

# MOISTURE CONTENT-WATER POTENTIAL CHARACTERISTIC CURVES FOR RED OAK AND LOBLOLLY PINE

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## ABSTRACT

This report describes the results of a study performed to measure the water potential of loblolly pine and red oak over the full range of moisture content during desorption. The matric potential as measured by the tension plate, pressure plate, and pressure membrane methods exhibited good continuity with the total water potential as measured by the isopiestic method. This not only proves the validity of the water potential measurements but also shows that the osmotic potential component of the total water potential is negligible at low moisture content. The characteristic curves allow characterization of water in wood at high moisture contents and thus avoid the need to extrapolate sorption isotherm beyond the 98% relative humidity level as was done in previous sorption studies. The results also show that, at a given water potential, the moisture contents of both species decrease with a rise in temperature. This may be due partly to the temperature dependence of the surface tension of water and to the fact that entrapped air expands when heated, thus displacing water out of the capillaries. The temperature dependence of water potential was used to calculate the enthalpy change, the free energy change, and the product of absolute temperature and entropy change associated with moisture sorption. The data show that the logarithms of these thermodynamic properties vary linearly with moisture content in the hygroscopic range but are nonlinear in the capillary range.

*Keywords:* Sorption, water potential, characteristic curve, isotherm, free energy, enthalpy, entropy, red oak, loblolly pine.

## INTRODUCTION

The water present in wood affects many of its properties. In most instances, the interaction between wood and water gives rise to the numerous practical problems associated with the processing and utilization of wood. For these reasons, the characterization of moisture in wood is of fundamental importance. While moisture content proves to be a very convenient parameter for expressing the amount of

water contained in a piece of wood, it fails to describe the energy state of water in the material. A more fundamental property that describes such state is obtained from basic thermodynamic principles. This property is called the water potential.

The concept of water energy in porous media finds its origin in Buckingham's work on soils (Buckingham 1907). He introduced the idea that flow of water in soil results from a difference in capillary potential between two points in the soil. This mechanical approach, however, failed to relate capillary potential to

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the energy state of water and thus prevented the approach from effectively analyzing the various transport phenomena associated with soil solutions. Buckingham realized that a rigorous treatment of the subject, with no restrictions imposed on either the water content or the soluble salt content of the soil, would have to use thermodynamic reasoning. Various proposals were forwarded in an attempt to satisfy this demand (Schofield 1935; Veihmeyer and Edlefsen 1937; Wadleigh and Ayers 1945; Day 1947). Although they came under different names, these proposals are all expressions of the chemical potential of water in soil relative to that of free water at the same temperature. This concept proved to be of immeasurable value in the scientific study of water in soils and in other porous media. Before Buckingham's work, the only way to describe water in materials was simply as the 'water content.' With the introduction of the water potential concept and using the formalisms of thermodynamics, water in a medium can now be characterized in terms of its energy state (Iwata et al. 1995).

To fully describe the state of a system, classical thermodynamics provides a mathematical expression relating a thermodynamic potential with the independent variables of state. If temperature  $T$ , pressure  $P$ , and the set of component masses  $\{m_i\}$  are the chosen independent variables, the thermodynamic potential is called the Gibbs free energy  $G$ . In differential form, the Gibbs free energy is given by the expression

$$dG = -SdT + VdP + \sum_i \mu_i dm_i \quad (1)$$

where  $S$  is the entropy,  $V$  the volume, and  $\mu_i$  the chemical potential of the  $i$ th component. If water is one of the  $i$  components, the above equation becomes

$$dG = -SdT + VdP + \mu_w dm_w + \sum_j \mu_j dm_j \quad (2)$$

Since the chemical potential or partial specific free energy of water  $\mu_w (= \partial G / \partial m_w)$  represents one of the equations of state that correspond to the Gibbs free energy, then it is also dependent on the variables  $T$ ,  $P$ , and  $\{m_i\}$ :

$$d\mu_w = \frac{\partial \mu_w}{\partial T} dT + \frac{\partial \mu_w}{\partial P} dP + \frac{\partial \mu_w}{\partial m_w} dm_w + \sum_j \frac{\partial \mu_w}{\partial m_j} dm_j \quad (3)$$

