | 12.02                | 12.0159       | 0.00411           |
|           | 0.68072                     | 305.37          | 305.614       | -0.24437          | 0.57023                        | 13.26                | 13.4517       | -0.19170          |
|           | 0.45974                     | 302.96          | 303.164       | -0.20359          | 0.34671                        | 15.96                | 15.8621       | 0.09788           |
|           | 0.23368                     | 300.56          | 300.656       | -0.09647          | 0.11684                        | 21.86                | 21.8727       | -0.01267          |
|           | 0.00000                     | 298.64          | 298.065       | 0.57516           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| X8        | 1.70434                     | 318.92          | 318.278       | 0.64230           | 1.59639                        | 7.20                 | 7.2450        | -0.04501          |
|           | 1.48844                     | 315.84          | 315.739       | 0.10108           |                                |                      |               |                   |
|           | 1.28524                     | 313.07          | 313.349       | -0.27948          | 1.18364                        | 9.37                 | 9.3311        | 0.03894           |
|           | 1.08204                     | 310.53          | 310.960       | -0.43004          | 0.98171                        | 10.46                | 10.3867       | 0.07325           |
|           | 0.88138                     | 308.13          | 308.600       | -0.47046          | 0.77851                        | 11.56                | 11.5421       | 0.01794           |
|           | 0.67564                     | 306.14          | 306.181       | -0.04115          | 0.57023                        | 12.88                | 13.0272       | -0.14724          |
|           | 0.46482                     | 303.71          | 303.702       | 0.00789           | 0.35179                        | 15.71                | 15.6393       | 0.07068           |
|           | 0.23876                     | 301.12          | 301.044       | 0.07615           | 0.11938                        | 22.46                | 22.4686       | -0.00857          |
|           | 0.00000                     | 298.63          | 298.236       | 0.39374           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |

| Sample ID | Thermo-couple Location (cm) | Temperature (K) | $\hat{T}$ (K) | $T - \hat{T}$ (K) | Moisture Content Location (cm) | Moisture Content (%) | $\hat{M}$ (%) | $M - \hat{M}$ (%) |
|-----------|-----------------------------|-----------------|---------------|-------------------|--------------------------------|----------------------|---------------|-------------------|
| Z3        | 1.64084                     | 317.00          | 316.908       | 0.09215           | 1.54051                        | 8.13                 | 8.0928        | 0.03723           |
|           | 1.44018                     | 314.39          | 314.595       | -0.20491          |                                |                      |               |                   |
|           | 1.23444                     | 312.54          | 312.223       | 0.31659           | 1.13792                        | 10.60                | 10.7210       | -0.12103          |
|           | 1.04140                     | 310.09          | 309.998       | 0.09170           | 0.94107                        | 12.07                | 12.0443       | 0.02567           |
|           | 0.84074                     | 307.59          | 307.685       | -0.09536          | 0.73533                        | 13.71                | 13.5600       | 0.14998           |
|           | 0.62992                     | 305.10          | 305.255       | -0.15531          | 0.52451                        | 15.53                | 15.6531       | -0.12305          |
|           | 0.41910                     | 302.52          | 302.825       | -0.30526          | 0.31369                        | 19.93                | 19.8955       | 0.03448           |
|           | 0.20828                     | 300.22          | 300.395       | -0.17520          | 0.10414                        | 32.52                | 32.5233       | -0.00327          |
|           | 0.00000                     | 298.43          | 297.994       | 0.43557           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| Y3        | 1.77292                     | 318.56          | 318.082       | 0.47830           | 1.66751                        | 7.82                 | 7.6672        | 0.15278           |
|           | 1.56210                     | 315.88          | 315.688       | 0.19238           |                                |                      |               |                   |
|           | 1.34874                     | 313.25          | 313.265       | -0.01469          | 1.23571                        | 10.21                | 10.4276       | -0.21763          |
|           | 1.12268                     | 310.49          | 310.698       | -0.20754          | 1.01346                        | 11.76                | 11.8560       | -0.09598          |
|           | 0.90424                     | 307.84          | 308.217       | -0.37692          | 0.79121                        | 13.38                | 13.3307       | 0.04928           |
|           | 0.67818                     | 305.20          | 305.650       | -0.44977          | 0.56769                        | 15.28                | 15.1242       | 0.15583           |
|           | 0.45720                     | 302.56          | 303.140       | -0.58031          | 0.34417                        | 18.94                | 18.9877       | -0.04768          |
|           | 0.23114                     | 300.64          | 300.573       | 0.06684           | 0.11557                        | 37.53                | 37.5266       | 0.00340           |
|           | 0.00000                     | 298.84          | 297.948       | 0.89168           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |
| X6        | 1.78562                     | 317.35          | 316.997       | 0.35349           | 1.67513                        | 8.46                 | 8.3800        | 0.07998           |
|           | 1.56464                     | 314.80          | 314.643       | 0.15693           |                                |                      |               |                   |
|           | 1.35382                     | 312.39          | 312.398       | -0.00783          | 1.24206                        | 10.80                | 10.9645       | -0.16451          |
|           | 1.13030                     | 309.81          | 310.017       | -0.20734          | 1.01727                        | 12.33                | 12.3241       | 0.00590           |
|           | 0.90424                     | 307.35          | 307.610       | -0.25980          | 0.79502                        | 13.82                | 13.7456       | 0.07436           |
|           | 0.68580                     | 304.83          | 305.283       | -0.45341          | 0.57785                        | 15.50                | 15.4817       | 0.01833           |
|           | 0.46990                     | 302.89          | 302.984       | -0.09407          | 0.35179                        | 19.00                | 19.0158       | -0.01578          |
|           | 0.23368                     | 300.29          | 300.468       | -0.17832          | 0.11684                        | 31.91                | 31.9083       | 0.00172           |
|           | 0.00000                     | 298.67          | 297.980       | 0.69038           |                                |                      |               |                   |
|           |                             |                 |               |                   |                                |                      |               |                   |

