

# UNSTEADY-STATE WATER VAPOR ADSORPTION IN WOOD: AN EXPERIMENTAL STUDY<sup>1</sup>

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## ABSTRACT

This paper concerns transient sorption measurements in two intervals (54 to 75% and 75 to 84% relative humidity) made on samples of pine, spruce, ash, aspen, cherry, and willow, with the flow in different directions. In the lower interval, the sorption behavior is quite Fickian; but in the higher interval, it is largely governed by other processes—e.g., the slow sorption in the cell walls. Different simple methods of evaluating such non-Fickian sorption curves are proposed and tested.

*Keywords:* Water vapor, adsorption, sorption, measurements, evaluation, non-Fickian behavior, *Pinus silvestris*, *Picea abies*, *Fraxinus excelsior*, *Populus tremula*, *Prunus avium*, *Salix* sp.

## INTRODUCTION

Moisture movement in wood is of great interest in both wood science and technology and in building physics. It is therefore of prime importance that reliable theories of moisture phenomena in wood are used. It is also essential that the models and theories in use are continuously tested and verified.

This paper mainly concerns new ways of evaluating transient sorption measurements on wood, as it has been shown that the commonly used Fickian approach does not accurately describe some sorption processes in wood. It is, however, not the aim of this paper to investigate the physical processes governing the anomalous sorption.

Transient adsorption measurements on 78 wood samples have been made by recording the weight change of the samples following an abrupt change in relative humidity (RH) from an initial RH with which the samples were in equilibrium. This method is common in wood science for evaluating diffusivities (Stamm 1960; White 1979; Droin-Josserand et al. 1989). In polymer science, it has also been used for studying deviations from the normally assumed Fickian behavior (Long and Richman 1960; Jacobs and Jones 1989). Similar studies have also been made on wood (Christensen and Kelsey 1959; Comstock 1963; Kelly and Hart 1970; Skaar et al. 1970).

The present measurements were made with an instrument that is described in some detail in Wadsö (1993e). An error analysis of the method and some results from a first series of measurements have also been reported (Wadsö 1993a, b, 1993f).

The nomenclature is given at the beginning of this article. Abbreviations are used for type of specimen, e.g., "pine S T 5.6 mm" is a sapwood pine specimen with a half thickness of 5.6 mm, measured in the tangential direction.

## EXPERIMENTAL PROCEDURE

Experiments have been performed in a purpose-built wind tunnel in which temperature and relative humidity (RH) can be held constant for long periods of time. The RH is controlled by

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<sup>1</sup> Taken from the author's Doctoral Dissertation, Lund University, Lund, Sweden, May 1993.

## NOMENCLATURE

Some notations are explained only in the text.

$a$	non-Fickian fraction of total sorption	
$c$	concentration of water in wood	kg/m <sup>3</sup>
$D_c$	diffusivity with concentration $c$ as potential	m <sup>2</sup> /s
$D_c^*$	apparent diffusivity with concentration $c$ as potential	m <sup>2</sup> /s
$E$	fractional weight change ( $\Delta M_t/\Delta M_\infty$ , where $\Delta M_t$ and $\Delta M_\infty$ are the weight changes at time $t$ and at final equilibrium)	
$l$	half thickness of sample	m
$t$	time	s
$t_h$	time to half sorption	s
$\tau$	relaxation time (Eq. 6)	s
The following abbreviations are also used for type of specimen:		
L	longitudinal flow direction	
R	radial flow direction	
T	tangential flow direction	
TR	transversal (a mixture of T and R)	
S	sapwood	
H	heartwood	

1.6 m<sup>2</sup> of saturated salt solutions in the wind tunnel. A total of 117 specimens are placed in holders that may be lifted and moved with an electromagnet placed outside the wind tunnel. By this arrangement, they may be moved from the wind tunnel to the balance and back again without being touched by the experimenter or taken out of the controlled environment. A more detailed description of the instrumentation is given in Wadsö (1993e).

The temperature was  $23.0 \pm 0.1$  C during the measurements and the air velocity was  $3 \pm 0.5$  m/sec (measured a few centimeters from the sample surfaces). Note that the main aim of this work was not to calculate diffusivities, but to study the sorption behavior of wood. The measurements at each RH-level have therefore continued for more than 100 days in order to detect even very slow sorption processes not included in the generally used models of moisture movement in wood.

The RH-intervals in which the measurements were made were the same as those used earlier (Wadsö 1993f):

Step A: from 33 to 54% RH

Step B: from 54 to 75% RH

Step C: from 75 to 84% RH.

These RH-intervals will be referred to as “Step A,” “Step B,” and “Step C.”

Step A was mainly a preparatory step to ensure that Steps B and C were made on the adsorption isotherm. It is also thought that Step A has decreased any memory of the earlier moisture history of the samples. Step A is not discussed here further.

For comparison, steady-state cup measurements on duplicate pine samples were made at the building Materials Laboratory at the Danish Technical University (Hansen 1991). These measurements have been corrected for internal resistances in the measuring cups and for the effect of a masked edge between the specimen and the cup. Measurements on spruce by the same method by Tveit (1966), Skaar et al. (1970), and Bertelsen (1983) have also been used in this paper. These cup diffusivities are believed to be true steady-state transport coefficients, which

are not much influenced by the non-Fickian behavior discussed later. This is reasonable as the flow of water molecules (both bound and in vapor phase) during a cup measurement should be the same independently of the cell wall being in complete sorption equilibrium or only near equilibrium. As discussed later, a sorption measurement may give a completely different diffusivity if the cell-wall absorption is slow. Steady-state measurements, however, give true diffusivities in the sense that they may be used in Fick's law to calculate steady-state flow.