This total differential equation could then be integrated from selected standard conditions (designated by superscript  $o$ ) resulting in the following equation:

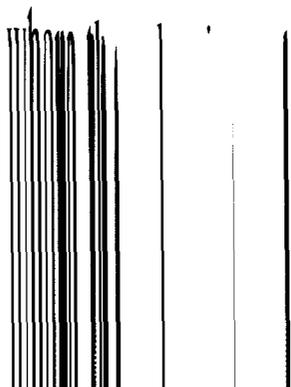
$$\begin{aligned} \mu_w - \mu_w^o = & - \int_{T^o}^T \bar{S}_w dT + \int_{P^o}^P \bar{V}_w dP \\ & + \int_{m_w^o}^{m_w} \frac{\partial \mu_w}{\partial m_w} dm_w \\ & + \sum \int_{m_j^o}^{m_j} \frac{\partial \mu_w}{\partial m_j} dm_j \end{aligned} \quad (4)$$

where  $\bar{S}_w = \partial \mu_w / \partial T = \partial(\partial G / \partial m_w) / \partial T = \partial(\partial G / \partial T) / \partial m_w = \partial S / \partial m_w$  is the partial specific entropy of water,  $J \text{ kg}^{-1} \text{ K}^{-1}$ ; and  $\bar{V}_w = \partial \mu_w / \partial P = \partial(\partial G / \partial m_w) / \partial P = \partial(\partial G / \partial P) / \partial m_w = \partial V / \partial m_w$  is the partial specific volume of water,  $J \text{ kg}^{-1} \text{ Pa}^{-1}$  or  $\text{m}^3 \text{ kg}^{-1}$ . The quantity  $(\mu_w - \mu_w^o)$  is called the water potential (denoted by  $\psi$ ) and has the units of  $J \text{ kg}^{-1}$ ; while the terms on the right-hand side of Eq. (4) are the temperature  $\psi_T$ , pneumatic  $\psi_P$ , matric  $\psi_m$ , and osmotic  $\psi_o$  components, respectively. Introducing these notations into the integrated form of the chemical potential Eq. (4) yields

$$\psi = \psi_T + \psi_P + \psi_m + \psi_o \quad (5)$$

In soil physics, the standard reference state generally used is a hypothetical pool of pure free water at atmospheric pressure, at a given elevation, and at the same temperature as that of the water in the soil; hence the temperature

potential disappears from Eq. (5). The new



scribes the combined effect of the capillary and sorptive forces arising from the presence of the solid matrix; and the osmotic potential takes into account the presence of solutes in the water (Fortin 1979). While the above equation for water potential was derived using only temperature, pressure, and the set of component masses as the chosen independent variables of state, other parameters may be included to arrive at a more general equation with component terms dealing with gravitational potential, surface interaction potential, electrical potential, etc. (Iwata et al. 1995). However, under normal service conditions of wood, the use of T, P, and  $\{m_i\}$  is sufficient.

Though originally developed in soil science, the water potential concept has found wide acceptance for the analysis of the interaction between water and other porous materials and, therefore, should also find broad applications in wood research and utilization. It is expected to shed light on many issues in wood-moisture relationship which, to date, have not been resolved by more traditional approaches. Specifically, it should provide insight into the fundamental driving force for the transport of water in wood both below and above the fiber saturation point; eliminate ambiguities regarding the arbitrary assignment of the fiber saturation point; clarify the arbitrary categorizations that prevail in wood science and that purport to classify different forms of wood moisture (free water, capillary water, hygroscopic water); and enable wood scientists to compare quantitatively, with the same scale, the state of water in various types of wood (i.e., untreated, chemically modified, composites, etc.).