**Table A6. Parameter estimates of the temperature and moisture content models for the nonisothermal steady-state temperature and moisture content profiles.**

| ID | Temperature    |                | Moisture Content |                |                |                |
|----|----------------|----------------|------------------|----------------|----------------|----------------|
|    | A <sub>T</sub> | B <sub>T</sub> | A <sub>M</sub>   | B <sub>M</sub> | C <sub>M</sub> | D <sub>M</sub> |
| A5 | 287.450        | 12.916         | 10.858           | -3.190         | 6.066          | 5.910          |
| B4 | 287.561        | 12.961         | 10.371           | -2.932         | 6.641          | 5.868          |
| C4 | 287.659        | 12.704         | 10.510           | -2.919         | 5.700          | 5.709          |
| A7 | 287.675        | 12.486         | 10.772           | -2.976         | 6.483          | 5.487          |
| H1 | 287.562        | 12.778         | 14.594           | -4.881         | 15.404         | 6.386          |
| C1 | 287.323        | 12.642         | 14.804           | -4.972         | 19.943         | 6.999          |
| F1 | 287.789        | 12.023         | 14.863           | -4.630         | 12.429         | 5.533          |
| E1 | 287.804        | 12.403         | 14.979           | -4.882         | 11.510         | 5.918          |
| B3 | 287.394        | 13.261         | 17.259           | -6.826         | 106.273        | 12.877         |
| H2 | 287.412        | 12.429         | 17.425           | -6.610         | 108.479        | 12.977         |
| A6 | 297.151        | 13.034         | 10.819           | -3.338         | 5.824          | 4.201          |
| B5 | 297.612        | 13.539         | 10.041           | -3.080         | 6.344          | 4.126          |
| E3 | 297.956        | 11.795         | 10.541           | -2.833         | 5.147          | 4.368          |
| C5 | 297.208        | 13.269         | 9.972            | -2.838         | 7.006          | 3.729          |
| B1 | 297.627        | 13.317         | 14.111           | -5.108         | 15.295         | 6.187          |
| A2 | 297.712        | 12.658         | 14.768           | -5.194         | 19.055         | 6.354          |
| E2 | 297.916        | 11.619         | 14.822           | -4.996         | 13.842         | 5.491          |
| A1 | 297.751        | 12.019         | 14.378           | -4.841         | 15.139         | 5.566          |
| B2 | 297.326        | 12.509         | 16.294           | -6.456         | 85.572         | 11.179         |
| A4 | 297.633        | 12.374         | 16.921           | -6.595         | 99.578         | 11.130         |
| C3 | 297.254        | 13.056         | 16.329           | -6.233         | 97.249         | 11.802         |
| J1 | 297.753        | 12.065         | 17.674           | -6.708         | 74.739         | 9.939          |
| X1 | 289.399        | 10.444         | 11.327           | -2.571         | 3.618          | 5.755          |
| Z1 | 289.190        | 10.571         | 11.094           | -2.642         | 3.972          | 5.374          |
| X3 | 288.872        | 10.671         | 11.346           | -2.423         | 3.956          | 4.414          |
| Y1 | 288.801        | 11.308         | 11.424           | -2.670         | 4.517          | 4.880          |