#### MATERIAL

Wood from six species was used in the present study: pine (*Pinus silvestris*), spruce (*Picea abies*), ash (*Fraxinus excelsior*), aspen (*Populus tremula*), cherry (*Prunus avium*), and willow (*Salix* sp.). The parallelepipedic samples were coated on four surfaces to give one-dimensional flow in one of the three principal directions: longitudinal (L), tangential (T), or radial (R), or in the transversal direction (TR, an unspecified mixture of T and R). They had thicknesses from 3.8 to 22.8 mm, and the other two dimensions were approximately  $5 \times 5$  cm<sup>2</sup>. All samples had planed or, in some cases, sanded surfaces. They had not been dried below 33% RH before the measurements.

The origin of the wood was as follows. The pine from the south of Sweden was gently dried in our laboratory directly after felling. The same applies to the spruce, which was collected by Mårtensson (1992). The aspen, cherry, and willow were also from the south of Sweden, but these were dried outdoors under roof and indoors. The ash of unknown origin was bought from a local importer.

The samples of ash, aspen, and willow were made of sapwood (S), and the cherry and spruce samples were made of heartwood (H). For the pine, both sapwood and heartwood specimens were used.

#### EXPERIMENTAL CONDITIONS

Unless otherwise noted, the experiments reported were conducted as described in Wadsö (1993e, f). The following differences should be noted:

1. The teflon parts on the stainless steel sample holders were changed to polyethylene-tape, as the teflon generated too much static electricity at low RH, which affected the weighings.
2. As before, the RH was controlled by saturated salt solutions, but the rate of the step change in RH, which was not satisfactory during the earlier measurements, was made much faster. This was achieved by manually entering humid air into the apparatus during the first hours of each step. It was then possible to control the new RH-level until the adsorption in the samples became so low that the saturated salt solutions were able to maintain the new higher RH-level in the apparatus. The result of the manual control was checked with a capacitive humidity sensor (Vaisala, Finland) and a dew-point sensor (Protimeter, UK). The measured RH in the apparatus during the first hour of Steps B and C is shown in Fig. 1.
3. The stability of RH and temperature was very good except during the end of Step B when the temperature was lowered to 21.5 C for some weeks, due to a failure in the temperature regulator. As this happened when the samples were near equilibrium, a period in which not many measurements were made, it has been hard to find out if this has influenced the final moisture content of Step B. A calculation (Wadsö 1993b) indicates that the measured final moisture content of this step might be 0.08 moisture-content-% too high. This is, however, only 2% of the total moisture content increase during Step B.
4. The samples were treated with a fungicide to lessen the risk of mold growth during the long exposure to high RH. The treatment (0.30 and 0.15 g dichlofluanid/m<sup>2</sup> wood surface for longitudinal and transversal samples, respectively) was shown not to influence the sorption

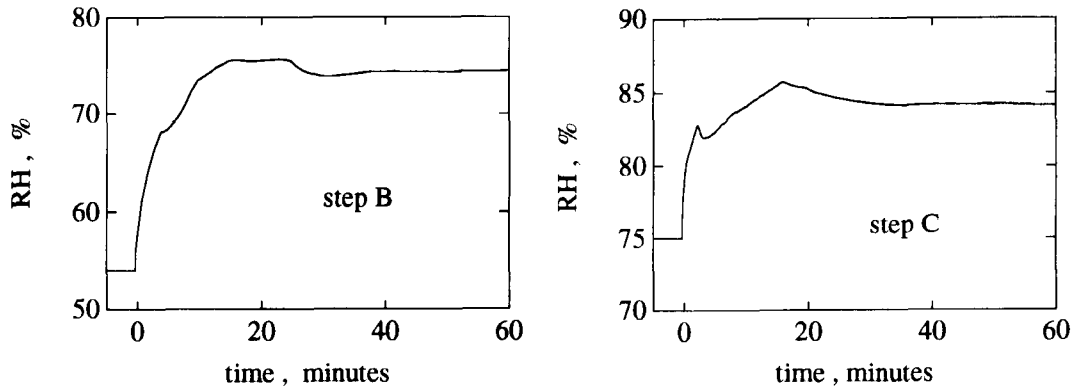


FIG. 1. Measured steps in relative humidity. The start of each measurement is at time zero.

behavior of the samples (Wadsö 1993b). This treatment did not, however, stop the mold growth completely. At the end of the 105 days at 84% RH (Step C), all samples of pine sapwood with flow in the longitudinal and radial directions were covered with a thin layer of mold. Some samples of pine sapwood with flow in the tangential direction also had some slight signs of mold growth, whereas the other samples were free from any visible mold.

It does not seem as if this mold growth influenced the transient sorption curves. First, duplicate samples, with and without mold, show the same sorption behavior (Fig. 2a). Second, the samples with most mold growth show the same slow approach to equilibrium as do all the other samples (Fig. 2b). It is, however, thought that mold could disturb the initial fast sorption as it will give an extra surface resistance to moisture flow. This was not the case during Step C, as the first mold was seen more than 50 days after this step was initiated.