Due to a limited number of studies, not much is known about water potential as far as wood is concerned. Though some studies were performed in the 1960s (Penner 1963; Stone and Scallan 1967), most of the information on this parameter as it relates to solid wood came out only recently from studies conducted in Canada (Fortin 1979; Cloutier and Fortin 1991; Cloutier et al. 1992; Cloutier and Fortin 1993, 1994; Cloutier et al. 1995; Tremblay et al. 1996). Much remains to be learned about

this parameter: how it varies relative to such variables as species, temperature, and moisture content; how it relates to the transport characteristics of wood; and how it applies to the various fields of wood technology. This paper covers the more fundamental scope of the former and thus reports the results of a study (Zhang 1997) that investigated the effects of moisture content and temperature on the water potential of red oak (*Quercus* spp.) and loblolly pine (*Pinus taeda*).

#### MATERIALS AND METHODS

This study focused on the determination of the water potential of red oak and loblolly pine during moisture desorption using the tension-plate, pressure-plate, and pressure-membrane methods. These methods were supplemented by equilibration over saturated salt solutions (isopiestic method) so that a characteristic curve covering the entire moisture content range was obtained. The measurements were performed at 30° and 55°C. All equilibrations were carried out inside a chamber whose temperature was maintained to within  $\pm 1.0^\circ\text{C}$  of the set temperature.

Green red oak and loblolly pine boards were purchased from local sawmills and stored, while wrapped in plastic, in a room maintained at 0°C until ready for processing. The average specific gravity (based on oven-dry weight and green volume) of the red oak and loblolly pine samples was 0.51 and 0.45, respectively. The specimens used for the isopiestic method were cut to 50 mm (R)  $\times$  50 mm (T)  $\times$  5 mm (L), while the specimens for the tension-plate, pressure-plate, and pressure-membrane methods were cut to 25 mm (R)  $\times$  25-mm (T)  $\times$  10 mm (L). Larger samples were used in the former so as to increase weight measurement sensitivity. The smaller sample size in the latter was a compromise between weight measurement sensitivity and the time required for the samples to reach moisture equilibrium. Each experiment was performed using four replicates of each species. The samples used in the tension-plate,

pressure-plate, and pressure-membrane experiments were saturated in distilled water using several cycles of vacuum and atmospheric pressure maintained for 12 h each. Complete saturation was assumed to have been achieved when no air bubbles were observed during subsequent vacuum application. The moisture contents of saturated loblolly pine and red oak specimens were approximately 160% and 120%, respectively.

The tension plate apparatus used in this study was similar to the device constructed by Cloutier and Fortin (1991). It consisted of a tension cell, a hanging water column, and a constant water level outflow device. The bottom of the tension cell is composed of a plexiglas base with holes for water outflow, a plastic screen separating a saturated filter paper from the base, and a layer of saturated clay on top of the filter paper. The saturated sample is placed in contact with the clay layer. By varying the elevation of the constant water level outflow device relative to the sample, various water potential values above  $-10 \text{ J kg}^{-1}$  could be attained.

For the pressure plate experiments, the procedure described in the American Society for Testing and Materials (ASTM) Standard D 2325-68 (ASTM 1998a) for soil was adapted to wood. A saturated porous-disk plate with a bubbling pressure of 1,500 kPa was covered on one face with a saturated clay layer about 2 mm thick to ensure good hydraulic contact between the specimen and the porous plate. With the wet samples sitting on its top, the porous plate was installed in a pressure chamber. The bottom of the plate was in contact with water enclosed in a rubber receptacle that is connected through a drain tube to the chamber outlet. After hermetically sealing the chamber, a desired air pressure was admitted into the chamber expelling some of the water from the wet assembly through the chamber outlet into a graduated receiver. Once water outflow had ceased (indicating equilibrium state), the pressure reading was taken. A clamp was placed on the outflow tube to prevent water backflow into the specimen. The

pressure inside the chamber was then released, the chamber opened, and the sample removed for weighing. The air pressure maintained inside the chamber was converted to its matric potential  $\psi_m$  equivalent using the equation:

$$\psi_m = -\bar{v}_m P_m \quad (6)$$

where  $\bar{v}_m$  = specific volume of water,  $\text{m}^3 \text{ kg}^{-1}$ ; and  $P_m$  = pressure inside the chamber,  $\text{N m}^{-2}$ . The process was repeated at successively higher pressure levels until a matric potential of  $-200 \text{ J kg}^{-1}$  was attained.