| W3 | 287.960        | 11.387         | 15.335           | -4.543         | 10.727         | 5.714          |
| X7 | 288.374        | 11.056         | 15.424           | -4.507         | 12.573         | 6.974          |
| X9 | 288.597        | 10.632         | 15.531           | -4.418         | 9.927          | 6.417          |
| X5 | 287.320        | 11.359         | 18.198           | -5.832         | 19.120         | 6.055          |
| Z4 | 288.000        | 11.065         | 19.009           | -6.191         | 28.039         | 7.284          |
| W2 | 287.459        | 11.147         | 18.973           | -6.131         | 23.650         | 7.096          |
| X2 | 299.384        | 10.516         | 11.306           | -2.833         | 4.055          | 4.259          |
| Z2 | 299.108        | 11.337         | 11.182           | -2.970         | 3.879          | 3.743          |
| X4 | 298.516        | 10.838         | 11.124           | -2.745         | 3.738          | 3.407          |
| W1 | 299.274        | 11.775         | 11.410           | -3.180         | 2.956          | 3.646          |
| W4 | 298.055        | 12.139         | 15.053           | -4.836         | 13.284         | 5.398          |
| Y2 | 298.065        | 11.090         | 15.566           | -4.686         | 13.085         | 5.535          |
| X8 | 298.236        | 11.759         | 15.236           | -5.007         | 15.156         | 5.531          |
| Z3 | 297.994        | 11.527         | 18.086           | -6.488         | 29.839         | 6.532          |
| Y3 | 297.948        | 11.356         | 18.322           | -6.389         | 53.188         | 8.488          |
| X6 | 297.980        | 10.650         | 18.357           | -5.956         | 32.260         | 6.995          |

**Table A7. Hailwood-Horrobin parameters of the composite curves for the nonisothermal steady-state samples.**

| ID       | Hailwood-Horrobin Parameters |         |          |         |          |            |
|----------|------------------------------|---------|----------|---------|----------|------------|
|          | $M_p$                        | $K_1$   | $K_2$    | A       | B        | C          |
| A5B4C4A7 | 326.824                      | 12.7849 | 0.781320 | 1.68582 | 0.155226 | 0.00131572 |
| H1C1F1E1 | 300.254                      | 10.7020 | 0.763691 | 1.86654 | 0.138298 | 0.00116503 |
| B3H2     | 301.098                      | 10.4349 | 0.764783 | 1.91277 | 0.138019 | 0.00116743 |
| A6B5E3C5 | 327.848                      | 12.8293 | 0.782078 | 1.68403 | 0.155797 | 0.00132146 |
| B1A2E2A1 | 302.797                      | 10.5695 | 0.766030 | 1.89809 | 0.139140 | 0.00117724 |
| B2A4C3J1 | 303.224                      | 10.5804 | 0.766540 | 1.89772 | 0.139364 | 0.00117979 |
| X1Z1X3Y1 | 306.439                      | 11.9850 | 0.759858 | 1.72543 | 0.144022 | 0.00119399 |
| W3X7X9   | 276.972                      | 9.5002  | 0.737473 | 1.98710 | 0.124565 | 0.00102670 |
| X5Z4W2   | 267.870                      | 8.7949  | 0.728576 | 2.08533 | 0.118430 | 0.00097355 |
| X2Z2X4W1 | 308.855                      | 12.1309 | 0.761955 | 1.71498 | 0.145451 | 0.00120784 |
| W4Y2X8   | 280.501                      | 9.7200  | 0.740869 | 1.96213 | 0.126760 | 0.00104683 |
| Z3Y3X6   | 272.484                      | 9.1378  | 0.733135 | 2.03676 | 0.121515 | 0.00100035 |

