

WATER VAPOR SORPTION RATES BY WOOD CELL WALLS¹

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ABSTRACT

Rates of water vapor adsorption and desorption by the cell walls of yellow poplar (*Liriodendron tulipifera* L.) and white oak (*Quercus alba* L.) were measured at 40 C in the absence of air. The rates were much lower than would be expected for Fickian diffusion of bound water. Species had little effect, but desorption was faster than adsorption, especially at higher humidities. The shapes of the rate versus remaining moisture content curves were also decidedly non-Fickian in nature. Heat transfer to the specimen was found to play an important role. An empirical equation was found to fit the data with a high degree of accuracy, but only limited success was achieved in relating the constants of the equation to the corresponding relative humidity levels.

INTRODUCTION

The objective of this study was to examine the water vapor sorption kinetics of small wood specimens in the absence of air. Fick's laws of diffusion have been generally used to describe the movement of moisture through wood, but it has recently been reported that they do not adequately describe moisture movement in small wood specimens (Christensen 1960; Christensen and Kelsey 1959; Prichananda 1966). A suggested explanation for this non-Fickian behavior has been stress relaxation of the structural wood matrix (Christensen and Kelsey 1959). Temperature change, as a result of the heat generated on adsorption and consumed on desorption, has not been adequately examined in studies on the wood-water interaction. The work reported here was conducted to determine what factor or factors control moisture movement through the cell walls of wood specimens, with particular emphasis on the heat transfer aspects of the problem.

Fick's first and second laws of diffusion (Crank 1956) have usually been used in

drying studies on wood (Comstock 1963; Prichananda 1966; Stamm 1959, 1960). The data from wood-moisture studies have usually been presented by plotting the fraction of the total moisture content change (E) for a given relative humidity step versus the square root of time (t) from the beginning of drying. Rogers (1965) has pointed out criteria which are indicative of Fickian diffusion. They are:

1. E versus $(t)^{\frac{1}{2}}$ plots are linear for 50% or more of the total change for each adsorption or desorption step.
2. The curve is always concave to the time axis; *i.e.*, there is no inflection point.
3. When data for specimens of different thicknesses undergoing the same adsorption or desorption step are plotted as E versus $(t/x^2)^{\frac{1}{2}}$, the curves are superimposed (x is the specimen thickness in the direction of diffusion).
4. When the diffusion coefficient increases with concentration, desorption is always slower than adsorption.
5. The concentration of adsorbate at the surface instantaneously attains the equilibrium value.

Non-Fickian diffusion behavior has been frequently found for adsorption of organic vapors by polymers and for water adsorp-

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tion by hydrophilic polymers such as cotton and wool (Downes and Mackay 1958; Long and Richman 1960; Newns 1956; Yokota 1959). Non-Fickian diffusion is especially evident with penetrants which swell the polymer. Rogers (1965) has classified non-Fickian adsorption and desorption curves into three distinct types: (1) pseudo-Fickian, where the E versus $(t/x^2)^{1/2}$ plot resembles Fickian diffusion but the approach to equilibrium is retarded and the initial linear portion is reduced; (2) two-stage, in which the E versus $(t/x^2)^{1/2}$ plot exhibits an initial rapid portion followed by a much slower rate to equilibrium; and (3) sigmoid, where the E versus $(t/x^2)^{1/2}$ plot is sigmoid.

Christensen and Kelsey (1959) found the rate of water vapor adsorption in the absence of air, by wood sections 20 micrometers (μm) and 1 millimeter (mm) thick, decreased as the moisture content increased. The rate of adsorption was also independent of thickness, indicating non-Fickian diffusion. Prichananda (1966) also found non-Fickian behavior for small specimens, but as the specimen size increased, Fickian diffusion was evident.

Adsorption of water vapor by wood is highly exothermic, since not only is the heat of condensation for water vapor released, but there is also a large differential heat of adsorption, especially at low moisture contents. The heat of adsorption of water vapor by wood is the sum of the differential heat of adsorption and the heat of condensation of water vapor. The differential heat of adsorption decreases as the moisture content increases and approaches zero at the fiber saturation point.

The heat evolved as a result of water vapor adsorption by wood has to be rapidly removed from the material to maintain isothermal conditions. An increase in the temperature of the sorbing material will change the environmental vapor pressure gradient, since the vapor pressure of the cell-wall water is strongly temperature dependent. To our knowledge, for small specimens in vacuum there has been but one attempt to study the temperature change

in wood as a result of water vapor adsorption and no attempt to study the temperature change as the result of desorption. Christensen and Kelsey (1959) reported a temperature increase of 13 C for an adsorption step of 0–14% relative humidity, for small wood sections sorbing water vapor in the absence of air. The heat accounting for this temperature rise was dissipated rapidly and the temperature returned to within 0.5 C of ambient within approximately 20 minutes. However, the time necessary to reach sorption equilibrium was approximately the same as the time necessary for thermal equilibrium. For adsorption steps at higher relative humidities, the temperature of the wood returned to ambient much quicker than sorption equilibrium was approached. Therefore, they discounted the possibility that temperature effects could account for any of the non-Fickian diffusion behavior they observed, with the possible exception of adsorption from the dry condition.

King and Cassie (1940), from their study of water adsorption by wool fibers, concluded that their moisture content versus time curves were due to heat dissipation and were independent of the rate of moisture diffusion in the fibers. They believed that the time necessary for moisture equilibrium in the fibers, after a change in the environmental conditions, was negligible compared with the time required for dissipation of the generated heat.

EXPERIMENTAL

A high vacuum glass apparatus, similar to that of Spalt (1957), was designed to be completely immersed in a constant temperature water bath. Twelve sorption tubes approximately 50 cm long were attached to a manifold by ground-glass joints. Wood specimens were suspended from quartz helices and placed in nine of these tubes for weight change observation. In the remaining three tubes, a small calibrated thermistor was placed within the specimens for measurement of the wood temperature. A mercury manometer for vapor pressure measurements was also attached to the

manifold. The vapor pressure within the apparatus was controlled by a series of saturated salt solutions which could be changed without lowering the water in the water bath. Circulation of the salt solution was accomplished by a magnetic stirrer. The water bath was heated with a thermistor-controlled intermittent 1000-watt immersible heater. Water circulation was accomplished by a three-inch propeller driven by an electric motor. The temperature cycle, from the time the heaters turned off until they began to heat again, was less than 0.2 C at 40 C.

