# Diffusion in the cellwalls of softwoods

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1988

*Citation for published version (APA):*
Wadsö, L. (1988). *Diffusion in the cellwalls of softwoods*. (Report TVBM; Vol. 3033). Division of Building Materials, LTH, Lund University.

*Total number of authors:*
1

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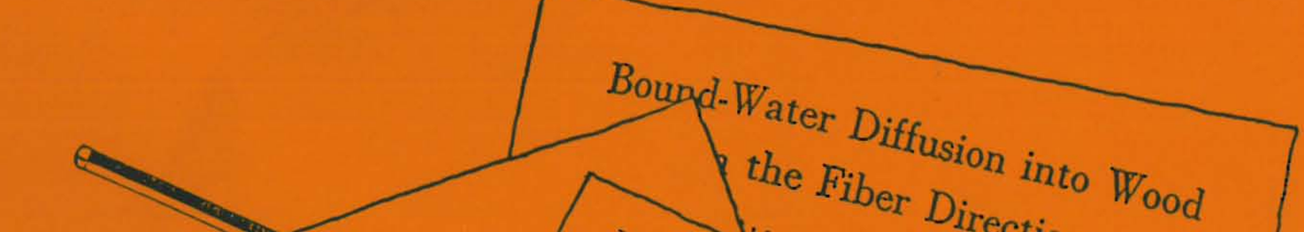
# DIFFUSION IN THE CELLWALLS OF SOFTWOODS

## Lars Wadsö



REPORT TVBM-3033 LUND, SWEDEN, 1988

CODEN: LUTVDG/(TVBM-3033)/1-26/(1988)

# DIFFUSION IN THE CELLWALLS OF SOFTWOODS

Lars Wadsö

*This research is supported by the Swedish Council for Building Research (research grant 85 09 77 - 9).*

*Printed on Munken Panda Copier, a paper containing less than 25% pulp bleached with chlorine.*

ISSN 0348-7911

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# DIFFUSION IN THE FIBRE WALLS OF SOFTWOODS

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## ABSTRACT

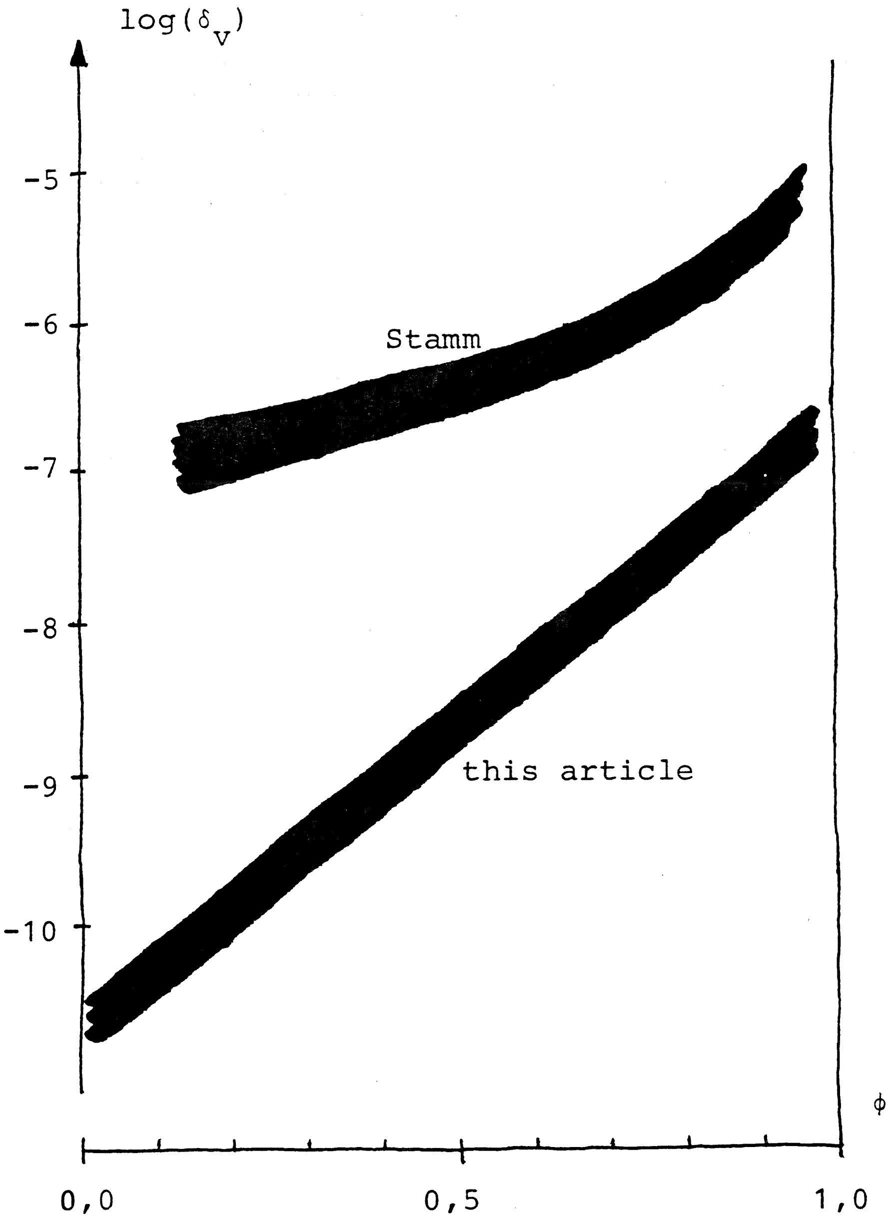
I have tried to calculate the bound water diffusion coefficient from what is known about the components of the cell wall and its structure. I then get a much lower cell wall diffusivity than Stamm (1959, 1960) got from his measurements. Even though my calculations are very rough, I think they might indicate that the bound water diffusion coefficient is lower than has been assumed for the last 25 years.