At lower matric potential values, the pressure-membrane apparatus was employed as described in ASTM Standard D 3152-72 (ASTM 1998b), which is similar to that of the pressure-plate system; the only difference being the replacement of the pressure plate with a saturated porous membrane resting on a screen disk. The porous membrane is made of cellulose acetate with a bubbling pressure of 10,000 kPa. The pressure inside the chamber was increased stepwise to obtain matric potential values ranging from  $-400 \text{ J kg}^{-1}$  to  $-4,000 \text{ J kg}^{-1}$ .

The isopiestic method involved placing samples in a chamber of constant relative humidity. At equilibrium, it is assumed that the potential of water in the sample is the same as that of the water in the solution and in the air. Thus, by knowing the relative humidity of the air, the total water potential  $\psi$  can be calculated as follows:

$$\psi = \frac{RT}{M_w} \ln\left(\frac{H}{100}\right) \quad (7)$$

where  $R$  = universal gas constant,  $\text{J mol}^{-1} \text{ K}^{-1}$ ;  $T$  = absolute temperature,  $\text{K}$ ;  $M_w$  = molecular weight of water,  $\text{kg mol}^{-1}$ ; and  $H$  = relative humidity,  $\%$ . In this study, four samples of each species were enclosed in a desiccator whose atmosphere was maintained at a constant relative humidity by a saturated salt solution (Peralta 1995). Once equilibrium was attained, the samples were weighed to obtain their moisture contents. Saturated aqueous solutions of different salts were prepared to ob-

TABLE 1. Water potential and moisture content data for loblolly pine and red oak at 30°C.

$\psi$ (J kg <sup>-1</sup> )	H (%)	Method <sup>a</sup>	Loblolly Pine		Red Oak	
			MC (%)	SD <sup>b</sup>	MC (%)	SD <sup>b</sup>
-5	99.996	TP	159.20	3.19	**	**
-20	99.986	PP	**	**	99.50	0.76
-26	99.981	PP	110.10	7.63	98.62	0.57
-50	99.964	PP	49.58	4.57	**	**
-400	99.715	PM	32.01	0.79	79.69	1.87
-3,200	97.741	PM	28.76	0.21	65.99	4.31
-4,265	97.000	K <sub>2</sub> SO <sub>4</sub> <sup>c</sup>	28.13	0.25	62.32	1.28
-11,200	92.313	KNO <sub>3</sub> <sup>c</sup>	24.21	1.10	41.04	0.38
-25,000	83.649	KCl <sup>c</sup>	20.61	0.19	21.40	0.16
-40,100	75.098	NaCl <sup>c</sup>	16.99	0.29	16.14	0.02
-81,100	56.036	NaBr <sup>c</sup>	12.16	0.11	11.55	0.07
-117,600	43.178	K <sub>2</sub> CO <sub>3</sub> <sup>c</sup>	10.03	0.11	9.44	0.06
-157,600	32.449	Mg <sub>2</sub> Cl <sup>c</sup>	8.61	0.09	7.85	0.03
-214,500	21.614	CH <sub>3</sub> COOK <sup>c</sup>	6.68	0.06	6.03	0.05
-305,500	11.285	LiCl <sup>c</sup>	4.40	0.05	3.84	0.09

<sup>a</sup> TP = tension plate; PP = pressure plate; PM = pressure membrane.

<sup>b</sup> SD = standard deviation based on 4 specimens.

<sup>c</sup> Saturated aqueous solution of the listed chemical.

tain water potentials ranging from -4,000 to -350,000 J kg<sup>-1</sup>. The salts were all certified ACS, meaning that they met or exceeded the latest American Chemical Society specifications. The salts that were used include potassium sulfate, potassium nitrite, potassium

chloride, sodium nitrite, sodium bromide, potassium carbonate, magnesium chloride, potassium acetate, and lithium chloride. The relative humidity and water potential that correspond to each of these salts are shown in Tables 1 and 2.

