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## Studies of water vapor transport and sorption in wood

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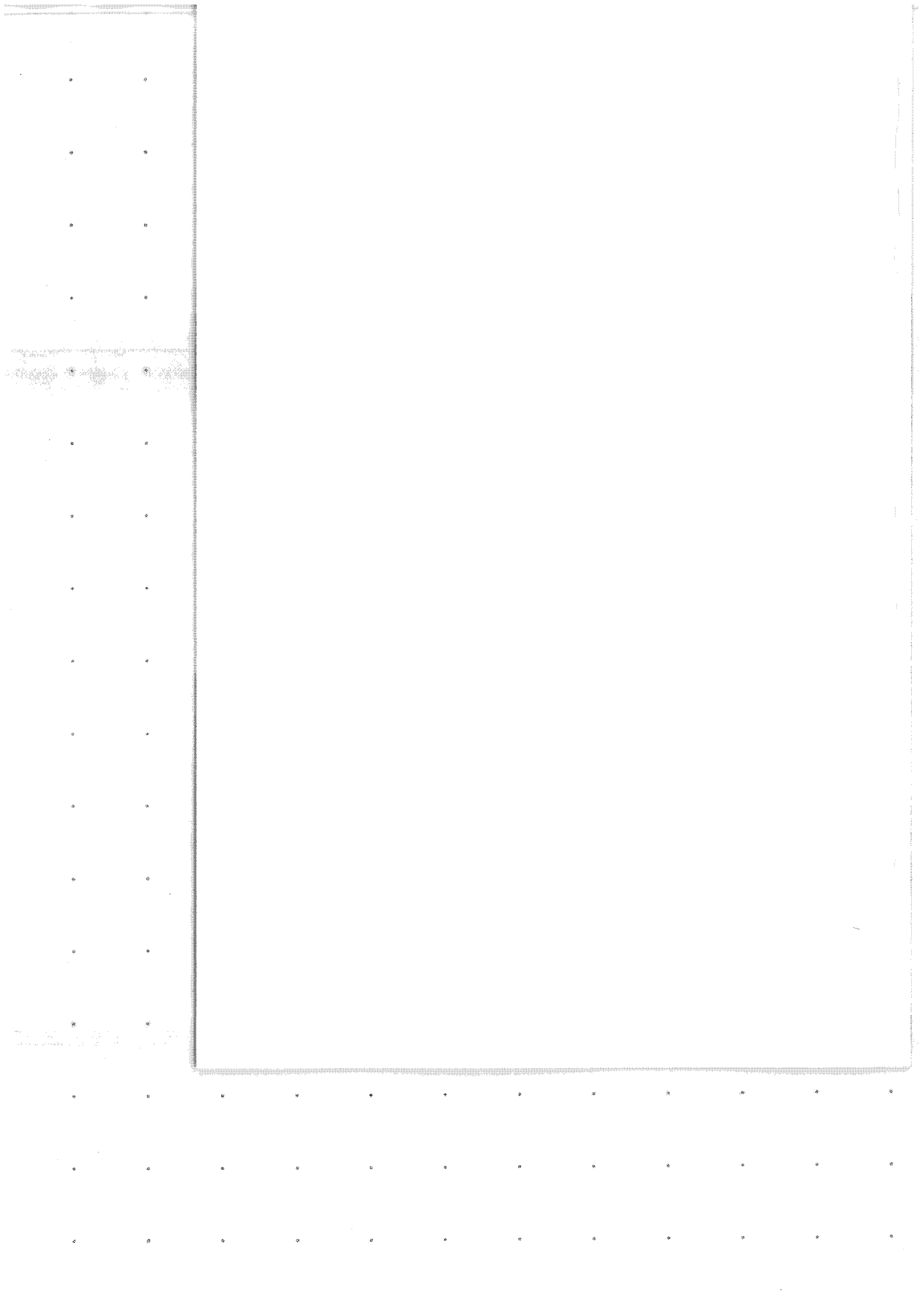
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**Studies of Water Vapor  
Transport and Sorption in Wood**

**Lars Wadsö**

**Doctoral Dissertation**



Studies of Water Vapor  
Transport and Sorption in Wood

Lars Wadsö



Doctoral Dissertation, Report TVBM-1013  
Building Materials, Lund University  
Lund 1993

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Transport and Sorption in Wood

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To Kerstin

Since then there has been a lot more mathematical analysis, but hardly any careful drying experimentation has been carried out to verify it. In general one wonders what the use is of solving all these equations, in particular if there is no indication as to which types of real systems the equations are applicable.

J. van Brakel (1980)



## Summary

This thesis deals with the evaluation of measurements of water vapor transport and sorption in wood. It mainly concerns measurements of the weight response of a sample after a step change in relative humidity (here called a "sorption measurement"). The thesis consists of an introduction and eight papers. The eight papers have the following contents:

- I A description of the instrumentation used and its performance characteristics.
- II Some first results on sorption in spruce wood. Non-Fickian behavior is observed above 75% relative humidity.
- III In this part the main experimental results are presented. At lower relative humidity (absorption from 54 to 75%) the conventional Fickian approach can describe the major part of the sorption process. At higher relative humidity (from 75 to 84%), however, the major part of the sorption is very slow and governed by non-Fickian effects, which are not dependent on direction of flow, sample size or wood species. The slow sorption of water vapor in the cell wall is believed to cause this phenomenon.
- IV A test of the effect of different disturbances (e.g. the surface resistance) on the conventional methods of evaluating sorption measurements is presented. It is shown that resulting errors in the calculated diffusivities may become large, and that different disturbances affect the tested methods in different ways.
- V In this paper problems concerning measurements of surface mass transfer coefficients are discussed. It is concluded that most measurements of such coefficients on wood surfaces are disturbed by the sorption being governed not only by a diffusivity and a mass transfer coefficient. The results from such measurements on wood surfaces are therefore uncertain. However, the size of surface mass transfer coefficients are known from theory and from measurements on other materials.
- VI The slow sorption of water vapor in the cell walls is a serious complication to sorption measurements, as the Fickian approach becomes invalid. This paper discusses how non-Fickian behavior in wood could be measured and modelled.
- VII An error analysis of a transient sorption measurement is developed. A number of error sources are treated one by one.
- VIII The error analysis is applied on two measurements from paper III.

These papers demonstrate that sorption measurements must be evaluated with great care. It is probable that many published measurements of diffusivities by the sorption method are disturbed, not only by the limited surface mass transfer, but also by non-Fickian effects and other disturbances like the temperature changes caused by the heat of sorption.





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a. Minor changes have been made in this paper since its publication.



# Studies of Water Vapor Transport and Sorption in Wood: An Introductory Paper

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## The thesis

The original aim of this study was to show that steady-state ("cup") and unsteady-state ("sorption") measurements were equivalent, i.e. that diffusivities may be evaluated from either one of them. This subject was chosen because the possibility of calculating moisture transfer in wood is of great importance for the design of wooden structures and building components. Therefore there is a need of good moisture transport data for both steady and unsteady conditions.

There were examples in the literature of experiments in which deviations between diffusivities evaluated from cup and sorption measurements had been found. I initially thought that these differences could be eliminated by careful experiments and evaluation of the results. This, however, was not completely possible.

For this study both cup and sorption measurements have been made (although the emphasis is on evaluation of sorption measurements). In the sorption method the diffusivity is evaluated from measurements of the weight change of a sample after an initial step change in relative humidity. In the cup method the diffusivity is evaluated from the measured flow through the sample at steady-state. I believe that cup measurements give true diffusivities in the sense that they may be used in Fick's law of diffusivity to calculate mass transport through wood, at least during steady-state conditions.

The diffusivity evaluated from a sorption

measurement usually differs from that of a cup measurement, even if the measurements were made on duplicate samples and under similar conditions. There are two reasons for this. Firstly, there are many sources of error which disturb sorption measurements, especially on fast sorbing samples. Secondly, the cup and the sorption methods work by different principles which are not always comparable.

The main sources of error in the present sorption measurements were the surface mass transfer coefficient, the heat of sorption and the imperfect relative humidity step. These are discussed in the thesis, and I believe their effects are known and may in some cases be compensated for.