#### EVALUATION OF SORPTION CURVES

Sorption measurements are usually evaluated by the calculation of diffusivities with methods based on Fick's law. It has, however, been shown that Fick's law does not accurately describe transport and sorption in wood because of the slow sorption of water vapor in the wood cell

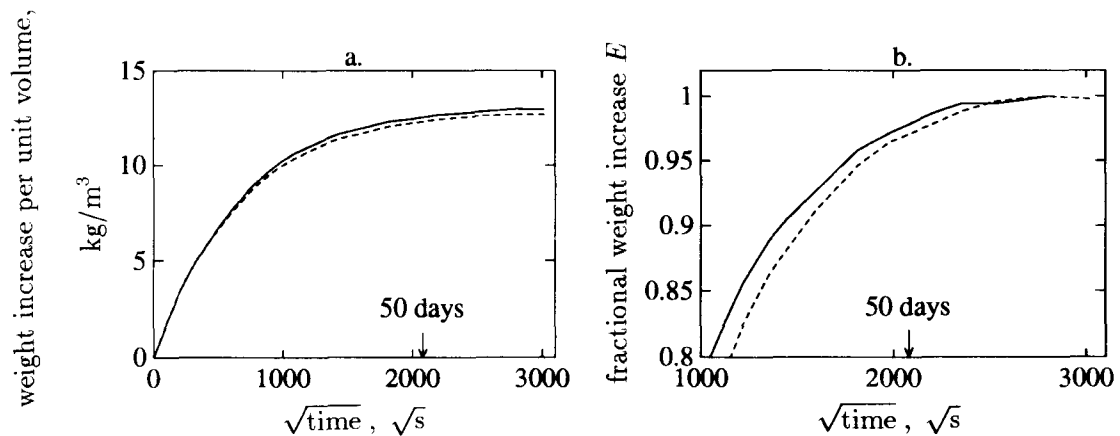


FIG. 2. Examples of the absence of any effect of mold on the sorption. a. Duplicate samples (pine S T 5.0 mm), with mold (solid line) and without mold (broken line). b. The slow approach to equilibrium for samples with mold (pine S R 6.7 mm, solid line) and without mold (pine H TR 5.2 mm, broken line).

walls (Christensen 1965). It has also been shown that the methods generally used for evaluating sorption curves are sensitive to different types of disturbances (Wadsö 1992). It is clear that it is hard to evaluate the true diffusivity, i.e., the steady-state diffusivity, from a sorption measurement. Below, two other methods of evaluating sorption curves are presented.

In this paper the term "Fickian" denotes a process that is governed by Fick's law (also when the diffusivity is concentration-dependent and the sorption isotherm is not linear). A "non-Fickian" process is not only governed by Fick's, but also by other internal processes (not external ones like a surface resistance).

#### *Finding the non-Fickian fraction*

Diffusivities may be calculated from the slope of the sorption curve plotted versus the square root of time (cf. p. 244 in Crank 1975):

$$D_c^* = \frac{\pi l^2}{4} \left( \frac{dE}{d\sqrt{t}} \right)^2 \quad (1)$$

Here  $D_c^*$  is the apparent diffusivity,  $l$  is half the thickness of the sample,  $t$  is the time, and  $E$  is the fractional weight change ( $E = \Delta M_t / \Delta M_\infty$ , where  $\Delta M_t$  and  $\Delta M_\infty$  are the weight changes at time  $t$  and at final equilibrium, respectively). The word "apparent" is used to indicate that  $D_c^*$  might not be a true (steady-state) diffusivity.

If there is a fraction of the sorption that is due only to the slow sorption in the cell walls, the true diffusivity may be evaluated by correcting the slope in Eq. (1):

$$D_c = \frac{\pi l^2}{4} \left( \frac{1}{1-a} \cdot \frac{dE}{d\sqrt{t}} \right)^2 \quad (2)$$

Here  $D_c$  is the true (steady-state) diffusivity and  $a$  is the fraction of the final weight change that is non-Fickian. The slope  $dE/d\sqrt{t}$  should be evaluated as early as possible during the sorption process (e.g., at  $E < 0.2$ ).

The sorption curve is here assumed to be composed of a first Fickian sorption on fast sorption sites (fraction  $1 - a$ ) and a second non-Fickian part of fraction  $a$  which is governed by the slow sorption in the cell wall:

$$E = (1 - a) \cdot E_F + a \cdot E_{NF} \quad (3)$$

Here  $E_F$  and  $E_{NF}$  are Fickian and non-Fickian parts of the sorption process [cf. Eq (6)]. It is assumed that the non-Fickian process does not influence the initial Fickian sorption. This is true if the two processes are uncoupled, i.e., have very different time scales [cf. Eq (9)].

The use of Eqs. (1) and (2) is twofold. First, if the true and apparent diffusivities are known, the non-Fickian fraction  $a$  can be calculated:

$$a = 1 - \sqrt{D_c^* / D_c} \quad (4)$$

Second, the ratios of diffusivities in different directions may be calculated if it is assumed that  $a$  is independent on direction of flow:

$$\frac{D_c^L}{D_c^T} = \frac{D_c^{*L}}{D_c^{*T}} \quad (5)$$

Here the indices  $L$  and  $T$  are used as examples of two directions.

It cannot be expected that Eqs. (4) and (5) will hold exactly in practice, but they should be useful for an estimate of the parameters investigated.