**Table A8.** Coefficients of the equations relating the Nelson sorption parameters to the absolute temperature.

| ID       | $B_n = A_B + B_B T$ |         | $\ln \Delta\mu_o = A_i + B_i T + C_i T^2$ |         |                        |
|----------|---------------------|---------|-------------------------------------------|---------|------------------------|
|          | $A_B$               | $B_B$   | $A_i$                                     | $B_i$   | $C_i$                  |
| A5B4C4A7 | 6.6317              | -0.0913 | 11.9774                                   | -0.0266 | $4.246 \times 10^{-5}$ |
| H1C1F1E1 | 4.1643              | -0.0813 | 11.5444                                   | -0.0235 | $3.722 \times 10^{-5}$ |
| B3H2     | 4.0820              | -0.0809 | 11.4780                                   | -0.0230 | $3.622 \times 10^{-5}$ |
| A6B5E3C5 | 15.1700             | -0.1195 | 15.4940                                   | -0.0498 | $8.063 \times 10^{-5}$ |
| B1A2E2A1 | 11.3287             | -0.1049 | 14.3713                                   | -0.0421 | $6.769 \times 10^{-5}$ |
| B2A4C3J1 | 11.2858             | -0.1047 | 14.3467                                   | -0.0419 | $6.737 \times 10^{-5}$ |
| X1Z1X3Y1 | 7.49869             | -0.0951 | 12.6056                                   | -0.0312 | $5.139 \times 10^{-5}$ |
| W3X7X9   | 4.4854              | -0.0828 | 11.9653                                   | -0.0266 | $4.331 \times 10^{-5}$ |
| X5Z4W2   | 3.9213              | -0.0804 | 11.8859                                   | -0.0260 | $4.230 \times 10^{-5}$ |
| X2Z2X4W1 | 16.7111             | -0.1256 | 16.8034                                   | -0.0588 | $9.693 \times 10^{-5}$ |
| W4Y2X8   | 12.1291             | -0.1081 | 15.32899                                  | -0.0488 | $7.985 \times 10^{-5}$ |
| Z3Y3X6   | 11.4247             | -0.1054 | 15.18145                                  | -0.0478 | $7.818 \times 10^{-5}$ |

## Appendix C. List of Symbols

|           |                                                     |
|-----------|-----------------------------------------------------|
| $a$       | water activity                                      |
| $B_n$     | parameter in the Nelson sorption model              |
| $C$       | concentration                                       |
| $C_i$     | mass fraction of component $i$                      |
| $C_p$     | heat capacity at constant pressure                  |
| $C_p$     | heat capacity of water vapor at constant pressure   |
| $D$       | diffusion coefficient                               |
| $\bar{D}$ | mean or apparent diffusion coefficient              |
| $D_a$     | coefficient of interdiffusion of water vapor in air |
| $D_{eff}$ | effective vapor diffusivity in wood                 |
| $D_{gT}$  | diffusion coefficient of water vapor through wood   |
| $D_T$     | thermal-diffusion coefficient                       |