The differences between the principles of cup and sorption measurements will also lead to differences in the evaluated diffusivities. If the diffusivity is concentration-dependent the two methods will average the diffusivity differently. This is, however, a small problem if the measurements are made in small relative humidity intervals.

A greater problem is the non-Fickian behavior, i.e. that Fick's law of diffusivity cannot always describe a process of transport and sorption in wood. When Fick's law is used for wood it is assumed that the cell wall sorption is fast, so that it does not disturb the Fickian behavior of the sample of whole wood. This assumption is not always true, as the sorption in the cell wall is a rather slow process, especially at higher relative humidities. In line with earlier investigations I show that at higher relative humidities the sorption is

largely governed by the cell wall, and not by the diffusion in the whole sample.

Below, I make a short description of wood, and moisture sorption and transport. The eight papers I-VIII, which form the main part of the thesis, and proposals for future work are also discussed.

## Wood

The properties of wood are governed by its structure and chemical composition, which will therefore be briefly discussed. Where no references are given, the account is based on standard textbooks, such as Kollman and Côté (1968), Siau (1984) and Skaar (1988).

### The living tree

The thousands of tree species on earth are divided into two main groups: conifers or softwoods, and dicotyledonous angiosperms or hardwoods. The softwoods have needles and the hardwoods have leaves (Fig. 1). Usually, but not always, the wood of a hardwood is harder than the wood of a softwood. Softwoods found in Sweden are pine, spruce and larch. Common hardwoods are birch, aspen, alder, oak and beech.

Most of the measurements presented in this study have been made on the two most common Swedish softwoods:

spruce (*Picea abies*)  
pine (*Pinus silvestris*)

Some measurements have also been made on four hardwoods:

ash (*Fraxinus excelsior*)  
aspen (*Populus tremula*)  
cherry (*Prunus avium*)  
willow (*Salix* sp.)

A tree consists of several parts with different functions. The root holds the tree to the ground and absorbs water and nutrient salts. The trunk, which is protected by the bark, transports the water to the branches and the leaves or the needles, where the energy of the

sunlight is captured through photosynthesis. The compounds formed are then transported down the inner bark and into the ray cells in the stem for storage. The center of the stem, which contains the first formed cells at each level of the trunk, is called the pith. Figure 2 shows a cross-section of a stem.

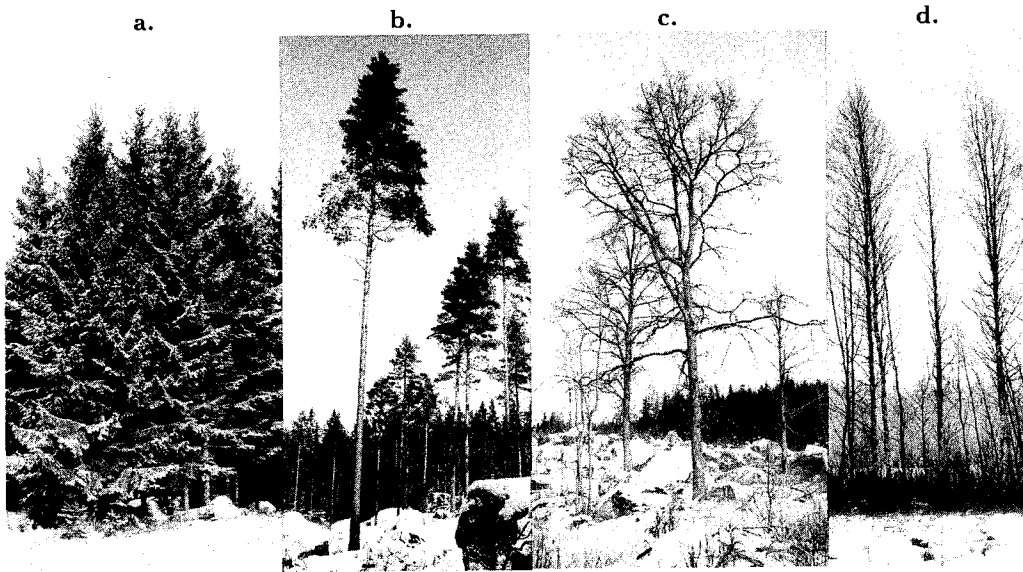
All parts of a tree are composed of cells of different types and sizes, which are formed by cell divisions in the cambium. This is a layer of living cells between the wood and the bark, i.e. the tree grows by adding new cells to the outside of the wood.

The major part (90-95%) of a softwood is made up of a type of cells called fibers, which are aligned more or less vertically. They give strength to the tree and serve as ducts for the transport of water from the ground to the crown.

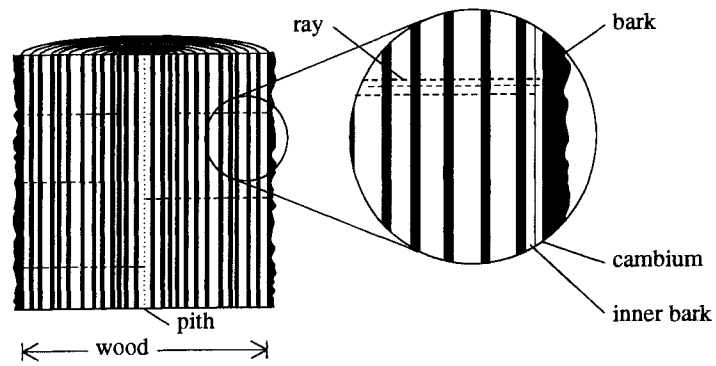
The cell nucleus of a wood fiber dies a short time after the cell has stopped growing. The fiber can, however, still function as a pathway for water transport, and as long as it does this it is part of the sapwood of the tree. In most trees (e.g. spruce, pine and oak) the fibers are cut off from the water transport after some decades of service. In pine and spruce this happens about 40 years after the fiber was formed. They then become part of the heartwood. In some species like pine and oak this has a darker color than the outer sapwood (Fig. 3). The heartwood may also become water repellent or more resistant to fungal attack. In some species, like spruce, there are, however, no visible differences between sapwood and heartwood.

The heartwood in a tree is cut off from the water transport, and has a lower moisture content than the sapwood (Table 1). This is clearly seen in newly felled trees, where the sap wets the sapwood while the heartwood remains dry.

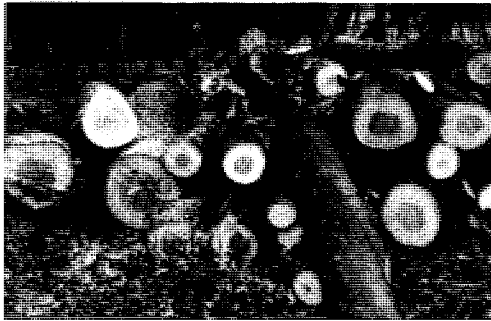
The water transport from the root to the leaves is by means of suction. As water evaporates from the leaves a negative pressure is developed in the leaves which sucks water through the fibers of the sapwood. This is



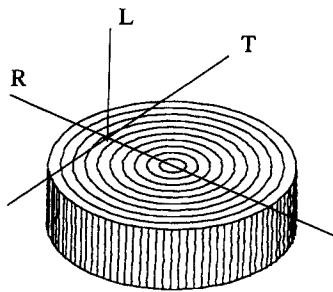
**Figure 1.** Four tree species photographed in wintertime in the southern part of Sweden. Spruce (a) and pine (b) are softwoods which retain their needles in wintertime. Oak (c) and birch (d) are hardwoods which shed their leaves for the winter.



**Figure 2.** Schematic cross-section of a softwood stem.



**Figure 3.** The sapwood and the darker heartwood are clearly seen in these logs of oak.



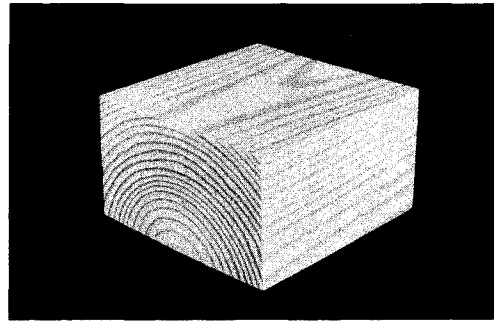
**Figure 4.** The directions in wood in the point where the three lines intersect (L is longitudinal, R is radial and T is tangential).

made possible by the structure of the very small tubes for water transport in wood (Zimmermann 1983).