Boiled slices of yellow poplar sapwood (*Liriodendron tulipifera* L.) and white oak heartwood (*Quercus alba* L.) 1 mm in the longitudinal direction (less than average fiber length), and approximately 2.5 cm by 1.0 cm in the radial and tangential directions, respectively, were closely matched within species. It was desired to have approximately 0.5 g of oven-dry wood in each sorption tube and to have two levels of surface area to weight ratios. Therefore, in approximately half of the sorption tubes, the slices were placed in a one-bundle form with the remaining sorption tubes containing the same weight of wood, but in a two-bundle form. Adjacent slices in the bundles were in intimate contact, but not close enough to hinder the movement of water vapor molecules. About 4.5 slices gave the desired weight for the poplar and about 3.5 slices for the oak.

Table 1 contains the species, specimen form, and relative humidity steps for each sorption tube and, for each of the first nine tubes, the resultant equilibrium moisture content and the time for one-half of the moisture content change to occur. For each of the last three tubes, the thermistor-measured maximum temperature change is shown. Desorption steps were over virtually the same relative humidity changes as adsorption, with the exception of desorption to 63% relative humidity. The magnetic stirrer failed during this step, resulting in a relative humidity above the saturated salt solution of 66%.

The experimental design thus provided

for comparison between species and between adsorption and desorption for various relative humidity changes and for evaluation of heat transfer effects through the comparison of the one- and two-bundle forms. Further heat transfer data were provided by thermistor-measured temperature data on specimens closely matched to the weight-gain specimens on the helices and exposed to the same relative humidity changes.

The wood specimens were placed in the sorption tubes in the water-wet condition and dried by evacuation at room temperature to insure a reproducible dry-weight (Hergt and Christensen 1965). The water bath was then filled, the temperature was set at 40 C, and evacuation continued until the helices exhibited a constant extension, at which time the stopcocks to all sorption tubes were closed. A saturated salt solution was attached to the apparatus and, with the stopcock to the manifold closed, the air was removed from the solution by evacuation. The manifold stopcock was then re-opened and, after a period for the vapor pressure to equalize, the stopcock to a sorption tube was opened and the extension of the quartz helix, as the result of water vapor sorption by the wood, was followed with a cathetometer. Since the volume of each sorption tube was only about 2.5% of the system volume, the change in the system vapor pressure with the opening of a sorption tube was negligible. The time from the beginning of the adsorption or desorption step was recorded for each extension. When the helix extension was practically constant, this sorption tube was left open, and another sorption tube was opened to this relative humidity. All sorption tubes which were to be exposed to the same relative humidity were opened in this manner, and the helix extensions and corresponding times were recorded. When a given helix had a constant extension for at least 24 hr, the stopcock to the particular sorption tube was closed, and the vapor pressure of the system was determined with the mercury manometer.

TABLE 1. Relative humidity levels at which each specimen was successively conditioned, per cent equilibrium moisture content (EMC) attained and minutes of time ($T_{0.5}$) required for half of the moisture change to occur for specimens 1-9. For specimens 10-12, the maximum temperature change (C) is shown

Specimen ^a	Relative Humidity (per cent)													
	0	12	31	44	53	63	84	66	54	44	32	12	0	
1-YP-1	EMC	0	→	5.2	6.4	→	9.3	13.8	11.2	→	8.0	6.2	→	-0.1
	$T_{0.5}$	-	→	3.2	9.5	→	18.7	24.9	10.0	→	11.1	7.5	→	3.0
2-WO-1	EMC	0	→	5.4	6.7	→	9.6	14.2	11.9	→	8.5	6.7	→	0.0
	$T_{0.5}$	-	→	4.1	8.9	→	22.9	36.8	13.2	→	16.8	9.9	→	4.5
3-YP-2	EMC	0	→	5.1	→	7.6	9.3	13.8	11.3	9.7	→	6.2	→	0.0
	$T_{0.5}$	-	→	2.4	→	8.2	32.5	21.4	10.0	7.8	→	6.8	→	2.5
4-WO-2	EMC	0	2.2	→	→	7.6	8.8	13.4	11.1	9.8	→	→	3.0	0.1
	$T_{0.5}$	-	4.1	→	→	5.2	9.2	25.1	7.4	6.4	→	→	3.5	3.5
5-YP-1	EMC	0	2.3	→	6.6	→	→	14.5	→	→	8.0	→	3.2	0.0
	$T_{0.5}$	-	4.9	→	5.3	→	→	18.0	→	→	10.9	→	4.0	4.4
6-WO-1	EMC	0	2.1	→	6.4	→	→	14.2	→	→	7.7	→	3.0	0.0
	$T_{0.5}$	-	4.2	→	7.1	→	→	21.1	→	→	14.5	→	5.2	5.7
7-YP-2	EMC	0	2.1	→	→	→	9.5	14.1	11.4	→	→	→	2.9	0.1
	$T_{0.5}$	-	3.1	→	→	→	4.9	17.0	7.9	→	→	→	2.9	2.3
8-WO-2	EMC	0	→	4.9	→	7.3	→	13.5	→	9.4	→	6.1	→	0.0
	$T_{0.5}$	-	→	3.2	→	7.7	→	17.8	→	10.5	→	7.8	→	3.1
9-YP-2	EMC	0	→	→	→	7.8	→	14.1	→	9.5	→	→	→	0.0
	$T_{0.5}$	-	→	→	→	3.4	→	17.0	→	8.8	→	→	→	2.7
10-WO-1	°C	-	+8.7	→	+12.5	→	+4.2	+3.7	-3.6	→	-4.9	→	-13.3	-10.6
11-YP-1	°C	-	+9.3	→	+13.4	→	+4.3	+3.9	-4.1	→	-5.2	→	-13.6	-12.5
12-WO-2	°C	-	+7.0	→	→	+14.0	→	+5.3	→	-5.4	→	→	-14.3	-9.9

^a Specimen name indicates tube number (1-12), species (WO = white oak, YP = yellow poplar), and specimen form (1- or 2-bundle).