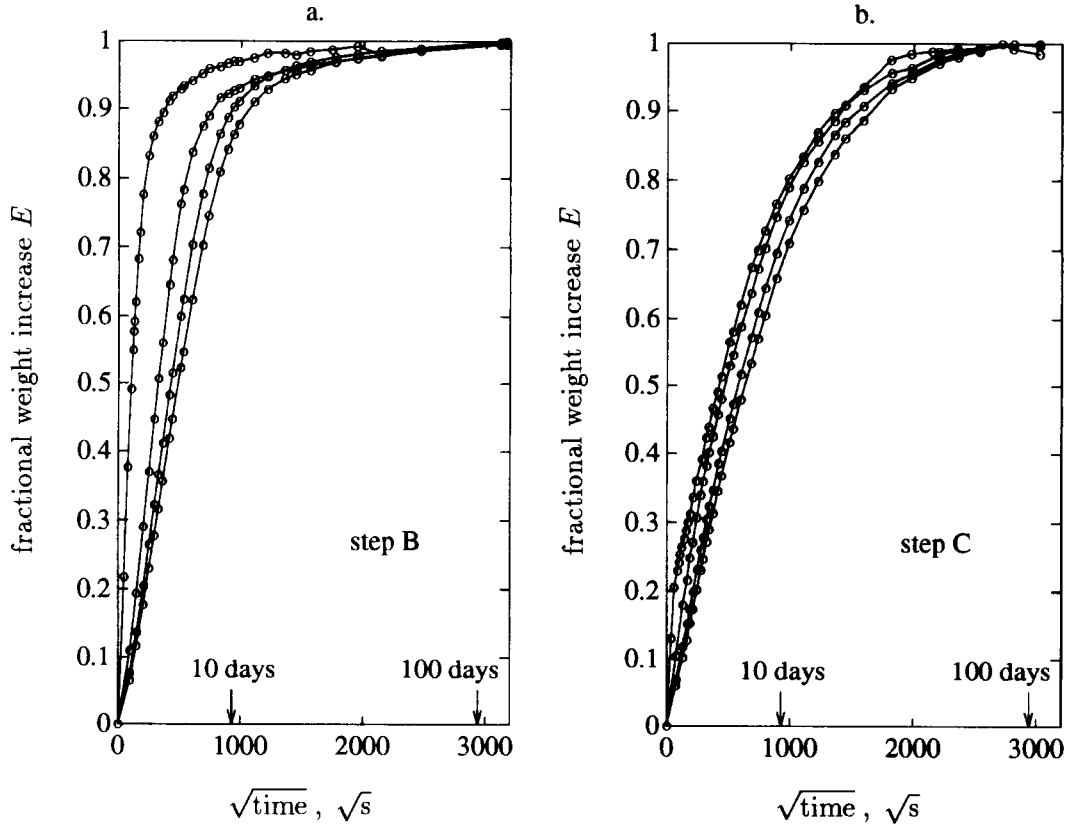


FIG. 3. Experimental sorption curves. a. Four samples of pine (S T) during Step B. The specimen with the highest rate of sorption consisted of thin flakes of wood contained in a basket of stainless steel. The other three samples had half thicknesses of 4.9, 7.0 and 8.1 mm. Thicker samples have a lower rate of sorption. b. same samples as a, but for Step C.

#### Curve fitting

If the sorption curves are non-Fickian, one may try to fit a model to the measured result. As the sorption is thought to be governed both by Fickian and non-Fickian processes, the sorption may be modelled as a sum of a Fickian sorption and one or more relaxation terms. The relaxation terms simulate the slow sorption in the cell wall. The following equation has been used by Berens and Hopfenberg (1978):

$$E = \left(1 - \sum_{i=1}^n a_i\right) E_F(D_c, l, t) + \sum_{i=1}^n a_i (1 - \exp(-t/\tau_i)). \quad (6)$$

Here  $E$  is the fractional weight change during a sorption measurement,  $n$  is the number of relaxation terms,  $a_i$  is the fraction of the relaxation process with a time constant  $\tau_i$ ,  $t$  is time, and  $E_F$  is the Fickian part of the fractional weight change (cf. p. 48 in Crank 1975):

$$E_F(t) = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \left( \frac{1}{(2m+1)^2} \cdot \exp\left\{-\frac{(2m+1)^2 \pi^2 D_c t}{4l^2}\right\} \right). \quad (7)$$

If  $D_c$  is unknown,  $n$  relaxation times gives  $2n + 1$  unknowns in Eq. (6) ( $D_c$  and  $n$  pairs of  $a$  and  $\tau$ ). If  $D_c$  is known, the number of unknowns may be reduced to  $2n$ . It should be noted that

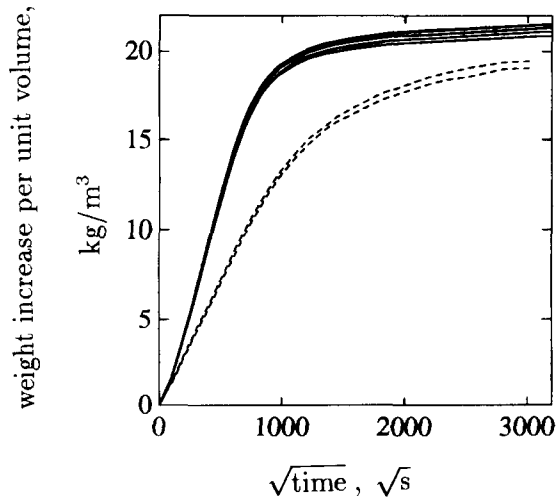


FIG. 4. Sorption curves of 5 duplicate samples of pine (S TR 7.6 mm) during Step B (solid line) and 2 duplicate samples of ash (T 4.8 mm) during Step C (broken line).

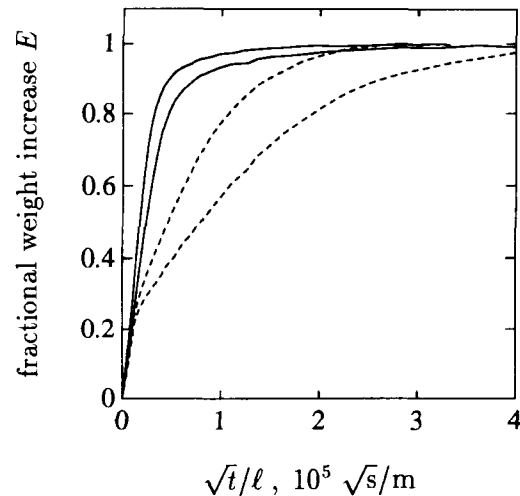


FIG. 5. A test of the Fickian behavior. The results of measurements on two pine samples (H L 5.4 mm and 9.9 mm) are shown for both Step B (solid line) and Step C (broken line). The curves corresponding to the thick sample are to the left of the curves for the thin sample.

it is assumed that the different processes are uncoupled, i.e., that they have very different time scales. Note also that  $\Sigma a$  in Eq. (6) has the same meaning as  $a$  in Eqs. (2) and (4), but as they are only parameters giving the approximate size of the non-Fickian part of an experimental sorption curve it can not be expected that these two methods should give exactly the same  $a$ -values.