TABLE 2. Water potential and moisture content data for loblolly pine and red oak at 55°C.

$\psi$ (J kg <sup>-1</sup> )	H (%)	Method <sup>a</sup>	Loblolly Pine		Red Oak	
			MC (%)	SD <sup>b</sup>	MC (%)	SD <sup>b</sup>
-5	99.997	TP	158.50	3.28	**	**
-11	99.993	PP	131.75	8.76	91.00	2.21
-20	99.987	PP	87.73	9.17	**	**
-25	99.984	PP	59.05	11.04	90.05	1.44
-50	99.967	PP	**	**	86.07	3.70
-103	99.932	PP	32.84	3.10	**	**
-393	99.741	PM	29.59	0.86	**	**
-896	99.411	PM	**	**	70.64	4.79
-2,000	98.689	PM	**	**	59.94	3.29
-3,200	97.911	PM	25.66	0.41	50.63	1.23
-6,950	95.518	K <sub>2</sub> SO <sub>4</sub> <sup>c</sup>	23.40	2.37	26.50	0.99
-29,100	82.532	KNO <sub>3</sub> <sup>c</sup>	16.67	0.27	15.76	0.13
-32,500	80.701	KCl <sup>c</sup>	15.16	0.10	**	**
-44,800	74.411	NaCl <sup>c</sup>	12.75	0.19	12.27	0.12
-104,600	50.153	NaBr <sup>c</sup>	8.13	0.11	7.93	0.15
-182,800	29.939	CH <sub>3</sub> COOK <sup>c</sup>	5.82	0.04	5.52	0.07
-334,100	11.034	LiCl <sup>c</sup>	3.00	0.02	2.74	0.09

<sup>a</sup> TP = tension plate; PP = pressure plate; PM = pressure membrane.

<sup>b</sup> SD = standard deviation based on 4 specimens.

<sup>c</sup> Saturated aqueous solution of the listed chemical.

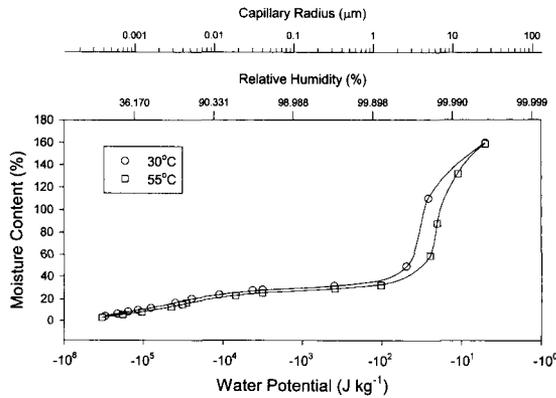


FIG. 1. Moisture content—water potential boundary desorption characteristic curve for loblolly pine at 30° and 55°C.

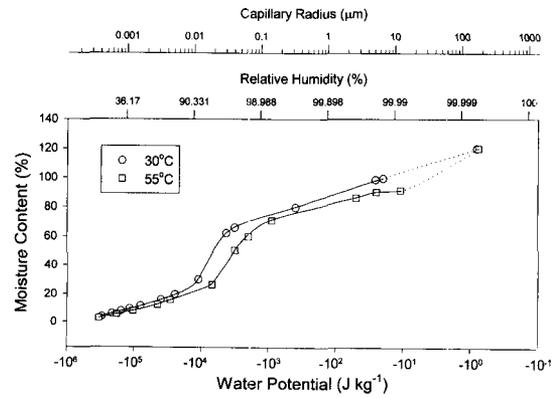


FIG. 2. Moisture content—water potential boundary desorption characteristic curve for red oak at 30° and 55°C.

#### RESULTS AND DISCUSSION

The moisture contents of loblolly pine and red oak at different water potentials are given in Tables 1 and 2 for the experimental temperatures of 30°C and 55°C, respectively. The data are also plotted in Figs. 1 and 2. It is apparent from the tables and figures that there is a good continuity in the data, especially that for loblolly pine, as the method of water potential measurement changes from the pressure plate/membrane method to the isopiestic method. This not only verifies the validity of the pressure plate/membrane approach to water potential measurement but clearly shows that at constant temperature and atmospheric pressure, matric potential is the primary component of the total water potential in wood, especially at low moisture contents.