RESULTS

As previously indicated, Table 1 shows the relative humidity steps employed for each specimen in this study, the resulting equilibrium moisture contents (EMC), and the times for half of the indicated moisture changes ($E = 0.5$) to occur. Assuming Fickian diffusion, the diffusion coefficient (D) as calculated from each of the time (t) and E values, is (Stamm 1960):

$$D = \pi a^2 E^2 / 4t, \tag{1}$$

where π is 3.14 and a is the cell wall thickness (which was measured microscopically on permanently mounted slides of matched material and averaged $6.5 \mu\text{m}$ for the oak and $5.7 \mu\text{m}$ for the yellow poplar). This equation is for a slab but is a reasonably accurate approximation for this application.

Also, the cell-wall thickness in permanently mounted slides probably lies somewhere between the green and the dry dimensions of the unaltered wood, but the exact relationship is conjectural. The diffusion coefficients, which were of the order of $10^{-10} \text{ cm}^2/\text{sec}$, were about 10^{-3} smaller than the reported values for bound water diffusion (Stamm 1959, 1960; Yokota 1959). This clearly indicates, as reported by Christensen (1960), that some mechanism or combination of mechanisms, other than diffusion as a result of a concentration gradient, limits the rate of adsorption and desorption of water vapor by small wood specimens.

From the equilibrium moisture content values in Table 1, it may be seen that, for the adsorption steps, the EMC at a given relative humidity was generally dependent

upon the size of the relative humidity increment by which the final relative humidity was reached, with the larger increment resulting in a higher EMC. For desorption the larger increments always had the same or lower EMC than the smaller increments to the same final relative humidity. Christensen (1960) showed adsorption EMC to be dependent upon increment size, and the data in this study indicate that the same phenomenon occurs in desorption.

Species was not found to have a pronounced effect on the rate of approach to equilibrium as the E versus $(t)^{1/2}$ plots for the two species over corresponding relative humidity steps were nearly superimposable, although the poplar did generally exhibit slightly faster rates. The oak, of course, was of considerably higher average specific gravity (0.63 green volume, 0.74 oven-dry volume, and weight basis) than the yellow poplar (0.46 and 0.56), but the actual average cell-wall thickness of the oak ($6.5 \mu\text{m}$) was only slightly greater than the poplar ($5.7 \mu\text{m}$), although the fibers of the oak were of much smaller diameter, averaging $20.7 \mu\text{m}$ for the oak versus $35.2 \mu\text{m}$ for the poplar. In both species, the total oven-dry sample weight was the same (0.5 g). The specimens were boiled during preparation to relieve growth stresses, and this undoubtedly served to remove water-soluble extractives which, if left undisturbed, may have contributed to a species difference. However, if the rate of cell-wall deformation is a controlling mechanism of the rate of moisture change, then this phenomenon could well be independent of species.

If the behavior of the specimens were truly Fickian, the time to $E = 0.5$ values would accurately reflect the relative sorption curves of the specimens. However, none of the plots of E versus $(t)^{1/2}$ appeared to fit the Fickian criteria of an initial linear portion with a rapid approach to equilibrium, except for the adsorption step from 0 to 31% relative humidity. Most of the plots exhibited some evidence of a two-stage behavior. Figure 1 for the one-bundle form of yellow poplar adsorbing and de-

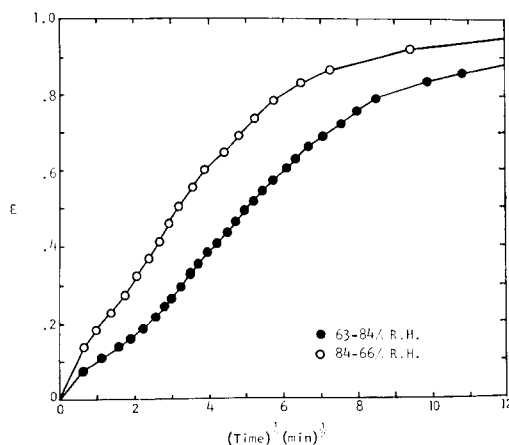


FIG. 1. E vs. $(t)^{1/2}$ for a one-bundle form of yellow poplar (1-YP-1) adsorbing and desorbing water vapor over approximately the same relative humidity step.

sorbing water vapor over approximately the same relative humidity step illustrates this two-stage behavior. From this plot, it is also evident that desorption over the same relative humidity range is faster than adsorption. This may be observed in 25 of the 30 comparisons of time to $E = 0.5$ in Table 1 and the other 5 differ only slightly, so the more rapid rate of desorption is clearly indicated. The difference between the two was pronounced in the steps above 54% relative humidity but generally quite small below this level.

From Table 1 the times to $E = 0.5$ may be compared for the one-bundle versus two-bundle forms in the same relative humidity step, on a within-species basis. For adsorption, the one-bundle time exceeds the two-bundle time in all seven of the possible comparisons with the average being 33% more time. For desorption, six of the seven comparisons show more time required for the one bundle (one comparison shows them equal), with the average being over 51% more time. Since the two-bundle surface area effectively available for heat transfer to the water bath is 60% greater than that of the one-bundle form, it appears that heat transfer is a most important controlling factor in desorption and is of lesser but still significant importance in adsorp-

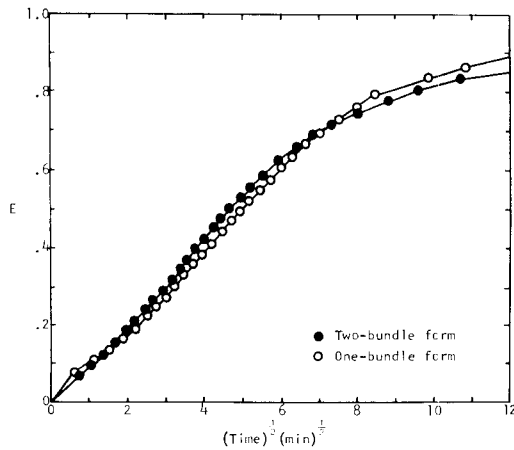


FIG. 2. E vs. $(t)^{1/2}$ for two yellow poplar specimens (1-YP-1 and 3-YP-2) adsorbing water vapor over the relative humidity step of 63–84%.