#### RESULTS AND DISCUSSION

Figure 3 shows sorption curves for four pine samples (S T). These curves show the general behavior of all measurements during Steps B and C. It is seen that each sorption curve was measured in about 30 points, the first measurement being made within one hour of the step change in RH.

##### *Similar samples give similar results*

In this investigation it was found that samples of the same type show identical sorption curves within the limits of accuracy of the determinations of the sample dimensions. Figure 4 gives some examples of this. The standard deviations of the determined parameters (Tables 2, 3 and 5) are also low. Further, it was shown (Wadsö 1993b) that results from the present series of measurements are in full agreement with measurements made earlier on the same samples (Wadsö 1993f).

##### *Is the sorption Fickian?*

When Fick's law is used for wood, it is assumed that there is an instantaneous equilibrium between the relative humidity in the cell cavity and the moisture content of the cell walls surrounding the cavity. This assumption has been shown not to hold at higher relative humidities (Christensen 1965). Non-Fickian behavior found in wood is therefore thought to be caused by the slow sorption in the cell walls.

TABLE 1. Ratio of the diffusivity in different directions calculated by Eq. (5). The diffusivities were calculated with Eq. (1) at the maximum slope for Step B and when  $E < 0.2$  for Step C.

	Step B			Step C		
	$D_L/D_T$	$D_L/D_R$	$D_L/D_{TR}$	$D_L/D_T$	$D_L/D_R$	$D_L/D_{TR}$
pine S	13	10	12	10	9	12
pine H			12			13
ash	13	6		11	5	
aspen			16			12
cherry			4			5
willow			6			9
pine <sup>a</sup>	29	19	23	8	9	9
spruce <sup>b</sup>			28			11
birch <sup>c</sup>	12					

<sup>a</sup> Calculated from steady-state diffusivities measured by Hansen (1991) (cf. Table 2).

<sup>b</sup> Calculated from steady-state diffusivities measured by Tveit (1966).

<sup>c</sup> Calculated from steady-state diffusivities measured by Skaar et al. (1970).

If a sorption process is governed by Fick's law, the following three statements should hold true:

1. Sorption curves plotted as a function of the square root of time should have an initial linear part (at least up to  $E = 0.6$ ).
2. Curves for different thicknesses should be the same if plotted as a function of the square root of time divided by the thickness of the sample.
3. Transient sorption measurements should give similar results as steady-state cup measurements.

None of these statements is fulfilled in the present case, especially not for Step C. Statement 3 has been tested in Wadsö (1993c) (cf. Table 2 below) and statement 2 is tested in Fig. 5.

It should be noted that seemingly non-Fickian behavior can be caused by other factors than the sorption not obeying Fick's law (e.g., a large surface resistance or carelessly made experiments). In the present case it has been shown, however, that that major part of the deviations are in fact caused by the sorption itself not being accurately described by Fick's law (Wadsö 1993 b, c, d). Note that a surface (boundary layer) resistance cannot give as large effects as shown in Fig. 5.

#### *Influence of thickness*

The influence of thickness on the sorption curves is shown in Fig. 3. For Step B it is seen that the rate of the (fractional) sorption decreases as the thickness of the samples increases, but Fig. 5 shows that the dependence on the thickness is not exactly according to Fick's law. During Step C it is only the initial sorption that is dependent on thickness, as the curves for different thicknesses show similar behavior after a few hours. The influence of thickness is thus not very large during Step C.

#### *Influence of direction of flow*

It is well known that the diffusivity in wood is direction-dependent. I have calculated the ratios of diffusivities in different directions with Eq. (5). Table 1 shows the result. As a comparison, ratios of steady-state diffusivities from steady-state cup measurements on pine, spruce, and birch are also given in the same table. These values show a good agreement with the



TABLE 2. Comparison of diffusivities measured by sorption and cup methods. The apparent diffusivities ( $D_c^*$ ) are evaluated from the present measurements with Eq. (1) using the maximum slope for Step B and the mean slope when  $E < 0.2$  for Step C. The standard deviations are given for values calculated from the sorption curves.

Number and types of samples	Step B		Step C		
	$D_c^*$ $10^{-12} \text{ m}^2/\text{s}$	$D_c$ $10^{-12} \text{ m}^2/\text{s}$	$D_c^*$ $10^{-12} \text{ m}^2/\text{s}$	$D_c$ $10^{-12} \text{ m}^2/\text{s}$	$a$ Eq. 4
7 pine S L	$840 \pm 200$	1,900 <sup>a</sup>	$340 \pm 55$	1,530 <sup>a</sup>	$0.53 \pm 0.04$
6 pine S R	$88 \pm 7$	100 <sup>a</sup>	$39 \pm 7$	163 <sup>a</sup>	$0.51 \pm 0.05$
7 pine S TR	$72 \pm 6$	82 <sup>a</sup>	$27 \pm 3$	173 <sup>a</sup>	$0.60 \pm 0.02$
13 pine S T	$66 \pm 5$	65 <sup>a</sup>	$33 \pm 2$	183 <sup>a</sup>	$0.57 \pm 0.01$
4 spruce H T	$67 \pm 20$	259 <sup>b</sup>	$51 \pm 1$	358 <sup>b</sup>	$0.62 \pm 0.004$

<sup>a</sup> From cup measurements on duplicate samples in the same RH-ranges (Hansen 1991).