The graph relating moisture content and water potential (Figs. 1 and 2) is called the characteristic curve. This approach to presenting water in wood has a distinct advantage over the traditional sorption isotherm in that it shows the full range of moisture content that wood can attain. In constructing a sorption isotherm, that part of the curve between 98% and 100% relative humidity is usually extrapolated from lower humidities, resulting in a final moisture content of about 30% at the 100% relative humidity mark. This is done mainly because it is practically impossible to

stabilize relative humidities above 98% with the use of the traditional experimental method (Griffin 1977). Such approach is very misleading since it gives the impression that: (a) no significant change in the shape of the isotherm could occur over such high relative humidities; and (b) wood in equilibrium with 100% relative humidity would have a moisture content of only about 30%. Theoretically, however, equilibration at 100% relative humidity should cause the wood to attain full saturation (Siau 1984), which for many species corresponds to moisture contents higher than 150%. This means that a dramatic change in the shape of the sorption isotherm must occur at high relative humidities. Such is demonstrated in Figs. 1 and 2. Over a water potential range of  $-26 \text{ J kg}^{-1}$  to  $-3200 \text{ J kg}^{-1}$  (or the equivalent of relative humidity change from 99.98% to 98%), the equilibrium moisture content of red oak went down from 99% to 66% at 30°C and from 90% to 51% at 55°C. The reductions in the moisture content of loblolly pine over the same range of water potential were 110% to 29% and 59% to 26% at 30°C and 55°C, respectively. Similarly, abrupt changes in moisture content over a narrow range of water potentials above  $-3000 \text{ J kg}^{-1}$  were also observed by other investigators (Penner 1963; Stone and Scallan 1967; Griffin

1977; Fortin 1979; Cloutier and Fortin 1991; Cloutier et al. 1995; Tremblay et al. 1996).

In presenting the sorption isotherm for wood, linear axes are often used resulting in a sigmoid-shaped curve. The characteristic curve, on the other hand, uses a logarithmic scale on the x-axis, thereby spreading out the region between  $H = 98$  and  $100\%$ . It is over this range of relative humidities where free water exists in the gross anatomical structure of wood, making the water potential approach important in our understanding of the phenomena of capillary water movement, cell collapse, pit aspiration, and decay susceptibility (Siau 1995). To better understand why the traditional sorption isotherm approach to wood-water interaction is limited to the hygroscopic range, the data in Tables 1 and 2 are also presented in Figs. 1 and 2 using capillary radius  $r$  as independent variable. The values for this variable were obtained using the following equation, which is a combination of Eq. (6) and the Laplace capillary pressure equation:

$$r = -\bar{v}_m \frac{2\sigma}{\psi_m} \quad (8)$$

where  $\sigma$  = surface tension of water =  $0.0712 \text{ N m}^{-1}$  at  $30^\circ\text{C}$ . It is apparent from the equation and from Figs. 1 and 2 that a water potential of  $-3000 \text{ J kg}^{-1}$  (or  $H = 98\%$ ) corresponds to a capillary radius of approximately  $0.05 \text{ }\mu\text{m}$ . Hence when wood is subjected to the highest relative humidity attainable during the traditional isopiestic experiments, all capillaries with a radius less than  $0.05 \text{ }\mu\text{m}$  are filled with water while larger capillaries are devoid of water. Since  $0.05 \text{ }\mu\text{m}$  corresponds to the size of pit membrane openings, this means that pit chambers and cell lumina, including those of tracheids, vessels, and fibers, would be empty at  $98\%$  relative humidity. Any free water present in the wood at this condition will be found mainly in the pit openings. But considering the small volume of voids ( $0.05 \text{ }\mu\text{m}$  radius and  $0.2 \text{ }\mu\text{m}$  thick) represented by the pit openings, the contribution of this free water to the wood moisture content is negligible (Siau 1984).