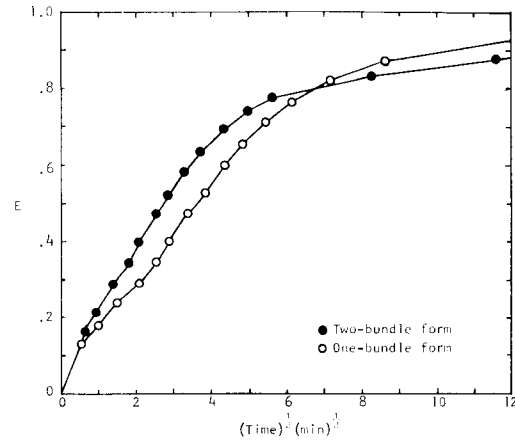


FIG. 3. E vs. $(t)^{1/2}$ for two white oak specimens (2-WO-1 and 4-WO-2) desorbing water vapor over the relative humidity step of 84–66%.

tion. But there is an inconsistency, as illustrated by Fig. 2 for adsorption and Fig. 3 for desorption. Both sets of curves cross over before reaching equilibrium. This definitely took place in three of the seven comparisons between 1- and 2-bundles for adsorption and in two of the seven comparisons for desorption, occurring in the $.70 < E < .85$ range for four of the comparisons and at $E = 0.51$ for the remaining one. Thus it appears that the faster rates resulting from improved heat transfer during the first half of the moisture change may often be counteracted by slower rates during the second half; hence the rate behavior remains clouded in this respect. It may be that greater stress levels are developed during the more rapid moisture change since there is less time for any time-dependent relaxation to occur, and this then retards the rates in the last half of sorption.

Table 1 also presents the maximum temperature change as recorded by the thermistors for adsorption and desorption over the given relative humidity steps. The largest temperature change occurred for adsorption and desorption over the 12 to 54 and the 54 to 12% relative humidity steps. This might be expected since they encompass both large moisture content changes and relative high heat of sorption values.

The adsorption maximum temperature change generally was only slightly less than the desorption value, with the greatest difference occurring in the comparison of 0–12% RH to the 12–0% step.

Evaluation of these thermistor-measured temperatures is best accomplished by examining the effect that the temperature change has upon the effective equilibrium moisture content. For example, desorption results in the consumption of heat which lowers the wood temperature, which also lowers the vapor pressure of the sorbed water. If the temperature is sufficiently reduced, the vapor pressure of the sorbed water will be equal to the vapor pressure in the environment, and no further desorption will occur until heat is transferred to the specimen and its temperature, and thus its vapor pressure, increases. The two-bundle specimen form allowed a higher heat transfer rate and, since desorption was faster for the two-bundle specimen form, the possibility of heat transfer's limiting desorption was investigated.

The determination of the moisture content in equilibrium with the given specimen temperature was accomplished by first constructing an equilibrium adsorption-desorption isotherm for all specimens containing thermistors. This was done by using the

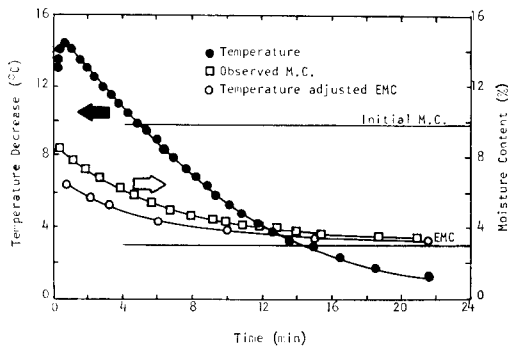


FIG. 4. Temperature, moisture content, and temperature adjusted EMC vs. time for matched two-bundle form of white oak desorbing water vapor over 54–12% RH (4-WO-2 and 12-WO-2).

EMC values of matched specimens on quartz helices. The measured temperature decrease on desorption will reduce the vapor pressure of the sorbed water in the specimen, but the ambient vapor pressure remains constant. From psychrometric graphs (Smith 1956), the effect of this temperature reduction on the ambient EMC can be determined and then adjusted to the particular EMC of the individual specimen. Figure 4 presents the temperature adjusted EMC as well as the observed moisture content and temperature, all plotted against time, for a two-bundle specimen form of white oak. It appears that heat transfer has a strong effect on the desorption rate since at any given time the temperature adjusted EMC is closer to the observed moisture content than to the final EMC value. The same calculations were made for the adsorption steps, but here the temperature-adjusted EMC reached the true equilibrium moisture content long before the specimen moisture content did. This may result partly from the lesser differential heat of sorption when approaching equilibrium at the higher relative humidity.