<sup>b</sup> From cup measurements on spruce H T samples in the same RH-ranges (Bertelsen 1983).

diffusivity ratios calculated from Step C, but the ratios obtained from Step B are generally lower than the same ratios determined at steady-state.

#### Evaluating true diffusivities from Step B

As the sorption curves from Step B look quite Fickian, it may be possible to evaluate the true (steady-state) diffusivities from them by Eq. (1). Table 2 shows that the result is good for the pine (R, TR, and T), but not so good for the pine (L) and spruce (T). The latter samples were the ones with the highest rate of sorption. Therefore, they are more disturbed than the other samples by a surface resistance or heat effect due to adsorption (Wadsö 1993b).

#### Non-Fickian fraction during Step C

Table 2 also gives the apparent diffusivity  $D_c^*$  calculated for Step C at low values of  $E$ . These diffusivities are quite different from the steady-state measured diffusivities also shown in Table 2. The cup measurements by Bertelsen (1983) were not made on duplicate samples, but compare well with other similar studies on *Picea abies* (Tveit 1966; Vanek and Teischinger 1989). Using Eq. (4) the fraction ( $a$ ) of the total sorption that is non-Fickian has been calculated. There is a close agreement between these values of the fraction of non-Fickian sorption for the different pine and spruce samples. Note that the standard deviations in Table 2 are low, i.e., samples of the same type, but with different thicknesses, give similar results.

No values of  $a$  are given for Step B, as these are very much higher for the samples with the higher rate of sorption (pine L and spruce T) than for the other samples. It has been shown (Wadsö 1993b) that there are significant initial disturbances (heat effects and surface resistance) to the measurements of the samples with high rate of sorption. The initial sorption rate is lower for all samples during Step C than during Step B, as only about 40% ( $1 - a$ ) of the total adsorption is in response to the differences in concentration. This may, at least partly, explain the differences found. A dependence of  $D_c^*$  on thickness was also found for the faster samples during Step B, thicker samples having higher values of  $D_c^*$ . This is seen in the larger standard deviations for these samples.

#### Two stage sorption during Step C

For all specimens with flow in the longitudinal direction, and for some thin specimens tested in the other directions, a clear two-stage sorption is seen during Step C with one fast and one slow part, separated by a marked change in slope (Fig. 6). In Table 3, the samples for which this phenomenon occurred are indicated.

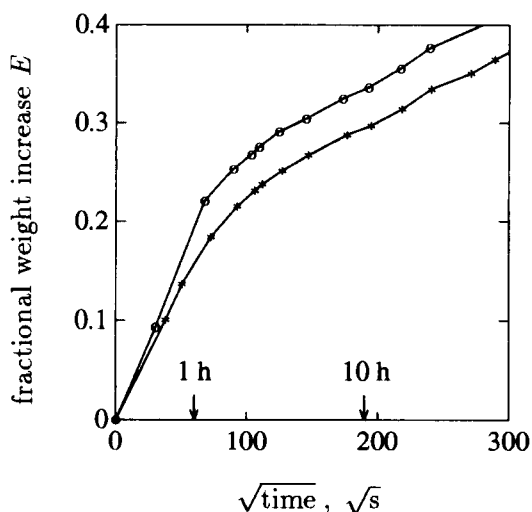


FIG. 6. Typical examples of two-stage sorption behavior during Step C. Samples of pine H L 5.4 mm (circles) and willow L 8.1 mm (stars).

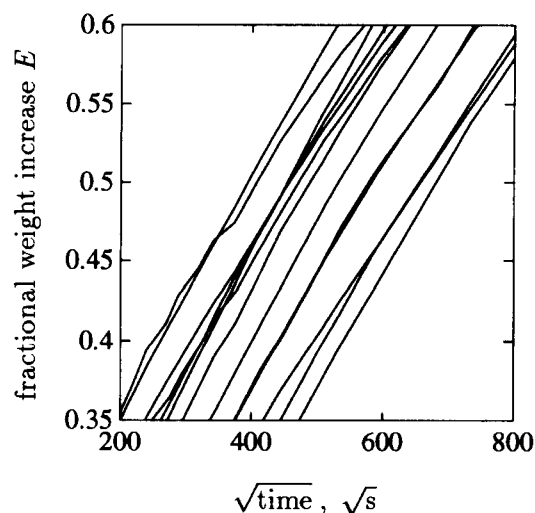


FIG. 7. The second slopes of 13 specimens of different woods, directions, and thicknesses are very similar in the interval  $0.35 < E < 0.6$  of Step C.

The initial slope lasts only about one hour and is fairly linear on a square root of time scale. It ends at approximately  $E = 0.2$ . The initial slope multiplied by the half thickness of the sample is given in Table 3. This parameter is similar for samples of the same type (but with different thickness). This indicates that the initial part of the sorption during Step C is governed by Fickian diffusion, as  $l \cdot dE/d\sqrt{t}$  is proportional to the square root of the diffusivity [Eqs. (1) and (2)].

The second slope in the sorption diagram is similar for all samples (Table 3). It is also quite linear (Fig. 7). In my opinion this is, however, not because the second stage of the sorption is governed by Fick's law. Not only Eq. (6), but many other functions  $f(x)$  with a decreasing slope when plotted versus  $x$  show large linear portions when plotted versus  $\sqrt{x}$ , e.g.,  $1 - \exp(-x)$ . As the wood used in this investigation is from six different woods, but still shows the same second-stage sorption behavior, it follows that this second stage of the sorption is probably not dependent on the wood anatomy, e.g., the cell-wall thickness. This is in accordance with the measurements of sorption on thin samples with very different cell-wall thicknesses by Christensen (1965). It should, however, be noted that it is somewhat strange that the slopes are so constant when they are plotted versus the square root of time.