Directions in a piece of wood are termed longitudinal (L), radial (R) and tangential (T) (Fig. 4). Note that the R- and T-directions are different for different locations in the tree. As the R- and T-directions in many respects show similar properties, they are often called the transversal directions.

### Macro-structure

The wood samples from the six tree species used in the present measurements have quite different properties. Pine and spruce are the two most common tree species in Sweden. They are mainly used as construction materi-



**Figure 5.** A piece of pine wood.

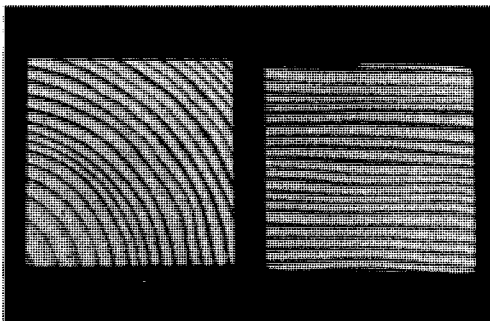
als (and as pulp for paper making). Ash and cherry are strong, heavy woods, used in furniture making and in other carpentry. Ash was formerly much used for mechanical parts, e.g. wheel spokes, and is still common in tool handles. Aspen is a low density wood which is well known for its use in matches. Willow is a weak, light wood which has not found much use except in basketry.

A defect free piece of a softwood is shown in Fig. 5. Conspicuous features are the alternating light and dark annual growth rings and the different surfaces, which show different growth ring patterns.

The growth rings contain fibers of two kinds: earlywood and latewood fibers. The earlywood fibers are formed in spring when the tree starts to grow after the winter. Their main task is to transport water and nutrient salts from the root to the leaves. They are therefore thin-walled, with large cell cavities (lumens).

The latewood fibers are formed during the summer when the tree has time to consolidate itself. They are thick-walled, with small lumens, and their main task seems to be to give strength to the tree. As the latewood cells contain a higher fraction of cell wall substance, they show up as dark bands in the wood, the lighter bands being the earlywood fibers.

The earlywood and the latewood have different properties, e.g. the density of the latewood is often twice that of the earlywood.



**Figure 6.** Samples of pine showing different curvatures of the growth rings.

In some hardwoods the vessel cells are much larger in the earlywood (cf. Figs. 9a and 9b).

Engineering materials are normally treated as isotropic, i.e. they are thought to have the same properties in all directions. Examples of such materials are metals and concrete.

Wood is always anisotropic, i.e. it has different properties in different directions (some properties in different directions of pine-wood are listed in Table 1). One must take this anisotropy into account when measuring material properties or simulating the behavior of wood.

Knots and other deviations from the regular growth ring structure are also part of the structure of wood. In mechanical calculations these are important, as a fracture often starts at a stress concentration caused by an irregularity of a structure. For moisture behavior such deviations are not as important, but in most experiments on wood one uses small specimens showing no knots or other deviations from the ideal structure.

As the curvature of the growth rings is lower near the bark than near the pith, samples in which one wants to measure a property in the radial or tangential direction are preferably made from wood near the bark (Fig. 6).

A common defect of wood is reaction wood. When a tree grows under stress (from the wind or because it is growing on a slope) the stem is not developed symmetrically. On one side compression wood is developed, and on the

**Table 1.** Typical values of properties and dimensions of Swedish pine and spruce. When a figure is given for a specific direction, this is marked by L, R, T or TR (transversal).

dry density	450 kg/m <sup>3</sup>
sapwood moisture content <sup>a</sup>	1,5 <sup>b</sup>
heartwood moisture content <sup>a</sup>	0,55 <sup>b</sup>
fiber saturation point <sup>a</sup>	0,3
moisture content <sup>a</sup> under roof <sup>c</sup>	0,15–0,25
moisture content <sup>a</sup> indoors <sup>c</sup>	0,05–0,1
fiber length	2 mm
earlywood fiber diameters	40×40 μm <sup>2</sup>
latewood fiber diameters	20×40 μm <sup>2</sup>
earlywood cell wall thickness	5 μm
latewood cell wall thickness	8 μm
heat conductivity (L)	0,25 W/(mK)
heat conductivity (TR)	0,1 W/(mK)
diffusivity <sup>d</sup> (L)	1,5·10 <sup>-9</sup> m <sup>2</sup> /s
diffusivity <sup>d</sup> (R)	0,3·10 <sup>-9</sup> m <sup>2</sup> /s
diffusivity <sup>d</sup> (T)	0,3·10 <sup>-9</sup> m <sup>2</sup> /s
compression strength <sup>e</sup> (L)	50 MPa
compression strength <sup>e</sup> (R)	8 MPa
tensile strength <sup>e</sup> (L)	100 MPa
elastic modulus <sup>e</sup> (L)	11 000 MPa
elastic modulus <sup>e</sup> (TR)	500 MPa
shrinkage <sup>f</sup> (%) (L)	0,4
shrinkage <sup>f</sup> (%) (R)	4
shrinkage <sup>f</sup> (%) (T)	8

a. kg water per kg dry wood.

b. At felling.

c. Scandinavian climate.

d.  $D_c$  at 75% RH and steady-state (cf. Eq. 1).

e. Small defect-free samples at 75% RH.

f. From saturated to dry conditions.

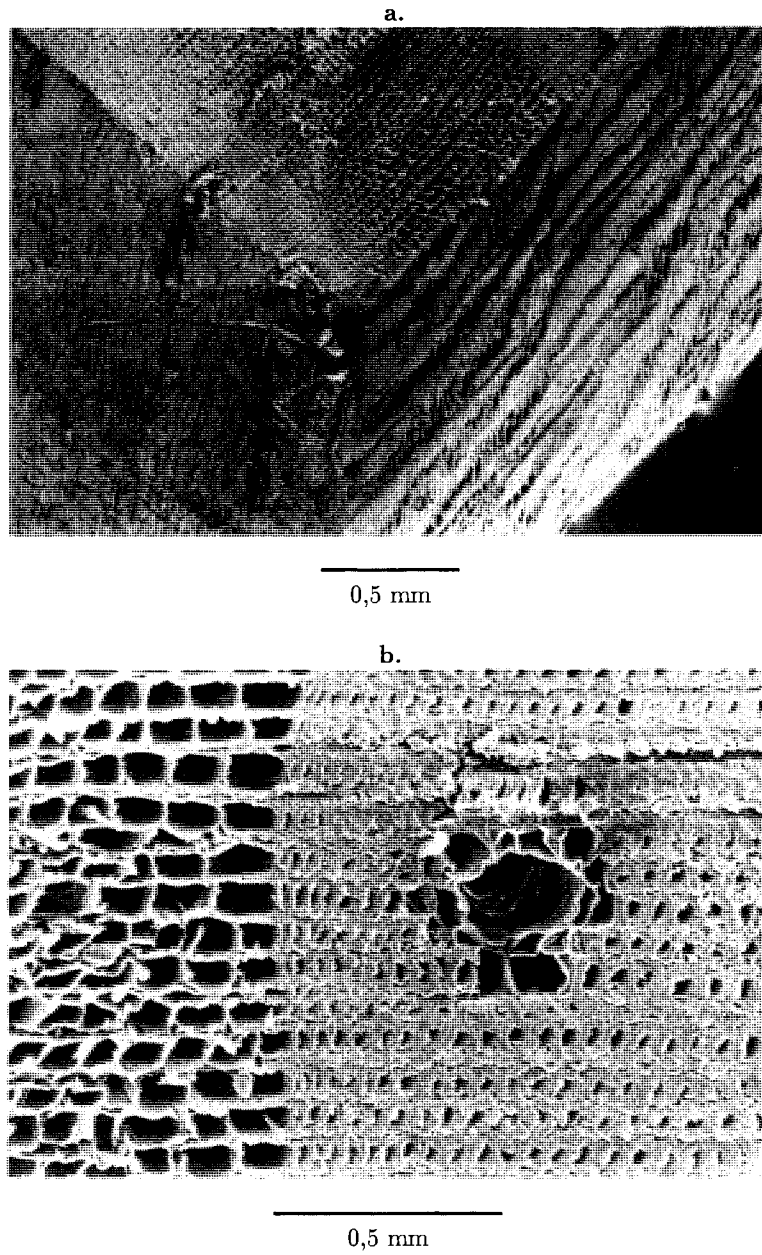
other side tension wood. These have different microstructure and properties (e.g. swelling and strength) than normal wood and may therefore cause problems when the wood is used. The samples used in this study do not contain reaction wood.