The non-uniformity of the E values versus $(t)^{1/2}$ plots for the adsorption and desorption data led to a search for a more meaningful way to characterize the data mathematically. A plot of the logarithm of dM_x/dt , the rate of moisture content change, versus the logarithm of the re-

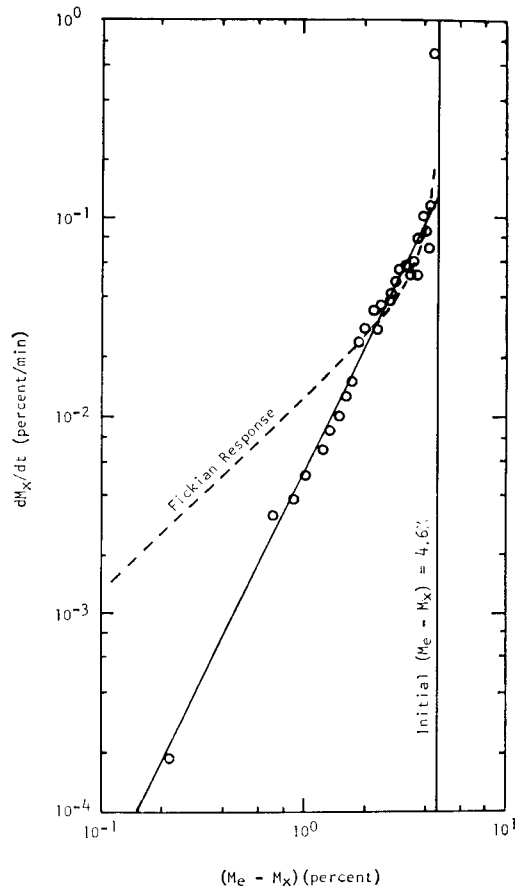


FIG. 5. Rate of change in moisture content vs. remaining moisture change for a one-bundle form of white oak (2-WO-1) adsorbing water vapor over the relative humidity step of 63–84%.

maining moisture content change to equilibrium, was constructed. The remaining moisture content change to equilibrium for adsorption is $(M_e - M_x)$ and for desorption is $(M_x - M_e)$, where M_x is the current moisture content and M_e the EMC. Because the dM_x/dt value is negative for desorption, the absolute value was plotted. All adsorption and desorption steps covered in this study were plotted in this manner. Figure 5 is typical of these plots.

A straight line was fitted to the data of the linear portion of these plots by the method of least squares. The initial one or two points at the high dM_x/dt values were omitted from the regression calculations

since it was obvious they would not fit the regression and there was insufficient data for fitting them to a separate regression. They apparently represented a very rapid first stage of short duration; thus, only the second stage is represented by the fitted regression. Designating the per cent moisture content change to equilibrium as Y , the equation for these regressions is

$$-\frac{dY}{dt} = AY^B. \quad (2)$$

The values of A and B for all adsorption and desorption steps are presented in Table 2. Within both adsorption and desorption, the specimen differences were highly significant for both of these coefficients.

Equation (2) can be integrated, and the resulting equation is of the following form, if B does not equal unity

$$\frac{Y^{1-B}}{B-1} = At + C, \quad (3)$$

where C = the constant of integration. If $B = 1$, the same form as for Fickian diffusion is obtained.

If the equations are forced through the initial moisture content change, Y_0 , at time zero, then the constant of integration becomes

$$C = \frac{Y_0^{1-B}}{B-1}. \quad (4)$$

However, in nearly all cases this results in the equation's lying above the data values because of the short period of very rapid moisture content change during the first stage, which is not accounted for in the equation. Thus, the initial intercept was changed by an amount, F , sufficient to bring the equation into average agreement with the data for the moisture content values between $0.3 \leq E \leq 0.7$ inclusive (Table 2). Thus, the final equation is

$$Y = [(B-1)At + (Y_0 - F)^{1-B}]^{1/(1-B)}. \quad (5)$$

In this equation, Y is asymptotic to zero.

In more generalized form, this equation may be written as

$$Y = (\alpha + \beta t)^\gamma, \quad (6)$$

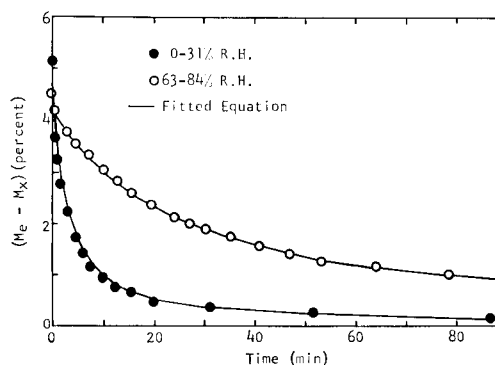


FIG. 6. $(M_e - M_x)$ vs. time for two adsorption steps of specimen 3-YP-2, showing the fit of the empirical equation to the data points.

where: Y = per cent moisture content change remaining at time t ,
 $= (M_e - M_x)$ for adsorption,
 $= (M_x - M_e)$ for desorption
 $\gamma = 1/(1-B)$
 $\alpha = (Y_0 - F)^{1-B}$
 Y_0 = initial per cent MC change
 F = correction factor (for first stage)
 $\beta = (B-1)A$.

Figure 6 is typical of the experimental data. The fit was good in most cases but generally poorest for some of the steps involving zero per cent relative humidity.

It must be stressed that the F values in Table 2 do not accurately reflect the true magnitude by which the first stage exceeded the second stage. This results from the characteristics of a least-squares fit on logarithmic data, plus the fact that some of the rate plots (Fig. 5) were slightly non-linear. Where the rate plots were slightly concave downward, the fitted lines exceeded the early data points and thus resulted in high predicted rates during the early part of the second stage. In a few cases this resulted in negative F values even though the actual first stage clearly exceeded the rate of the second stage as typically shown in Fig. 5 by the first point, which lies far above the regression. These negative F values would not have occurred if the logarithmic transformation had not been necessary. Thus the

TABLE 2. Values of A, B, and F for equations (5) and (6) and also values of $s'_{y,x}$ and number of observations, n