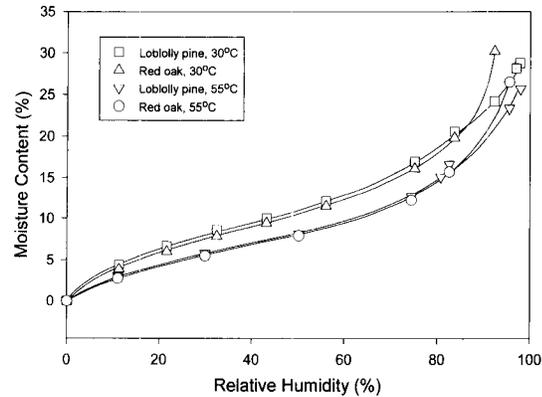


FIG. 3. Desorption isotherm of loblolly pine and red oak at  $30^\circ$  and  $55^\circ\text{C}$ .

It is apparent from Eqs. (2) and (4) that the water potential is equal to the negative of the change in free energy associated with liquid water intake. Nelson (1983), in deriving an empirical model for moisture sorption by cellulosic materials, observed a linear relationship between moisture content and the logarithm of the differential free energy of bound water sorption  $\Delta G_s$ . Nelson's observation is supported by the data in Figs. 1 and 2 in that the characteristic curve is approximately linear at moisture contents less than  $30\%$ . At high moisture contents, however, the curve rises sharply, making Nelson's model inadequate to describe the relationship. The appropriate function to use at high moisture content levels is the differential free energy of capillary sorption  $\Delta G_c$ . A relationship between moisture content and  $\Delta G_c$  has to be derived to adequately model the portion of the sorption isotherm or of the characteristic curve beyond the hygroscopic range. Based on the Kelvin equation, the model will have to be in the form of a cumulative distribution function, with the parameters varying from species to species depending upon the relative distribution of macro pore sizes. The large species dependence of the characteristic curve at high moisture contents is in contrast to that for moisture sorption in the hygroscopic range. Since the structure and hygroscopicity of the cell wall are more or less the same from species to species, the

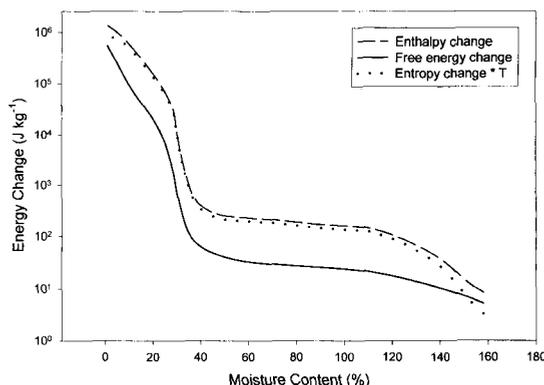


FIG. 4. Free energy change, enthalpy change, and product of absolute temperature and entropy change associated with moisture sorption by loblolly pine.

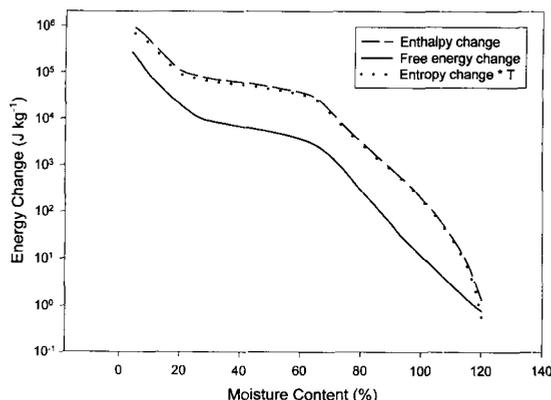


FIG. 5. Free energy change, enthalpy change, and product of absolute temperature and entropy change associated with moisture sorption by red oak.

sigmoid shape of the sorption isotherm is almost universal. Figure 3, for instance, shows that the sorption isotherm of loblolly pine almost coincides with, and is of the same shape as, that of red oak. But above 30% MC, the shapes of the characteristic curves (Figs. 1 and 2) of the two species are markedly different.