Table 1 gives examples of typical properties and dimensions of spruce and pine wood.

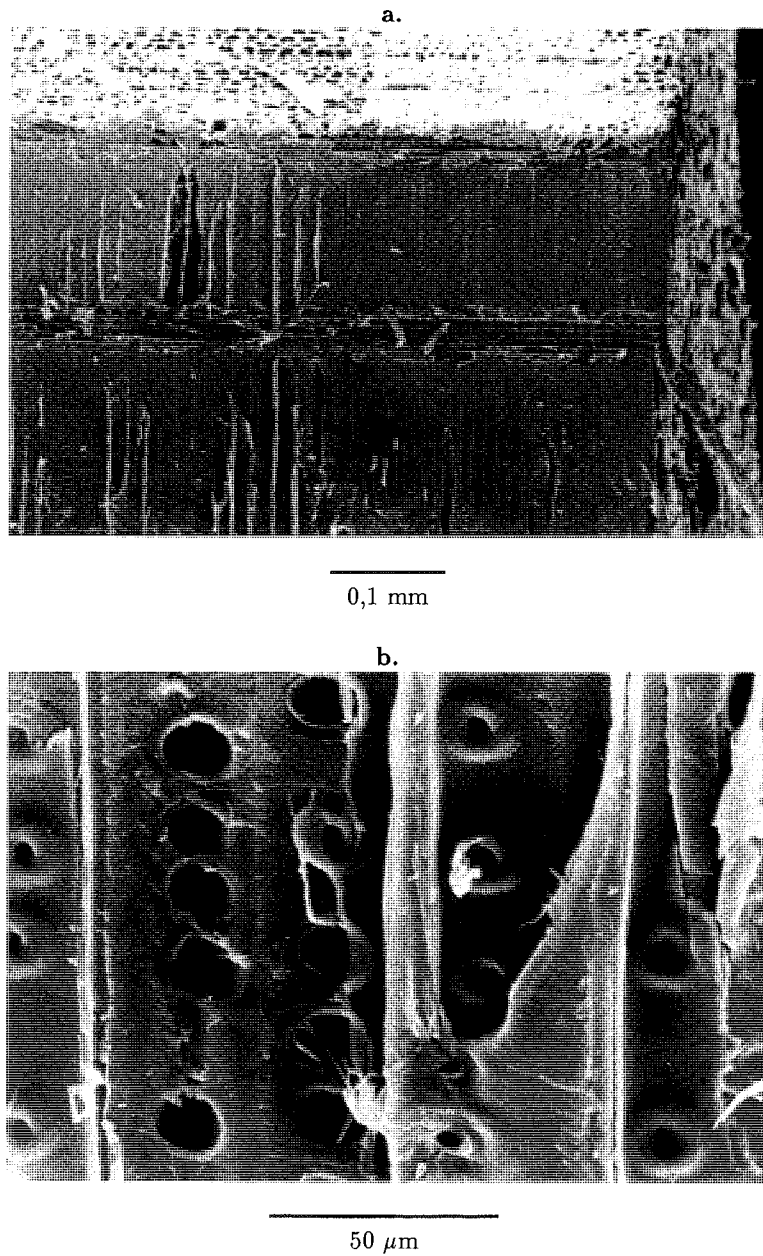
## Microstructure

The structure of wood is very complex when viewed through a microscope. Figures 7 to 10