Specimen ^a	Adsorption						Desorption					
	RH Step (%)	AX10 ²	B	F	$s'_{y,x}$	n	RH Step (%)	AX10 ²	B	F	$s'_{y,x}$	n
1-YP-1	0-31	6.48	1.784	0.85	0.0638	28	84-66	3.99	1.643	0.27	0.0238	22
	31-44	7.54	2.972	0.23	0.0320	13	66-44	2.34	2.133	0.34	0.0299	21
	44-63	1.89	1.881	0.15	0.0572	23	44-32	5.59	3.377	0.40	0.0737	14
	63-84	1.17	1.735	0.16	0.0642	33	32-0	4.83	2.063	-0.01	0.2380	31
2-WO-1	0-31	5.80	1.637	0.83	0.0526	30	84-66	3.14	1.887	0.22	0.0373	18
	31-44	8.47	3.072	0.30	0.0447	10	66-44	1.22	2.374	0.27	0.0436	21
	44-63	1.47	1.794	0.44	0.0426	19	44-32	3.65	3.449	0.39	0.0707	14
	63-84	0.50	2.071	0.40	0.0767	29	32-0	3.11	2.049	0.31	0.2078	32
3-YP-2	0-31	8.17	1.953	0.41	0.0634	24	84-66	2.99	2.661	0.15	0.0387	21
	31-53	3.92	2.127	0.25	0.0370	18	66-54	5.81	3.416	0.26	0.0412	14
	53-63	1.62	2.563	-0.19	0.2760	10	54-32	2.40	2.796	-0.09	0.1176	25
	63-84	0.99	1.959	0.33	0.0495	32	32-0	4.88	2.256	-0.32	0.2053	32
4-WO-2	0-12	2.06	1.511	0.95	0.1170	15	84-66	4.17	2.758	0.23	0.0380	19
	12-53	3.12	1.969	0.96	0.0986	31	66-54	8.69	2.450	0.36	0.0609	12
	53-63	4.71	2.186	0.26	0.0499	10	54-12	8.79	1.520	0.17	0.1613	38
	63-84	0.92	1.892	0.32	0.0331	36	12-0	4.07	3.202	0.63	0.1390	18
5-YP-1	0-12	2.54	2.071	0.88	0.1191	16	84-44	1.54	1.984	-0.17	0.2014	45
	12-44	3.72	1.997	0.56	0.0495	29	44-12	7.57	1.641	0.25	0.1393	30
	44-84	0.62	2.042	0.36	0.0811	52	12-0	3.60	2.906	0.35	0.0785	20
6-WO-1	0-12	2.38	1.361	0.92	0.1570	17	84-44	1.07	2.020	0.20	0.1314	44
	12-44	2.99	2.051	0.27	0.0657	29	44-12	5.93	1.621	0.34	0.1181	34
	44-84	1.14	1.586	0.46	0.0456	61	12-0	5.24	2.310	-0.03	0.1196	19
7-YP-2	0-12	1.03	0.392	0.99	0.2203	14	84-66	4.45	1.992	0.29	0.0153	19
	12-63	2.36	2.084	0.25	0.1042	33	66-12	14.37	1.210	0.74	0.1147	40
	63-84	1.75	1.733	0.22	0.0503	32	12-0	8.23	2.945	0.32	0.0959	16
8-WO-2	0-31	4.52	2.184	0.70	0.0615	26	84-54	1.18	2.718	0.38	0.0795	28
	31-53	4.49	1.832	0.42	0.0278	18	54-32	2.28	2.711	0.09	0.0755	22
	53-84	0.97	1.885	0.59	0.1222	44	32-0	4.54	2.146	-0.23	0.2182	32
9-YP-2	0-53	1.66	2.562	-1.17	0.1680	38	84-54	1.85	2.341	0.14	0.0772	33
	53-84	0.73	2.126	0.57	0.1676	46	54-0	7.31	1.586	1.19	0.1324	43
Average		2.99	2.021	0.42				4.63	2.378	0.25		

^a Specimen name indicates tube number (1-12), species (WO = white oak, YP = yellow poplar), and specimen form (1- and 2-bundle).

negative F values of Table 2 in no way detract from the evidence of two-stage behavior.

It may be noted from Table 2 that both A and B values display a fair amount of variation, the A values more so than the B. With one exception, attempts to relate this variation to the physical factors of the experiment were unsuccessful. The exception was with the A values for adsorption.

It was noted that the values tended to increase with decreasing final RH and also tended to be larger for larger changes in relative humidity. Thus when A was divided by the average per cent relative humidity of the given step and the logarithm of this quotient was plotted against the final per cent relative humidity, the plot indicated in Fig. 7 was obtained. Aside from the 0-12% relative humidity, the

linearity is quite good, but the zero to 12 does not seem to fit with the other data, possibly indicating a change in mechanism at very low moisture contents. The least-squares equation for this plot (including the 0-12% data) was:

$$A = 0.01017 \overline{RH} \exp(-0.0502 RH_f), \quad (7)$$

where the average (\overline{RH}) and final (RH_f) relative humidities are expressed in per cent and A is in per cent/minute.

Also shown in Table 2 is $s'_{y,x}$, the square root of the mean square deviation of the calculated M_x values from the actual data values. The M_x values were calculated from equation (5), and no correction of the number of observations for degrees of freedom was made. The first data point was omitted from this calculation since it was clearly a part of the first stage; thus the tabulated n is one greater than the actual number of observations used in this calculation. Most of the $s'_{y,x}$ values are less than 0.1% moisture content, indicating the good fit to the data as illustrated by Fig. 6.

DISCUSSION

If heat transfer had been the totally limiting factor in both adsorption and desorption, then there would be no evidence to support the suggestion that a time dependent relaxation phenomenon plays an important role. But since heat transfer clearly is not the sole limiting factor, although it has been demonstrated to be a partially limiting factor, then a time dependent phenomenon may well be an important factor in explaining the slow rates exhibited by the specimens.