## CONTENTS

## 1. RESULTS

I have tried to calculate the bound water diffusion coefficient from what is known about the components of the cell wall and its structure. I then get a much lower cell wall diffusivity than Stamm (1959, 1960) got from his measurements. Even though my calculations are very rough, I think they might indicate that the bound water diffusion coefficient is lower than has been assumed for the last 25 years.

Below is a diagram showing Stamm's measurements and the results of my calculations, as functions of relative humidity.



## 2 DIFFUSION IN POLYMERS

This paper deals with diffusion of water in the cell wall of a softwood. As the cell wall is composed of three polymers (cellulose (both crystalline and amorphous), hemicellulose and lignin) I will start with a few words about the phenomenon of diffusion in polymers.

In a polymer the water molecules diffuse without being either liquid or in vapour phase. They are bound to different bonding sites on the polymer, and move to a new site if they get enough energy to break the first bond.

Two factors control the rate of diffusion: temperature by controlling the speed of the water molecules and the mobility of the polymer chains, and the concentration by determining the distribution of binding energies. When concentration is low all water molecules are tightly bound and the diffusivity is low. When the concentration is increased some are still tightly bound, but more and more molecules are bound more loosely. As a consequence of this the coefficient of diffusion will increase.

Rogers (1984) and Stannett et al (1974) mention a large number of different theories for how the coefficient of diffusion changes with temperature and concentration, but those are probably not of much practical use.

A question that has been much debated over the years (not only by wood researchers) is what gradient should be used when working with diffusion. Some polymer scientists working with diffusion inside polymers prefer to use concentration as gradient. Then the coefficient of diffusion will not change dramaticly when the concentration is changed. This might seem to be the logical choice when dealing with polymers, as we can't say that there is for example a certain vapour pressure in the polymer. But we can still use other gradients as we have unambigous relations between for example vapour pressure and equilibrium concentration (apart from the hysteresis effect).

I have chosen to work with vapour content (kg of vapour per $m^3$ of air) as this is the natural choice when working with diffusion in air, and much of the diffusion in wood is diffusion in air. I therefore use the following notations (symbols conforms to ISO standard 9346:1987):

| | symbol | units |
|---|---|---|
| vapour content | $v$ | $kg/m^3$ |
| coefficient of diffusion | $\delta_v$ | $m^2/s$ |
| flow | $g$ | $kg/(m^2s)$ |
| distance | $x$ | $m$ |

When these are used together, the Ficks law of diffusion will look like this:

$$-g = \delta_v \, dv/dx$$

I hope that this explanation of the units I am using will make this paper less confusing than many others. Huglin and Zacharia (1983) found 29 different units for the diffusion coefficient when they read 80 articles on diffusivity in polymers (plus a few that were completely wrong). Many authors forget to mention which units they use, and in many cases I have found it quite hard to figure that out. For example, the unit of the diffusion coefficient is $m^2/s$ whether you use concentration or vapour content as gradient. In appendix 1 I have collected all unit tranformations that I have made (for chapter 5).