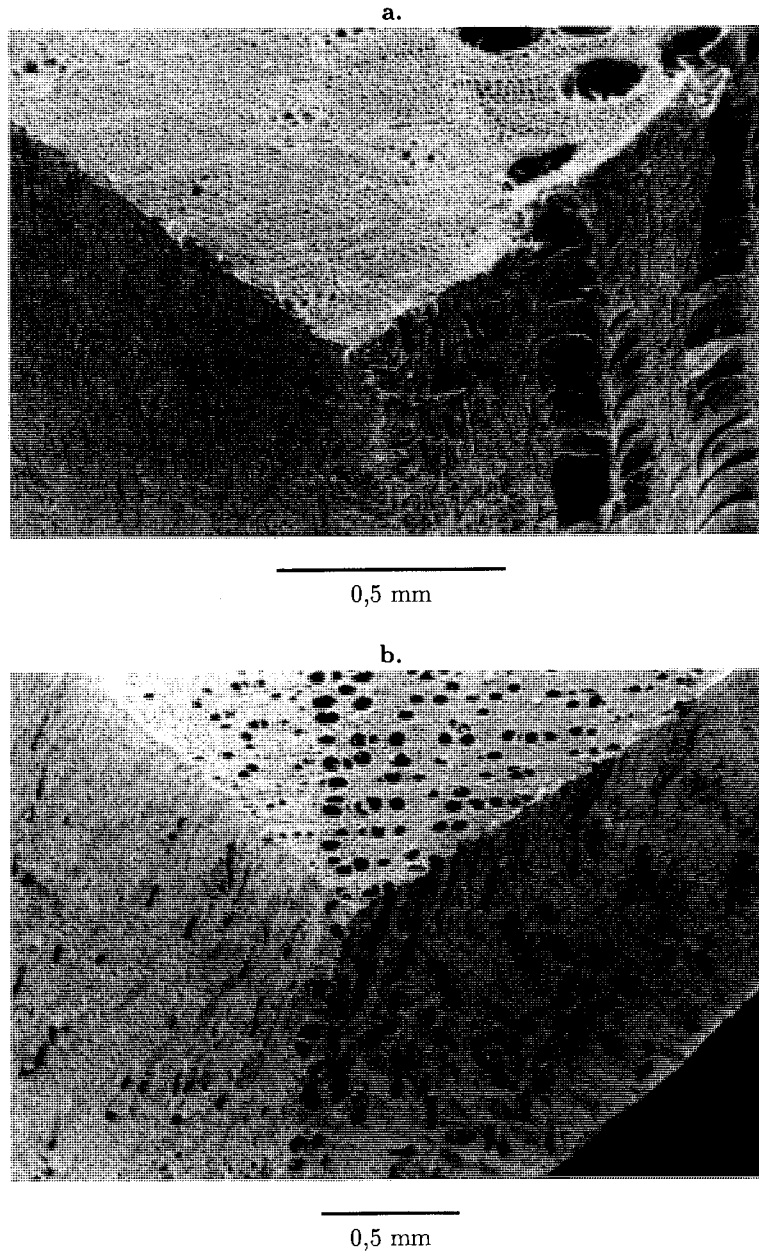




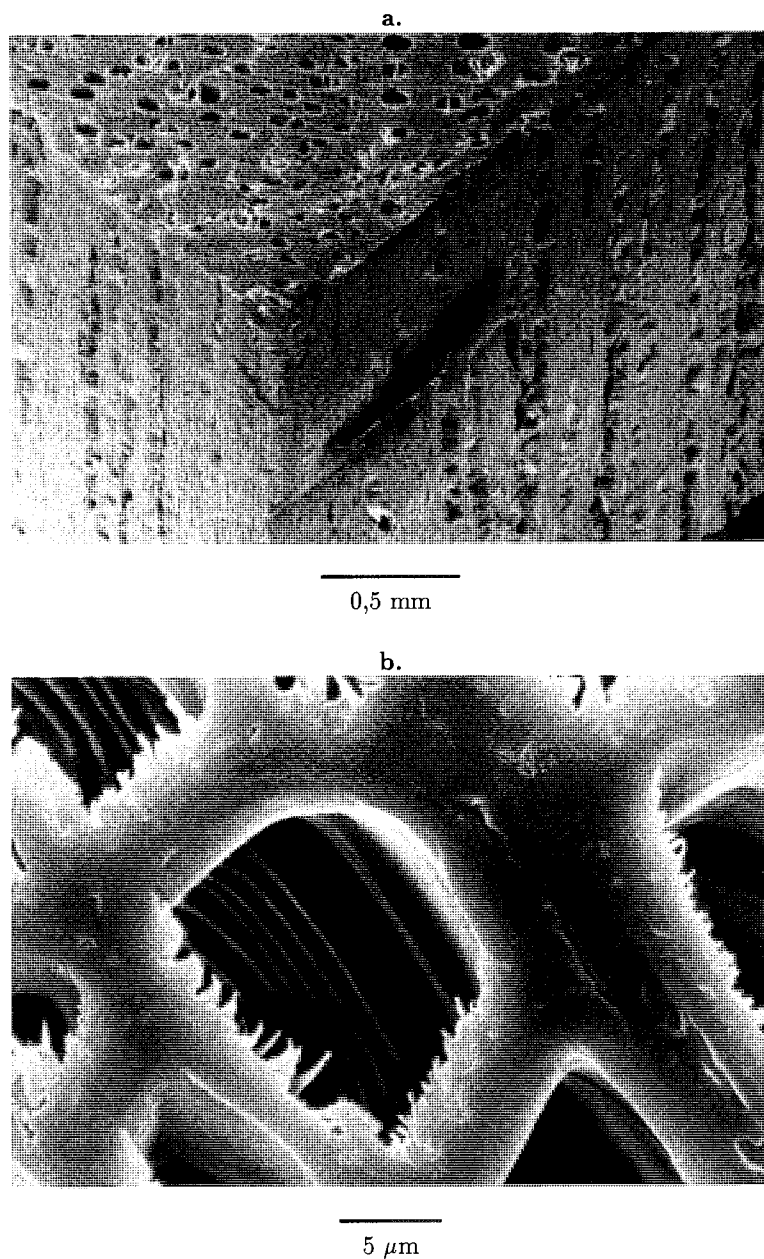
**Figure 7.** Pine wood (*Pinus silvestris*) used in this study as viewed with a scanning electron microscope (SEM). **a.** A corner with the three surfaces facing in approximately the three principal directions (top: longitudinal; left: radial; right: tangential) **b.** The abrupt transition from latewood (left) to earlywood (right) and the difference in dimensions in these two types of fibers are clearly seen, together with a resin duct.



**Figure 8.** Pine wood (*Pinus silvestris*) used in this study as viewed with a SEM. **a.** This close-up shows ray cells running perpendicular (horizontally in the picture) to the fibers. **b.** Pit pores on the tangential faces of the fibers. Note that some pores are closed by pore membranes (the missing membranes may have been removed in the preparation of the sample for the SEM).



**Figure 9.** SEM pictures of anatomical details of two of the hardwoods used in this study. The hardwood structure is more complex than the softwood structure (cf. Fig. 7a). The top surfaces on the samples are facing in the longitudinal direction. The other surfaces are facing in the transversal directions. Note the large anatomical differences between these two tree species (e.g. in cell size and in cell distribution). **a.** Ash (*Fraxinus excelsior*). **b.** Cherry (*Prunus avium*)



**Figure 10.** SEM pictures of anatomical details of the willow wood (*Salix caprea*) used in this study. **a.** The top surface is facing in the longitudinal direction. Note the high porosity in this light wood and that the cells of different sizes are distributed evenly. **b.** A closeup of a willow surface facing in the longitudinal direction. The insides of the cells are lined with rolls.

give examples of this. The earlywood fibers with thin walls and large lumens, and the latewood fibers with thick walls and smaller lumens, are clearly seen in Fig. 7b. As mentioned before, these cells make up the major part of a softwood. Resin ducts (Fig. 7b) and ray cells (Fig. 8a) are also prominent features of most softwoods.

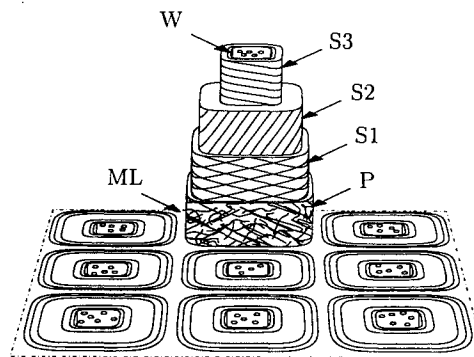
The lumens are connected by pores of different kinds. These are seen on the walls of the fibers facing in the tangential direction in Fig. 8b. Most pores have membranes which close when the wood is dried. If wood is water-stored for a long time, bacteria may destroy these membranes, leading to an increased capacity for the absorption of liquid water.

Figures 9 and 10 show anatomical details of ash, cherry and willow. These three species contain the same kinds of cells, but they are arranged in different ways. Hardwoods contain vessels, a kind of cells not present in softwoods, which are used for the transport of water. In some species, like ash and oak, these are large enough to be easily visible to the naked eye (Fig. 9a). In cherry (Fig. 9b) the vessels are found in both earlywood and latewood, although they are larger in the earlywood. In willow (Fig. 10a), which does not show much difference between its earlywood and latewood, similar vessels are found in all parts of the wood.

All wood cells have very complicated microstructures. A scanning electron microscope (SEM) reveals more of this as the magnification is increased, see e.g. Fig. 10b. With special preparation techniques, it is also possible to show that the cell wall consists of a number of layers (Fig. 11) which have different compositions and orientation of the cellulose microfibrils (described below).

### The cell wall constituents

Wood is mainly composed of three polymers: cellulose, hemicellulose and lignin. These are all very large molecules, but with different properties. The amounts of them in pine and



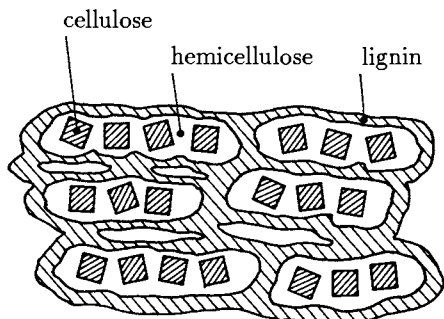
**Figure 11.** A schematic drawing of the main structural details of a wood fiber. It consists of a primary layer (P) and three secondary layers (S1, S2 and S3). The inside of the S3 layer is coated with a warty layer (W) which is very thin. The fibers are held together by the middle lamella (ML). The S2-layer makes up the major part of the cell (approximately 85% of the cell wall thickness in *Picea abies*). The microfibrillar angles are indicated by the lines in the different layers of the fiber wall.

spruce wood are approximately 42% cellulose, 26% hemicellulose and 30% lignin.

Different models have been proposed as to how the constituents are organized in the cell wall. Figure 12 shows one such model, which is not very detailed, but gives a general idea of the structure. Note that the polymers are not mixed, but arranged in separate entities.

Cellulose is a non-branched polymer consisting of some 5000–10 000 glucose units. It is a major part of all plant materials and the most occurrent polymer on earth. In wood, several cellulose molecules are arranged parallel to each other, like the strands of a sewing thread. These are called microfibrils. In some parts of a microfibril the cellulose chains are ordered with respect to each other (crystalline); in other parts they are not ordered (amorphous). The crystallinity of wood cellulose is approximately 50%.

Amorphous cellulose absorbs water vapor, i.e. it is hygroscopic. The water molecules attach themselves to the OH-groups on each



**Figure 12.** Schematic drawing of the organization of the components in the S2-layer of the fiber wall (adapted from Salmén 1991).

glucose unit. In the crystalline parts the absorption is very limited, as most OH-groups are bonded to OH-groups in neighboring cellulose chains. Cellulose in wood may therefore be regarded as two different substances with different moisture properties.

Hemicellulose is a branched polymer built from different kinds of sugar units. The proportions of these units are different for different kinds of tree species. Hemicellulose has about the same hygroscopicity as amorphous cellulose.

The third major component of wood is lignin. This is also a branched polymer, but it is composed of phenyl-propane units. Its structure is very complex and its hygroscopicity is lower than that of hemicellulose and amorphous cellulose.

Wood also consists of minor fractions of extractive substances. These are sugars, salts, fats, pectin, resin and others. Such substances may influence properties like durability, wettability and color, but do not affect mechanical properties and water vapor transport and sorption as much.

A cellulose microfibril is strong in tension, but weak in compression; just like a thread. The structure of the cell wall is, however, such that wood also can take some compression

stresses, but in contrast to many other materials wood is stronger in tension than in compression.