The fact that the equilibrium moisture content is shown to be dependent upon the step size for both adsorption and desorption is indicative of the role that stress plays in wood-moisture interactions. The slight difference in sorption rates between the oak and the yellow poplar indicates that there may be little species effect in the swelling deformation rates of cell walls although, since the two species differed so little in average cell-wall thickness, it cannot be con-

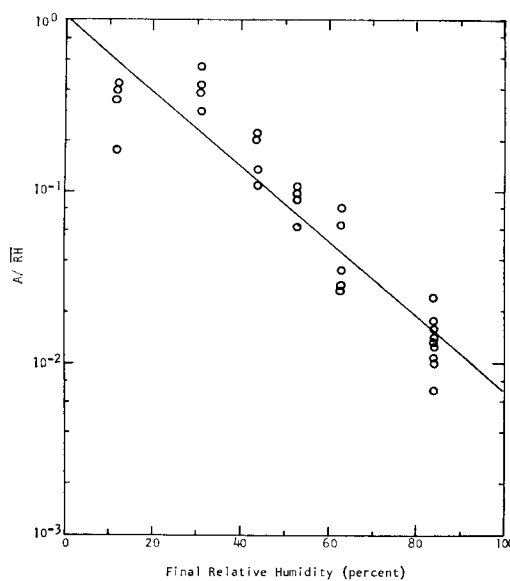


FIG. 7. A/\overline{RH} , plotted on a logarithmic scale, vs. final relative humidity for all sorption steps.

cluded that wall thickness does not affect the sorption rates.

The plots of E versus $(t)^{1/2}$ (Figs. 1-3) indicate a two-stage behavior, but the magnitude of the first stage was not great. In the rate plots typified by Fig. 5, the fact that one or more of the first data points lie far above the linear portion of the curve is not in itself indicative of non-Fickian behavior. In fact, for Fickian data, the first half of the data points, below $E = 0.5$, would tend to be asymptotic to the initial $M_e - M_x$ line and those above $E = 0.5$ would curve over into a virtually linear response with a slope of unity. The fact that the slopes of the experimental data plots averaged over two instead of one is highly indicative of the non-Fickian behavior of the data, as well as is the fact that nearly all of the data were in this linear portion instead of only the last half, as would be expected for Fickian diffusion. Figure 5 includes a Fickian curve calculated for the same time to $E = 0.5$ as the plotted experimental data.

In an earlier project in the study, Comstock (1963) found that for specimens of 0.63 centimeters half-thickness, the faster

rate of adsorption over desorption as predicted from steady-state movement did not apply to unsteady state movement at higher humidities although it did apply at lower humidities. The present project on movement into a cell-wall thickness showed desorption to be faster than adsorption over the entire relative humidity range, but the difference was less at lower humidities. For example, in Comstock's project the adsorption/desorption ratio of times to $E = 0.5$ was approximately 1.2 for the 84-53% relative humidity step and 0.6 for the 53-31% step while the present project showed ratios of 1.9 and 1.2 for the same humidity steps. The trend is the same in both cases, and it seems probable that a time-dependent relaxation phenomenon is effective in both but is much more of a controlling factor with the small specimens of the present study.

The faster rate of desorption over adsorption may arise from the possibility that retarded swelling affects adsorption more than retarded shrinkage affects desorption. Adsorption clearly cannot occur if there is no space to accommodate the water molecules, but the effect of retarded shrinkage is not so obvious. The lag in cell-wall shrinkage may well slow down desorption since there would presumably be more hydrogen bonding sites unsatisfied by bonding to adjacent sites. Upon the loss of one water molecule, such a site may more readily attract another water molecule if shrinkage does not bring it into closer proximity with another bonding site. But even if shrinkage were as necessary for desorption as swelling is for adsorption, why should shrinkage occur at a faster rate than swelling?

An answer to this question may lie in a comparison of the relative magnitudes of swelling pressure and shrinkage tension resulting from adsorption and desorption, respectively. The equation relating swelling pressure or tension to relative humidity change is (Tarkow and Turner 1958):

$$P = \frac{RT}{\bar{V}} \ln \frac{P_f}{P_i}, \quad (8)$$

where P = swelling pressure

R = gas constant

T = absolute temperature

\bar{V} = molar volume of the sorbed water

P_i = initial relative vapor pressure

P_f = final relative vapor pressure.

The initial theoretical swelling pressure for adsorption over a given relative humidity step, P_i to P_f , is the same as for desorption over the same step except that the negative sign for desorption indicates a tension stress. But as the initial wood moisture content changes to M_x , the vapor pressure of the sorbed water changes from P_i to P_x and the swelling pressure or tension is then proportional to $\ln (P_f/P_x)$. However, for a given change in moisture content, the change in swelling pressure (tension) is not the same for adsorption and desorption.

As an example of this, assume that a wood specimen in equilibrium with 10% relative humidity is exposed to a relative humidity of 80% at constant temperature. Assuming that the molar volume of the sorbed water is constant, 18 cc, and the temperature is a constant 40 C, the initial theoretical swelling pressure at constant temperature is then proportional to the logarithm of the ratio of the final to initial relative humidity. The theoretical initial swelling pressure for this example is proportional to the natural logarithm of 80/10 or 2.079; so the calculated value is $2.079 \times 20,975 = 43,607$ psi. The equilibrium moisture content as a function of temperature and relative humidity can be determined with the aid of the psychrometric graphs of Smith (1956). At 40 C the equilibrium moisture contents are 2.2 and 15% for relative humidities of 10 and 80%, respectively. When the wood has adsorbed moisture to where its average moisture content is 4.2%, the sorbed water has a vapor pressure which is in equilibrium with a 20% relative humidity. The theoretical swelling pressure at this relative humidity has been reduced to $1.386 \times 20,975$. This calculation can be continued up to 80% relative humidity for

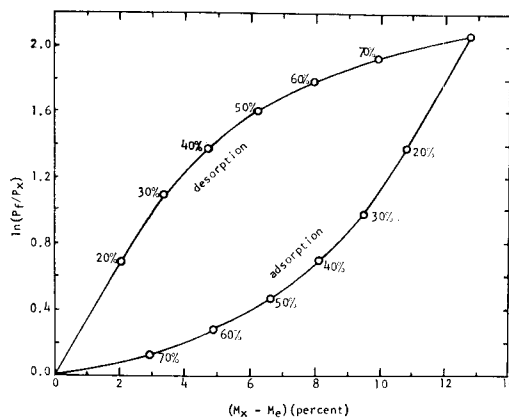


FIG. 8. Comparison of the theoretical swelling pressure, without the constant multiplier, between adsorption and desorption over the same relative humidity range of 10–80% (numbers on the graph refer to RH).

adsorption, and then back down to 10% relative humidity for desorption.