|                 |                                                                              |
|-----------------|------------------------------------------------------------------------------|
| $E_A$           | activation energy                                                            |
| $E_s$           | activation energy for bound water diffusion                                  |
| $F_i$           | external force per unit mass acting on component i                           |
| $g$             | gravitational force per unit mass                                            |
| $G_M$           | specific gravity of wood at moisture content M                               |
| $G_o$           | ovendry specific gravity of wood                                             |
| $G^\circ$       | free energy of water at absolute zero temperature                            |
| $G_s$           | free energy of sorbed water                                                  |
| $\Delta G_s$    | differential free energy of sorption                                         |
| $G_v$           | free energy of water vapor                                                   |
| $G_w$           | free energy of water                                                         |
| $h$             | relative vapor pressure                                                      |
| $\bar{h}$       | partial specific enthalpy                                                    |
| $H$             | relative humidity                                                            |
| $H^\circ$       | enthalpy of water at absolute zero temperature                               |
| $H_s$           | enthalpy of sorbed water                                                     |
| $H_v$           | enthalpy of water vapor                                                      |
| $H_w$           | enthalpy of water                                                            |
| $\Delta H_o$    | molar heat of vaporization of liquid water                                   |
| $\Delta H_{pc}$ | sum of enthalpy changes for phase transitions occurring<br>between 0 and T°K |
| $\Delta H_s$    | differential molar heat of sorption                                          |
| $\Delta H_v$    | molar heat of vaporization of sorbed water                                   |

|                          |                                                                                       |
|--------------------------|---------------------------------------------------------------------------------------|
| $J$                      | flux or rate of transfer per unit area                                                |
| $\vec{J}_i$              | flux of component $i$ relative to barycentric motion                                  |
| $J_q$                    | total energy flux                                                                     |
| $J'_q$                   | reduced heat flux                                                                     |
| $\vec{J}_q$              | heat flux vector                                                                      |
| $\vec{J}_s$              | entropy flux vector                                                                   |
| $\nabla \cdot \vec{J}_s$ | divergence of entropy flux                                                            |
| $J_w = J'_w$             | water flux                                                                            |
| $J_w^T$                  | moisture flux due to thermal diffusion                                                |
| $K_a$                    | moisture transport coefficient based on water activity gradient                       |
| $K_b$                    | bound water conductivity coefficient                                                  |
| $K_M$                    | moisture transport coefficient based on moisture content gradient                     |
| $K_\mu$                  | moisture transport coefficient based on chemical potential gradient                   |
| $K_p$                    | moisture transport coefficient based on vapor pressure gradient $t$                   |
| $K_\pi$                  | moisture transport coefficient based on osmotic pressure gradient                     |
| $K_\phi$                 | moisture transport coefficient based on spreading pressure gradient                   |
| $K_q$                    | thermal conductivity coefficient                                                      |
| $L_{jk}$                 | phenomenological coefficient                                                          |
| $L_{qq}$                 | phenomenological coefficient related to the heat conductivity coefficient             |
| $L_{qw}$                 | coupling coefficient associated with the flow of heat due to a concentration gradient |

|                 |                                                                                                  |
|-----------------|--------------------------------------------------------------------------------------------------|
| $L_{wq}$        | coupling coefficient associated with the flow of water due to a thermal gradient                 |
| $L_{ww}$        | phenomenological coefficient related to the diffusion coefficient                                |
| $m$             | fractional moisture content                                                                      |
| $m_i$           | mass of component i                                                                              |
| $m_v$           | molecular weight of water vapor                                                                  |
| M or MC         | percent moisture content                                                                         |
| $M_r$           | moisture content at fiber saturation                                                             |
| $M^*$           | content of activated water molecules in the cell wall                                            |
| $n$             | dimensionless exponent relating spreading pressure to vapor pressure                             |
| $n_b$           | flux of bound water                                                                              |
| $n_v$           | flux of water vapor through the air spaces in wood                                               |
| $N_A$           | molar flux of water vapor relative to stationary coordinates in a mixture of water vapor and air |
| $p$             | vapor pressure of sorbed water                                                                   |
| $p_o$           | vapor pressure of water                                                                          |
| $\frac{p}{p_t}$ | mole fraction of water vapor in air                                                              |
| $P$             | static pressure                                                                                  |
| $dq_{1o}$       | heat supplied to phase 1 from the outside                                                        |
| $dq_{11}$       | heat received by phase 1 from phase 2                                                            |