## Moisture sorption in wood

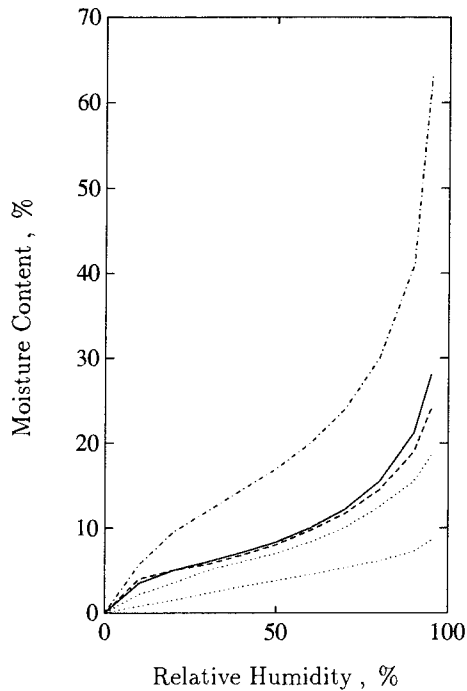
Wood is a hygroscopic material. Figure 13 shows how much water vapor wood absorbs at different relative humidities (—). This diagram is called a sorption isotherm or a moisture equilibrium curve. It is similar for all wood, as all tree species have similar cell wall composition.

The isotherms in Fig. 13 are for absorption. Corresponding curves for desorption lie above the curves for absorption, as there is a hysteresis in the sorption behavior.

The sorption isotherm gives the moisture content of wood up to relative humidities near 100%. At this point the cell walls of wood are saturated with moisture. The moisture content, the weight of water divided by the weight of the dry wood, is then around 30%. This is called the fiber saturation point. The lumens, however, may also be filled with water. This can be done by immersing the wood in liquid water. The moisture content may then increase up to a maximum of more than 200%.

This thesis deals with relative humidities up to 84%, i.e. there is no liquid water present. At such relative humidities all moisture is absorbed by the cell wall substance. The sorption is a sorption *in* the cell wall material.

By chemical processes it is possible to separate the cell wall components and measure their sorption isotherms. Figure 13 shows the result of such measurements, from which it is possible to construct the sorption isotherm of whole wood by adding the curves for the different components multiplied by their weight fractions in wood (Christensen and Kelsey 1959b, Takamura 1968). Note, however, that the chemical processes used to isolate the cell wall components will probably change the original structure of these polymers.



**Figure 13.** Absorption isotherms of wood and the wood constituents at 25°C: wood (—), hemicellulose (- - -), wood cellulose (- · -) and lignin (· · ·). Two curves are shown for lignin prepared in two different ways. Adapted from Christensen and Kelsey 1959b. Moisture content is here expressed as weight of water per weight of dry wood (%).

Many other hygroscopic materials sorb water by surface and capillary condensation. Very small pores can hold liquid water at low relative humidities, e.g. at 90% relative humidity a pore with a radius of  $0,01\mu\text{m}$  will be filled with water. An example of such a material is concrete. The pore system in concrete consists of minute pores which are thought to absorb large amounts of water. This is *not* the process by which water is absorbed in wood. The cell wall has only about 2% pore volume (Stamm 1964) and the lumens are too large for this kind of condensation to occur. Vapor sorption in wood is by sorption on binding sites in the wood constituents.

## Moisture transport in wood

### Theory

Water vapor transport in wood is by diffusion, i.e. the random motion of molecules tends to level out differences in concentration. This is a very common process which is found in all solids, liquids and vapors, e.g. hydrogen molecules in metals, sodium chloride ions in water, and odorants in still air.

Diffusion was first clearly understood by Adolf Fick (1855, see also Tyrell 1964). He studied diffusion of ions in water and found that the following law, which has since been called Fick's law, described the process:

$$F = -D_c \frac{\partial c}{\partial x} \quad (1)$$

Here  $F$  ( $\text{kg}/\text{m}^2\text{s}$ ) is the flux,  $D_c$  ( $\text{m}^2/\text{s}$ ) is the diffusivity,  $\partial c$  ( $\text{kg}/\text{m}^3$ ) is the difference in concentration over the distance  $\partial x$  (m). The ratio  $\partial c/\partial x$  is the gradient in moisture. The minus sign indicates that the transport is in the direction of negative gradient, i.e. from high to low concentration.

Actually, Fick did not state Eq. 1 (which is often called Fick's first law), but the following form:

$$\frac{\partial c}{\partial t} = D_c \frac{\partial^2 c}{\partial x^2} \quad (2)$$

Equation 2 is often called Fick's second law. It is found from Eq. 1 and the continuity equation (mass conservation):

$$\frac{\partial F}{\partial x} = -\frac{\partial c}{\partial t} \quad (3)$$

Fick's law is analogous to many other transport laws, like Ohm's law of electricity and Fourier's law of heat conduction. All these laws simply state that the transported amount of  $X$  is proportional to the gradient in a potential of  $X$ , the constant of proportionality being a conductivity.

For diffusion of ions in water the above equations are sufficient, but for Eq. 2 to be of any use in describing the sorption of vapor

into a material, the sorption isotherm must also be known:

$$c = f(\phi) \quad (4)$$

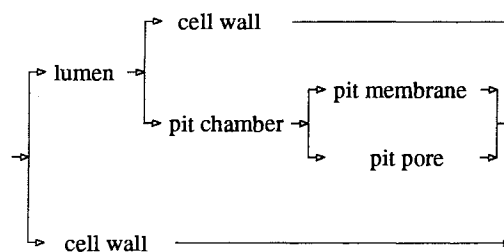
Here  $\phi$  is the relative humidity and  $f$  is a function describing the relationship between  $c$  and  $\phi$  (cf. Fig. 13). The sorption isotherm is needed as a relation between the moisture states of a specimen and its surroundings.

Fick's law is used with many different potentials, e.g. concentration (as in Eq. 1) or vapor pressure. This may cause confusion if it is not clearly stated which potential is used. The diffusivity has different numerical values and units for different potentials. In other transport laws, only one potential is normally used and no confusion is then possible. In the laws of Ohm and Fourier, voltage and temperature are the potentials. The index  $c$  in  $D_c$  is used to emphasize that the diffusivity is expressed with concentration of moisture in wood ( $c$ ) as potential.

Another complication connected with Fick's law is that the diffusivity is not a constant, but a function of the potential. Because of this, problems involving moisture diffusion are often harder to solve than problems involving heat conduction.

The transport of water molecules in wood is mainly by bound water flow and by water vapor diffusion. However, only the total flows may be measured. The flow of moisture in wood may be modelled by coupling the flows in the different components of the wood cell. Figure 14 shows such a model. It is illustrative, but it is difficult to determine the flows in the different components. Stamm (1959, 1960a) and Yokota (1959), for example, have made measurements of the diffusivity of the cell wall, which in my opinion are very uncertain.

If a sorption process is governed by Eqs. 1, 3 and 4 it is called "Fickian" in this thesis. A "non-Fickian" process is one which cannot be described only by these equations, as there are also other processes governing the transport and sorption within the wood. The most prob-



**Figure 14.** A model of the diffusion of water vapor and bound water in a softwood fiber (adapted from Stamm and Nelson 1961).

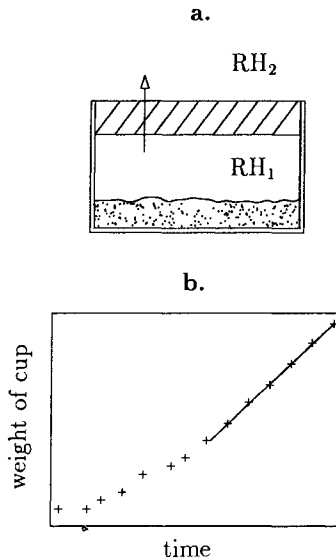
able cause of the non-Fickian behavior seen in wood is the slow or delayed sorption of moisture in the cell walls (Christensen 1965). The term "non-Fickian" has been used since the discovery of these phenomena in polymers (see e.g. Kishimoto et al. 1960, Petropoulos and Roussis 1974, Berens and Hopfenberg 1978, Crank 1975). It should, however, be noted that such non-Fickian behavior as is found in wood cannot occur in the simple system studied by Adolf Fick. The term "non-Fickian" is therefore not completely appropriate.