Figure 8 is a plot of the logarithm of the ratio of the final to current relative humidity versus the remaining moisture content change to equilibrium for adsorption and desorption over the relative humidity step of 10 to 80%. The values on the plot refer to the relative humidity at that point. At any given remaining moisture content change, swelling tension during desorption is at a higher level than is the swelling pressure for adsorption. Although these calculations are not exactly accurate for application to adsorption-desorption in wood (*e.g.*, the wood temperature is not constant), they are sufficient to indicate that a difference between the swelling pressure and the swelling tension may result in a difference between rate of swelling and rate of shrinkage and thus may account for a portion of the difference in adsorption and desorption rates.

The relationship between the *A* value and relative humidity, as shown by Fig. 7, shows that adsorption rates decrease rapidly with increasing final relative humidity. This may result from the lower swelling pressures associated with the higher humidities. But for a given final RH, a lower initial RH (and thus a lower \bar{RH} , the aver-

age of the initial and final RH values) results in a lower *A* value, even though this is a larger RH change and thus a greater initial swelling pressure. However, it must be remembered that the *A* value is actually the rate, dM_x/dt , when 1% moisture change remains. Thus if the initial MC change is 2%, *A* represents the adsorption rate at $E = 0.50$, but if the initial change were 4%, *A* would represent the adsorption rate at $E = 0.75$ and a slower rate might be expected at a higher *E* value, as does in fact occur. This indicates the probability that swelling pressure and heat transfer together are not the only rate-controlling mechanisms since they should largely be functions of the moisture change *remaining*, rather than functions of the *fractional* moisture change, *E*.

SUMMARY

Measurements of the adsorption and desorption of water vapor by the cell walls of wood have shown that the rates are approximately 10^{-3} smaller than would be expected for Fickian diffusion of bound water. The two species, yellow poplar and white oak, showed little difference in response, but they also differed little in average cell-wall thickness even though they differed substantially in density (the oak fibers were smaller in diameter). A two-stage behavior was indicated for both adsorption and desorption with the first stage displaying the more rapid rate, but this stage was of short duration. For the second stage, the logarithm of the rate of moisture change gave a linear plot against the logarithm of the remaining moisture content with an average slope of more than two as compared to unity for a similar plot of Fickian type data, thus emphasizing the non-Fickian nature of the response. Desorption was considerably faster than adsorption for relative humidity steps above 54% and only slightly faster below this level. Heat transfer to the specimen was found to play an important role in limiting the rate of moisture change, particularly in desorption, but there was some indication that better heat transfer and the resultant

faster rates during the first half of sorption may be largely offset by slower rates during the second half. An empirical equation was found to fit the experimental data with a high degree of accuracy, but only limited success was achieved in relating the constants of the equation to the corresponding relative humidity levels.

REFERENCES

- CHRISTENSEN, C. N. 1960. Kinetics of water vapor sorption by wood. I. The effect of sample thickness. *Australian J. Appl. Sci.* **11**: 294-304.
- , AND K. E. KELSEY. 1959. The rate of sorption of water vapor by wood. *Holz als Roh- und Werkstoff.* **17**: 178-188.
- COMSTOCK, G. L. 1963. Moisture diffusion coefficients in wood as calculated from adsorption, desorption and steady state data. *Forest Prod. J.* **13**: 97-103.
- CRANK, J. 1956. *Mathematics of diffusion.* Oxford Univ. Press, London.
- DOWNES, J. G., AND B. H. MACKAY. 1958. Sorption kinetics of water vapor in wool fibers. *J. Polymer Sci.* **28**: 45-67.
- HERGT, H. F. A., AND G. N. CHRISTENSEN. 1965. Variable retention of water by dry wood. *J. Appl. Polymer Sci.* **9**: 2345-2361.
- KING, G., AND A. B. D. CASSIE. 1940. Propagation of temperature changes through textiles in humid atmospheres. I. Rate of absorption of water vapor by wool fibers. *Trans. Faraday Soc.* **36**: 445-453.
- LONG, F. A., AND D. RICHMAN. 1960. Concentration gradients for diffusion of vapors in glassy polymers and their relation to time dependent diffusion phenomena. *J. Am. Chem. Soc.* **82**: 513-519.
- NEWS, A. C. 1956. The sorption and desorption kinetics of water in a regenerated cellulose. *Trans. Faraday Soc.* **52**: 1533-1545.
- PRICHANANDA, C. 1966. A study of some aspects of moisture sorption dynamics in wood. Unpublished Ph.D. Dissertation from New York State University, College of Forestry, Syracuse, New York.
- ROGERS, C. E. 1965. Solubility and diffusivity. Chapt. 6. In D. Fox, M. M. Labes, and A. Weissberger (ed.), *Physics and chemistry of the organic solid state*, Vol. 2. Interscience Publishers, New York.
- SMITH, H. H. 1956. Relative humidity and equilibrium moisture content graphs and tables for use in kiln drying lumber. U. S. Dept. Agr., Forest Service, Forest Prod. Lab. Rept. No. 1651.
- SPALT, H. A. 1957. The sorption of water vapor by domestic and tropical woods. *Forest Prod. J.* **7**: 331-335.
- STAMM, A. J. 1959. Bound water diffusion into wood in the fiber direction. *Forest Prod. J.* **9**: 27-32.
- . 1960. Bound water diffusion into wood in across the fiber direction. *Forest Prod. J.* **10**: 524-528.
- TARKOW, H., AND H. D. TURNER. 1958. The swelling pressure of wood. *Forest Prod. J.* **8**: 193-197.
- WATT, I. C. 1960. Kinetic studies of the wool-water system. II. The mechanism of two-stage absorption. *Text. Res. J.* **30**: 644-651.
- YOKOTA, T. 1959. Diffusion of sorption-water through the cell wall of wood. *J. Japan Wood Res. Soc.* **5**: 143-159.

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