The dependence of the characteristic curve on temperature is evident in Figs. 1 and 2. At a particular moisture content, the water potential at 55°C is always higher than that at 30°C. The temperature-dependence of the free energy of sorption is well documented in the literature (Stamm and Loughborough 1935; Kelsey and Clarke 1956; Nelson 1983). This energy is associated with the work needed to swell the wood structure during adsorption and is reversible since the energy can be restored to the vapor when it is compressed from the given vapor pressure to the saturated vapor pressure. At moisture contents above the fiber saturation point, Cloutier and Fortin (1991) considered the effect of temperature on the surface tension of water to explain the temperature dependence of water potential. When they compared the experimental temperature coefficient ( $\partial\psi/\partial T$ ) with the theoretical coefficient that takes surface tension into consideration, the former was consistently higher than the latter. The same was observed in this study, with the experimental quantity about an order of magnitude higher than the theoretical

value. In soil science, this discrepancy was explained in terms of the presence of trapped air in the samples and of surface-active contaminants at the air-water interface (Chahal 1965; Saha and Tripathi 1981).

The characteristic curves at 30°C and 55°C were used to calculate the differential molar enthalpy of bound water sorption  $\Delta H_s$  at  $\bar{T} = (30^\circ\text{C} + 55^\circ\text{C})/2 = 42.5^\circ\text{C} = 315.65\text{ K}$ . The calculation was carried out by applying the integral form of the Clausius-Clapeyron equation given below:

$$\Delta H_s = RT_1 T_2 \left[ \frac{\ln\left(\frac{h_2}{h_1}\right)}{T_2 - T_1} \right]_M \quad (9)$$

where  $R$  is the universal gas constant, and  $h_1$  and  $h_2$  are the relative vapor pressures at temperatures  $T_1$  and  $T_2$ , respectively, at a constant moisture content. The same equation may be used to calculate the differential molar enthalpy of capillary sorption  $\Delta H_c$ , thereby providing a picture of the variation of the change in the energy of sorption over the full moisture content range. As Siau (1995) stated: "it appears that the heat of capillary condensation provides essentially a continuous extension of the heat of (bound water) sorption into the capillary range." Figures 4 and 5 show how

the differential enthalpy of sorption varies with moisture content. Also shown is the curve for the entropy term associated with sorption  $T\Delta S$ , which was obtained by subtraction of the free energy change from the enthalpy change:  $T\Delta S = \Delta H - \Delta G$ . The value of the enthalpy change when the curve was extrapolated to zero moisture content was approximately  $1.45 \times 10^6 \text{ J kg}^{-1}$  for red oak and  $1.90 \times 10^6 \text{ J kg}^{-1}$  for loblolly pine. These values are close to that ( $1.2 \times 10^6 \text{ J kg}^{-1}$ ) reported by Stamm (1964) for a number of cellulosic materials and are within the range of the bonding energies associated with hydrogen bonds. Just as in the free energy change, the linear relationship between moisture content and the logarithm of enthalpy change that was observed by many researchers for moisture contents in the hygroscopic range does not apply above the fiber saturation point. The enthalpy change at high moisture contents, though small, is finite and represents the heat released when water is taken up in the wood capillaries. This much energy is thus needed to raise the energy level of capillary water to that of ordinary water. It is also evident in Figs. 4 and 5 that entropy change accompanies the sorption of both bound and capillary moisture by wood. At first, other investigators thought that the entropy change is negligible, probably within the range of experimental error. Subsequent studies have shown and this study has demonstrated that the values of free energy change are lower than the corresponding values of enthalpy change, indicating that a definite entropy reduction accompanies the sorption of moisture by wood.

#### CONCLUSIONS

1. The tension-plate, pressure-plate, and pressure-membrane methods supplement the isopiestic method in obtaining the water potential for wood over the full range of moisture content.
2. Water potential measurement methods allow characterization of water in wood above

the fiber saturation point without resorting to extrapolation of the sorption isotherm.

3. The logarithms of free energy change, of enthalpy change, and of the product of absolute temperature and entropy change are approximately linear in the hygroscopic range but are nonlinear in the capillary range.

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