### Measurements of vapor transport

There are basically two methods for measuring diffusivities in wood: the steady-state cup method and the transient (or unsteady-state) sorption method. Both these methods have been used in the present study, but the sorption method has been investigated in greater detail.

In cup measurements (Fig. 15) a sample of wood is fastened as a lid on a cup. Inside the cup is a saturated salt solution or a drying agent which regulates the relative humidity ( $RH_1$  in Fig. 15a). The cup is placed in an atmosphere with a relative humidity  $RH_2$ . If the relative humidity is higher inside the cup than outside, moisture will flow through the sample out of the cup. The weight of the cup will then decrease. The method may also be used with the highest RH outside the cup. In



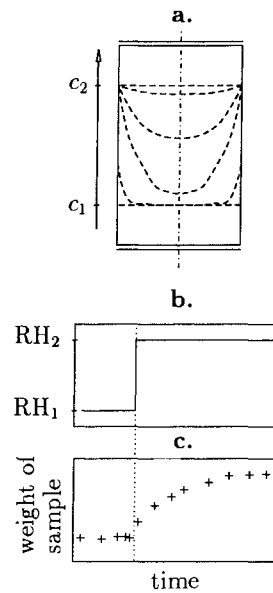


**Figure 15.** A schematic description of a cup measurement. **a.** The cup with an arrow indicating the moisture flow when  $RH_1 > RH_2$ . **b.** From the weight change of the cup as a function of time one may calculate the diffusivity.

that case, a weight gain is recorded. When the cup is weighed at regular intervals at steady-state the weight change is a linear function of time (Fig. 15b). From the slope of the weight change versus time, it is possible to calculate the diffusivity.

Cup measurements on wood were first performed by Martley (1926a), who also measured the moisture content profile of the sample at steady-state. Some examples of more recent measurements on wood with this method are Comstock (1963), Choong (1965), Tveit (1966), Hart (1970), Skaar et al. (1970), Kurjatko (1974), Schneider (1980), Bertelsen (1983), Liu Tong (1988, 1989), Vanek and Teischinger (1989), McLean et al. (1990), Thomas and Burch (1990) and Lee et al. (1991ab).

The cup measurements on pine used in this thesis were made by Kurt Kielsgaard Hansen (1991) at the Technical University of Denmark by use of an apparatus described in West and



**Figure 16.** A schematic description of a sorption measurement. **a.** A cross-section of a sample with concentration profiles during a sorption measurement. **b.** The step change of RH. **c.** The resulting weight change from which the true diffusivity can be calculated if Fick's law describes the sorption process.

Hansen (1988).

In sorption measurements (Fig. 16), the sample is first equilibrated in an initial relative humidity  $RH_1$  until it is at equilibrium with this and shows no weight change. The relative humidity outside the sample is then rapidly changed to a new value  $RH_2$ . As wood is hygroscopic the sample will absorb or desorb water vapor depending on whether  $RH_2$  is higher or lower than  $RH_1$ . This is measured by weighing the sample at regular intervals. The result, normally plotted as a function of the square root of time, is here called a sorption curve (cf. Crank 1975). From the initial slope of such a curve it is possible to calculate the diffusivity (which may not be a true diffusivity if the sorption process cannot be described with Fick's law only).

Tuttle (1925) was probably the first to describe the use of a sorption method to measure

moisture transport properties in wood. The measurements were made from above fiber saturation down to the hygroscopic region, i.e. there was initially liquid water present in the wood. Similar measurements were also made by Sherwood (1929), Bateman et al. (1939), Egner (1934), Voigt et al. (1940) and Ogura (1950ab). As moisture flow above the fiber saturation point is governed not only by diffusion, but also by capillary transport, the usefulness of the sorption method in such a case is rather doubtful. Maku (1951) may have been the first to make a sorption measurement in the hygroscopic range. Some more recent papers which describe sorption measurements on wood are: Stamm (1960b), Stamm and Nelson (1961), Comstock (1963), Biggerstaff (1965), Simpson (1974), Skaar et al. (1970), Droin et al. (1988), Droin-Josserand et al. (1988), Liu Tong (1988) and El Kouali and Vergnaud (1991).

There are also some less commonly used methods of measuring diffusivities, e.g. by studying the weight changes of two samples of different initial relative humidity which are put in contact with each other (Martley 1926b).

## Evaporation and condensation

This study also deals with the flow of moisture from a sample to the air, and flow from the air to a sample. This phenomenon was first fully understood by John Dalton (1802). He found that the evaporation from a liquid was proportional to the difference in vapor pressure at the surface of the liquid and in the air. This can be stated in a more general form as:

$$F = k_p(p_s - p_a) \quad (5)$$

Here  $F$  ( $\text{kg}/\text{m}^2\text{s}$ ) is flux (as in Eq. 1),  $k_p$  ( $\text{kg}/(\text{m}^2\text{s Pa})$ ) is the mass transfer coefficient, and  $p_s$  and  $p_a$  are the vapor pressures (Pa) at the surface and in the ambient air, respectively. The surface may be liquid or solid.

The mass transfer coefficient is dependent on external factors like air velocity, surface

roughness and the shape of the surface. It is not, however, dependent on the properties of the material in the sample.

When moisture transport, e.g. the drying of wood, is described one has to take both Eqs. 1 to 4, and 5, into account, the first ones for the internal diffusion and the last one for the external transport.

## Limitations of this study

This study has been made under the following conditions:

1. This thesis is a study of the sorption method as a method for measuring diffusivities.
2. The experiments were made at a temperature of  $23^\circ\text{C}$  and an air velocity of 3 m/s.
3. The measurements described were performed below 84% relative humidity, i.e. no liquid water was present.