Table 4 gives a literature survey of values of second slopes within approximately the same RH-range as my Step C. All these measurements were made in the absence of air and show distinct linear second stages. The second slope seems to be higher at higher temperatures.

It has been reported (Avramidis and Siau 1987) that the sorption can nearly cease at a quasi-equilibrium level before the onset of a second stage of the sorption. Such phenomena have also been reported for polymers sorbing solvent vapors (see e.g., News 1956; Berens 1978). No clear quasiequilibrium is seen in the results from the present measurements.

#### Final equilibrium

The measurements during both Steps B and C lasted for more than 100 days. Table 5 gives the moisture content changes during the two steps. It is also indicated if measurements have previously (Wadsö 1993f) been made on the sample ("old") or not ("new").

TABLE 3. Evaluation of first and second slopes during Step C. The first slope is calculated for  $E < 0.2$  and is multiplied by half the sample thickness. The second slope is calculated at  $0.35 < E < 0.6$ . Mean values and standard deviations are given for each group of samples.

Numbers and types of samples	First slope $l \cdot dE/d\sqrt{t}$ $10^{-6} \text{ m}/\sqrt{s}$	Second slope $dE/d\sqrt{t}$ $10^{-6} \text{ l}/\sqrt{s}$	Presence of an inflection point
7 pine S L 6.7–11.4 mm	21 ± 2	770 ± 20	yes
6 pine S R 4.1–6.7 mm	7.0 ± 0.7	760 ± 20	no
7 pine S TR 5.2–7.6 mm	5.9 ± 0.3	730 ± 30	no
13 pine S T 4.7–8.1 mm	6.5 ± 0.2	730 ± 30	no
6 pine H L 5.3–10.0 mm	19 ± 2	660 ± 10	yes
4 pine H TR 5.2–5.3 mm	5.1 ± 0.2	684 ± 4	no
4 spruce H T 1.9–3.8 mm	8.1 ± 0.1	640 ± 20	yes
4 ash L 5.0–10.1 mm	13 ± 1	750 ± 10	yes
4 ash R 5.0–9.7 mm	5.7 ± 0.4	650 ± 40	no
4 ash T 4.8–9.8 mm	3.9 ± 0.4	630 ± 80	no
2 aspen L 6.5–7.1 mm	14 ± 1	730 ± 30	yes
4 aspen TR 4.9–11.0 mm	4.1 ± 0.4	600 ± 70	no
4 cherry L 5.3–8.2 mm	15 ± 1	590 ± 10	yes
3 cherry TR 6.7–9.2 mm	6 ± 1	620 ± 10	no
3 willow L 5.1–8.1 mm	21 <sup>a</sup>	680 ± 10	yes
3 willow TR 5.8–10.5 mm	6.8 ± 0.6	660 ± 20	no

<sup>a</sup> Data from one sample only.

For Step B only minor differences between different types of samples may be noted: pine (H L and TR), ash (R), and cherry (L and TR) have lower total adsorption during Step B than the average sample. Aspen (TR) and willow (L and TR) have higher adsorption.

For Step C it is seen that “old” pine (S), pine (H L and TR), and spruce (H T) show a lower, and the “new” pine (S TR) and willow show a higher, total adsorption during Step C than the average sample.

It is not quite clear why the “old” pine (S) shows a lower adsorption during Step C than the “new” pine (S). As all samples were made from wood from the same log, there is probably not any great difference in the original material. The most probable explanation is that mold growing during the previous measurements with the “old” pine influenced the present experiment. During the previous measurement, all samples of pine (S) had mold after Step C. This does not, however, explain why a similar difference between “old” and “new” samples was not seen for Step B.

The moisture content changes during Steps B and C are not very different from the values from literature also given in Table 5, although they are on the low side.

#### Curve fitting

I have used two forms of Eq. (6) and calculated best fits by minimizing the square sum of the differences between measured and calculated data. This was done by a simplex procedure (Dennis and Woods 1987) on four curves from the present measurements. The evaluated parameters are found in Table 6.

In the first form, called M1,  $n = 2$  in Eq. (6), so there are five unknowns ( $D_c$ ,  $a_1$ ,  $\tau_1$ ,  $a_2$  and  $\tau_2$ ). Such a curve gives an accurate fit to the measured data, and the calculated diffusivity is in the same range as the steady-state diffusivity.

TABLE 4. Second slopes evaluated from data found in literature for sorption in approximately the same RH-interval as Step C.

			Second slope $\frac{dE/d\sqrt{t}}{10^{-6} \text{ l}/\sqrt{s}}$	Reference
1	40 C	74 → 89% RH	7,940	Christensen and Kelsey (1959)
2	25 C	70 → 82% RH	1,570	Christensen and Kelsey (1959)
3	25 C	77 → 88% RH	1,770	Christensen and Kelsey (1959)
4	25 C	83 → 90% RH	1,330	Christensen (1960)
5	40 C	63 → 84% RH	14,700	Kelly and Hart (1970)
6	23 C	75 → 84% RH	590–770	This paper (Table 3)

In the second form, called M2,  $n = 1$  in Eq. (6), but there are only two unknowns, as the diffusivity is held constant at a value taken from steady-state measurements. The results of M2 do not give as good a fit to the measured data, as do the results of M1.

The diffusivities calculated with M1 are in the same range as the values measured at steady-state. For Step C, the values of  $a$  are also similar to the values given in Table 2, and the time constants  $\tau$  found from the two models are in the same range. Both models thus seem to capture the main features of the anomalous sorption of Step C.

TABLE 5. Moisture content changes (kg water per kg dry wood) during steps B and C, compared with values from literature.