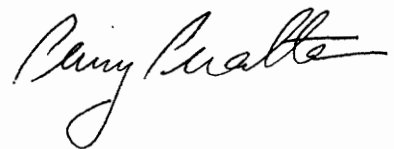
|                 |                                                                                         |
|-----------------|-----------------------------------------------------------------------------------------|
| $Q^*$           | heat of transfer                                                                        |
| $Q_2$           | empirical transfer quantity                                                             |
| $R$             | gas constant                                                                            |
| $s$             | specific entropy                                                                        |
| $\bar{s}$       | partial specific entropy                                                                |
| $s_v$           | molar entropy of water vapor                                                            |
| $S^0$           | entropy of water at absolute zero temperature                                           |
| $S_s$           | entropy of sorbed water                                                                 |
| $S_T$           | Soret coefficient                                                                       |
| $dS$            | entropy change for a system                                                             |
| $d_s S$         | change in entropy due to the interaction of the system<br>with the surrounding          |
| $d_i S$         | change in entropy due to entropy production inside the system                           |
| $\Delta S_{pc}$ | sum of entropy changes for all phase transitions occurring<br>between 0 and $T^\circ K$ |
| $\Delta S_s$    | differential entropy of sorption                                                        |
| $t$             | time                                                                                    |
| $T$             | Kelvin temperature                                                                      |
| $u$             | specific internal energy                                                                |
| $U$             | internal energy                                                                         |
| $U^*$           | energy of transfer                                                                      |

|               |                                                                                                        |
|---------------|--------------------------------------------------------------------------------------------------------|
| $v$           | specific volume                                                                                        |
| $V$           | volume                                                                                                 |
| $x$           | space coordinate                                                                                       |
| $X_i$         | thermodynamic force                                                                                    |
| $X'_q$        | thermodynamic potential for the flow of heat                                                           |
| $X'_w$        | thermodynamic potential for the flow of water                                                          |
| $\alpha$      | attenuation factor                                                                                     |
| $\beta^*$     | transfer quantity                                                                                      |
| $\nabla$      | del or nabla operator                                                                                  |
| $\varepsilon$ | fractional void volume of wood                                                                         |
| $\mu_b$       | chemical potential of bound water molecules                                                            |
| $\mu_i$       | specific chemical potential of component i                                                             |
| $\mu_w$       | specific water potential                                                                               |
| $\mu_{wc}$    | concentration-dependent component of the specific chemical potential of water                          |
| $\Delta\mu$   | change in the molar free energy of water from the adsorbed to the liquid state                         |
| $\Delta\mu_o$ | change in the molar free energy of water from the adsorbed state extrapolated to zero moisture content |
| $\rho$        | density of a pure substance or total density of a multicomponent system                                |
| $\rho_c$      | density of the cell wall at a fractional moisture content m                                            |
| $\rho_i$      | density of component i                                                                                 |
| $\rho_w$      | density of water                                                                                       |

|             |                                                           |
|-------------|-----------------------------------------------------------|
| $\sigma$    | rate of entropy production per unit volume                |
| $\tau$      | momentum flux                                             |
| $\tau_{ij}$ | normal stress if $i = j$ , and shear stress if $i \neq j$ |
| $\phi$      | spreading pressure                                        |
| $\Phi$      | energy dissipation function                               |

## Vita

Perry Nacnac Peralta was born on May 31, 1959 in Ilocos Norte, Philippines to Hector C. Peralta and Herminia N. Nacnac. He attended the University of the Philippines at Los Banos (UPLB), receiving a Bachelor of Science in Forest Products Engineering degree in 1980, and a Master of Science degree in 1985. After serving for five years as instructor at the Department of Wood Science and Technology, UPLB, the author went to Virginia Polytechnic Institute and State University in 1986 to pursue a doctorate in Wood Science and Forest Products, concentrating in wood physics.

A handwritten signature in black ink, reading "Perry Peralta". The signature is written in a cursive style with a large, stylized 'P' and 'P'.