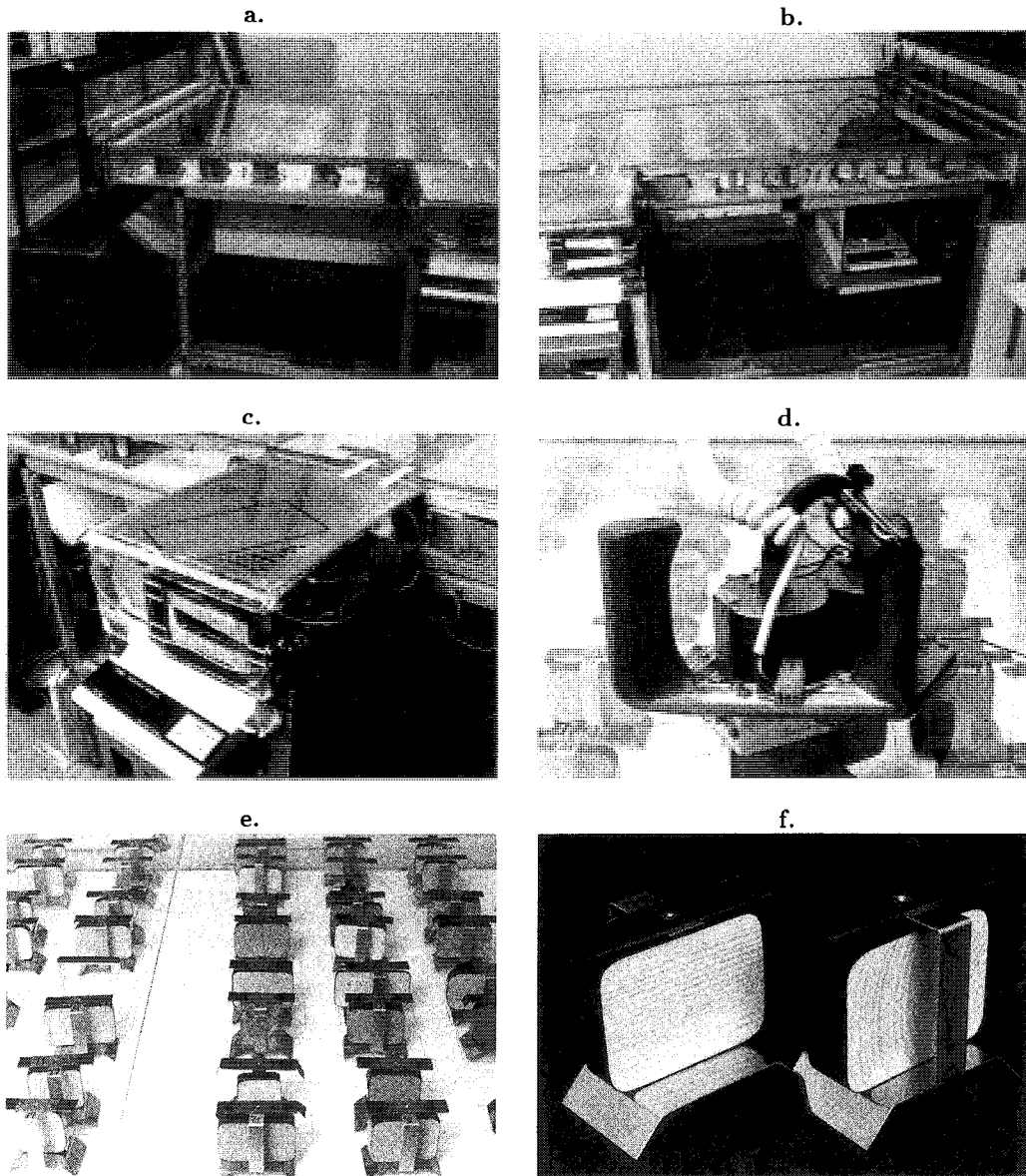
## Short summaries of the papers

This thesis consists of eight papers which are summarized below.

**Paper I. Instrumentation.** The apparatus is essentially a wind tunnel in which 117 specimens may be placed. The relative humidity is controlled by saturated salt solutions. Figure 17 shows different parts of the instrumentation. The paper contains a description of the instrument and its performance characteristics.

**Paper II. First results.** Results from a first run with the instrumentation are reported. It is shown that sorption at higher RH cannot be described with Fick's law. Only results from measurements on 4 and 8 mm tangential spruce samples are presented.

**Paper III. Main results.** Results from sorption measurements on 78 wood specimens are presented. The measurements were made in the intervals 54 to 75% and 75 to 84% RH on wood from pine, spruce, ash, aspen, cherry and willow. For each species, measurements



**Figure 17.** Photographs of the instrumentation used in the present study (cf. Figs. 1 and 2 in paper I). **a.** The left part of the apparatus with the fan in the lower left and the balance to the right. The salt pans are in the lower part and the samples are in the upper part. **b.** The right part of the apparatus. **c.** The balance and the weighing compartment. **d.** The electromagnet used for moving the samples. **e.** Samples in the apparatus. **f.** Two samples with frames.

were made on samples with different thicknesses and with the flow in different directions.

In the lower RH-range, the major part of the sorption was Fickian, although there was also a minor non-Fickian component.

In the higher RH-range, the major part of the sorption was governed by non-Fickian behavior. It was found that samples of different species, thicknesses and flow directions had approximately the same behavior after the first Fickian part. It is concluded that this second stage sorption is not governed by Fick's law, but by the slow sorption in the cell wall material.

**Paper IV. Evaluation.** In this paper simple methods to evaluate the diffusivity from a sorption measurement are tested when the sorption is disturbed by different disturbances (surface resistance, non-perfect step in RH, and non-Fickian effects). Differences are found among the different methods.

**Paper V. Surface mass transfer.** The orders of magnitude of surface mass transfer coefficients are relatively well known, even if they are dependent on many external factors (e.g. the shape of a surface). Measurements of surface mass transfer coefficients on wood surfaces have, however, given very low coefficients. In this paper it is shown that this may, at least partly, be explained by the fact that the methods used are sensitive to other disturbances than the surface mass transfer coefficient. In my opinion one may use the same mass transfer coefficients for wood as are used for other surfaces. One should also refrain from using moisture concentration of wood as the potential for the mass transfer coefficient, as this introduces unnecessary complications.

**Paper VI. Non-Fickian behavior.** Moisture transport and sorption in wood are not accurately described by Fick's law of diffusion. This paper discusses how a model of non-Fickian behavior (NFB) in wood should be constructed. Some measurements in which NFB in wood is clearly seen are also reviewed. A review of models of NFB in synthetic poly-

mers indicates that there is presently no such model which can be used for wood. The paper ends with a discussion of how such a model for wood could be constructed, and which measurements would have to be made to test such a model.

**Paper VII. Error analysis: theory.** All quantitative measurements should be accompanied by an error analysis. There are many factors which influence the result of a sorption measurement. In the error analysis developed in this paper the influences of several error sources are studied one by one. This is, in my opinion, superior to statistical methods applied to a large number of measurements. This physical approach is also useful in the design of experiments.

**Paper VIII. Error analysis: application.** The results in paper VII are applied on two sorption processes. The errors found are rather small. The largest problems come from the surface resistance and heat of sorption on fast sorbing samples, and non-Fickian behavior and other disturbances which are at least partly outside the control of the experimenter. Measurements made under less well-defined conditions can, however, have much larger errors than the present measurements.

## Proposals for future studies

Based on an analysis of the results given in the eight papers in this thesis I would propose two experiments to be made as a continuation of this project. Firstly one should redo the sorption measurements in the absence of air on single cell walls made by Christensen and Kelsey (1959ab) to establish a relation for the sorption of water vapor in the cell walls.

Secondly, one should make measurements of flow through a wood sample in a modified cup where the RH on one side of the specimen could be controlled accurately, and the RH on the other side accurately measured. With this experiment one would check if Fick's law and the modified cell wall sorption from the first experiment could describe the water va-

por flow through wood.

Both these experiments would have to run for long periods of time at different temperatures and relative humidities. They would serve as a base for new models of drying and absorption of moisture in wood. Below is a more detailed description of how instruments for these experiments may be constructed and which performance characteristics they would need to have.

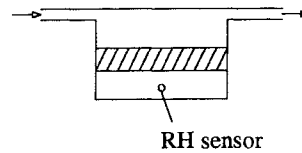
### Sorption in the cell wall

Christensen and Kelsey (1959a) made measurements of transient sorption in wood cell walls following a step change in RH. Their measurements were made in the absence of air. The very small weight changes were found by measuring the length changes of a quartz spring at which end the sample was fastened. This was a common method in polymer science.

This experiment may be automated if the weight is measured with an electronic microbalance for vacuum systems. Such a balance may, however, have problems working in a very humid environment. This can be solved by having the balance outside the vacuum system and using a magnetic connection through the wall of the container. Such systems can work without loss of accuracy in the weighings. If the balance is outside the system, a less expensive balance may also be used, and it is easier to weigh many samples with one balance.

Sorption measurements seem to always be made with step changes in vapor pressure. In my opinion, one has to also study other variations in RH to find a practicable relation for the sorption of the cell wall. Other possible RH changes are ramps between different levels or periodic variations. The exact forms these variations should have are not known, but it is very probable that the apparatus must be able to control the RH in the absence of air in a very general way.

The result from such an investigation is a



**Figure 18.** A schematic description of a modified cup instrument. The arrows indicate flow of moist air.

model for sorption in the cell wall. Such a relation has to be history dependent, i.e. it has to take earlier states of the sample into account. Such relations are discussed in connection with the modelling of non-Fickian behavior in polymers; see e.g. Kalospiros et al (1991).

The knowledge of the coupling of the different components may also help in designing a model for the sorption in the cell wall. A lot is known about the mechanical properties of the wood constituents, e.g. at which temperature and relative humidities they soften.

The result of this experiment would lead to an expression with which one can predict the water vapor concentration in a wood cell wall as a function of the present and past moisture states.

### A modified cup method

A second study could be designed to check the validity of Eqs. 1 to 4 coupled to a model of the non-Fickian behavior of the cell wall. This could be designed as a modified unsteady-state cup method as shown in Fig. 18. The RH on one side of the sample may be controlled and the RH in the chamber on the other side of the sample is measured. The flow through the sample is found as a function of the changes in RH. It is not known which forms these changes should have.

The RH in the incoming air can be accurately controlled by means of a valve that proportions dry and saturated air into a mixing chamber. The sorption on other parts of the

apparatus than the wood sample will probably also have to be taken into account. The limited surface mass transfer is also a problem. Either it must be very well known, or so small that it does not disturb the measurements.

## Acknowledgements

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