Number and types of samples		Moisture content change (%)	
		Step B	Step C
4 pine S L	old	4.13 ± 0.03	2.36 ± 0.02
3 pine S L	new	4.08 ± 0.02	2.63 ± 0.05
6 pine S R	old	4.12 ± 0.07	2.34 ± 0.09
7 pine S TR	new	4.11 ± 0.06	2.80 ± 0.09
13 pine S T	old	4.16 ± 0.03	2.45 ± 0.04
6 pine H L	new	3.78 ± 0.04	2.37 ± 0.02
4 pine H TR	new	3.82 ± 0.09	2.47 ± 0.05
4 spruce H T	old	4.15 ± 0.03	2.38 ± 0.03
4 ash L	new	4.06 ± 0.02	2.76 ± 0.01
4 ash R	new	3.89 ± 0.03	2.66 ± 0.05
4 ash T	new	4.07 ± 0.03	2.81 ± 0.01
2 aspen L	new	4.26 ± 0.02	2.69 ± 0.01
4 aspen TR	new	4.37 ± 0.15	2.76 ± 0.02
4 cherry L	new	4.04 ± 0.02	2.51 ± 0.02
3 cherry TR	new	4.02 ± 0.03	2.58 ± 0.03
3 willow L	new	4.37 ± 0.03	2.74 ± 0.03
3 willow TR	new	4.30 ± 0.02	2.82 ± 0.02
Bertelsen (1983) <sup>a</sup>		4.3	3.1
Okoh and Skaar (1980) <sup>b</sup>		4.1	2.9
USDA (1955) <sup>c</sup>		4.5	3.1

<sup>a</sup> Spruce in adsorption.

<sup>b</sup> Mean of ten North American hardwoods in adsorption.

<sup>c</sup> Mean of adsorption and desorption for different woods.

TABLE 6. Values of the parameters in Eq. (6) for two samples of pine. The models M1 and M2 have 5 and 2 unknowns, respectively.

Sample	No.	Step	Model	$D_c$ $10^{-12} \text{ m}^2/\text{s}$	$a_1$	$\tau_1$ $10^3 \text{ s}$	$a_2$	$\tau_2$ $10^3 \text{ s}$	$\tau_1/\tau_h$ Eq. 9
Pine (S L 6.7 mm)	1	B	M1	950	0.20	62	0.09	660	13
	2	B	M2	1,900 <sup>a</sup>	0.52	67	—	—	14
	3	C	M1	2,900	0.37	240	0.34	1,600	40
	4	C	M2	1,530 <sup>a</sup>	0.61	840	—	—	140
Pine (S T 4.9 mm)	5	B	M1	59	0.41	160	0.09	2,500	2
	6	B	M2	65 <sup>a</sup>	0.16	980	—	—	13
	7	C	M1	310	0.40	380	0.32	1,900	14
	8	C	M2	183 <sup>a</sup>	0.62	1,060	—	—	40

<sup>a</sup> Values measured at steady-state (Hansen 1991) used as input to the curve fitting procedure.

For Step B, the non-Fickian part seems to be overestimated in Simulations 2 and 5 (Table 6). In Simulation 2 this is probably because there are large disturbances to measurements in the longitudinal direction. For Simulation 5 the non-Fickian parts have partly taken over the Fickian part. The two other simulations for Step B (1 and 6) show lower values of the non-Fickian fraction. Equation (6) seems to give better results for curves from Step C, which are more anomalous, than for the curves from Step B.

The following limitations of the above curve fitting procedure have been noted:

1. If Eq. (6) is to have any physical meaning, the different processes must have very different time scales, as they are not coupled, but simply added. The Fickian part must also be the fastest. The time to reach half the weight change ( $t_h$ ) is a measure of the time scale of a Fickian sorption (p. 239 in Crank 1975):

$$t_h = 0.2 \frac{l^2}{D_c} \quad (8)$$

A nearly corresponding time scale of the relaxational part is  $\tau$ . I propose the following quite arbitrarily chosen criterion for regarding the processes as uncoupled:

$$\tau_1/t_h > 5 \quad (9)$$

This ratio is given in Table 6.

2. More than one set of  $D_c$ ,  $a_1$  and  $\tau_1$  may give approximately the same fit to a measured sorption curve (this problem is accentuated with two relaxation terms). Some of these will be nonphysical (like  $D_c < 0$  or  $a < 0$ ), but within the limits of accuracy of the measurements, there may exist several different, but nearly equivalent, solutions which are physically possible.

#### CONCLUSIONS

Measurements of water vapor adsorption on wood samples of many different wood types and thicknesses are presented. The wood samples were subjected to abrupt increases in relative humidity (RH) and the weights of the samples were measured for long periods of time.

The most important conclusion from these measurements is that Fick's law does not accurately describe the obtained sorption curves. Diffusivities calculated from sorption measurements using Fick's law may therefore be apparent coefficients, which should not be used uncritically in calculating moisture transport in wood.

New methods of evaluating sorption curves have been tested, leading to the following conclusions:

1. The adsorption from 54 to 75% RH is essentially Fickian, but the faster sorbing samples are influenced by initial disturbances (heat effect and surface resistance).
2. The adsorption from 75 to 84% RH is non-Fickian. It may be described as the sum of a Fickian component governed by the steady-state diffusivity, and a non-Fickian component. The non-Fickian fraction of the sorption was approximately 60% for all samples for which it was possible to calculate this fraction.
3. In the higher RH-interval mentioned above there is a second lower slope in the sorption curve. This second slope is similar for all samples. This indicates that the non-Fickian processes are independent of the cell-wall thickness and other structural differences between different kinds of wood. The slope is of the same order as slopes found in sorption curves in the literature.
4. Unexpectedly, it seems to be easier to evaluate the sorption curves which are more anomalous. The reason for this is probably that there are fewer disturbances to these measurements, as the rate of sorption is lower for this step.

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