# 3 COMPONENTS OF THE CELL WALL

## 3.1 Cellulose

Cellulose is a carbohydrate polymer with many OH-groups which makes it very hygroskopic, as these groups easily form hydrogen bonds with the water molecules.

Cellulose in wood and cotton, or regenerated cellulose is partly crystalline, partly amorphous. Kolseth (1983) gives the following approximate values for the percentage of crystalline cellulose in three different celluloses (as measured with X-ray diffraction):

| | |
|---|---|
| pulp | 60 % |
| cotton | 73 % |
| regenerated cellulose | 35 % |

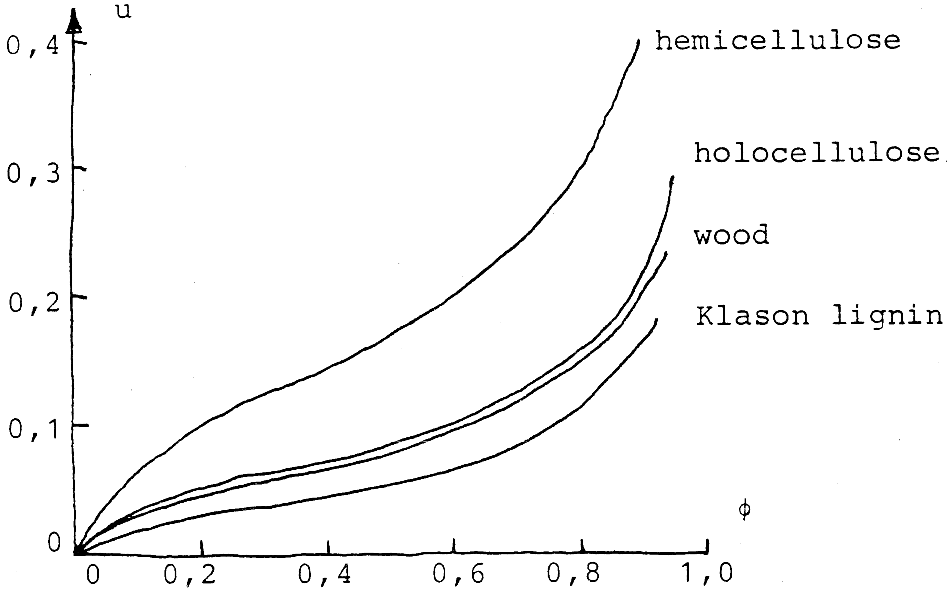
He also reports some very different values measured with other methods, but I think that these ones are approximately true as X-ray diffraction is one of the most used methods for studying the inner structure of fibres. Siau (1984) gives the value 50-60% for wood. Contrary to Kolseth, Stamm (1964) says that different methods are in good agreement. His values are very much like the ones above.

The crystalline zones of the cellulose are impermeable to the water molecules (Pizzi et al 1987a and Siau 1984). This is the same as for other crystalline polymers (Rogers 1984). Therefore the diffusion coefficient for water in crystalline cellulose is very low. Only on the surfaces of the crystallites can the water form hydrogen bonds with the OH-groups of the crystalline cellulose.

Native cellulose has a crystal structure called cellulose I. When it is recrystallised as regenarated cellulose it changes to the more stable form cellulose II. These two forms are here assumed to have the same properties.

The amorphous parts of the cellulose are permeable to water (Pizzi et al 1987b). Some measurements have been made with regenerated cellulose (see chapter 5).

Below are sorption curves for wood, holocellulose (cellulose and hemicellulose), hemicellulose and Klason-lignin (from Skaar 1974 and 1984):



## 3.2 Hemicellulose

The structure of hemicellulose is more complicated and more irregular than that of cellulose. Apart from that, hemicellulose is very similar to amorphous cellulose as these two polymers have nearly the same density and hygroscopisity (number of OH-groups per mole or kg). Pizzi et al (1987b) write: "as regards sorption characteristics of amorphous high molecular carbohydrates little difference is likely to exist between the behavior of amorphous cellulose and hemicellulose. These two should behave similarily".

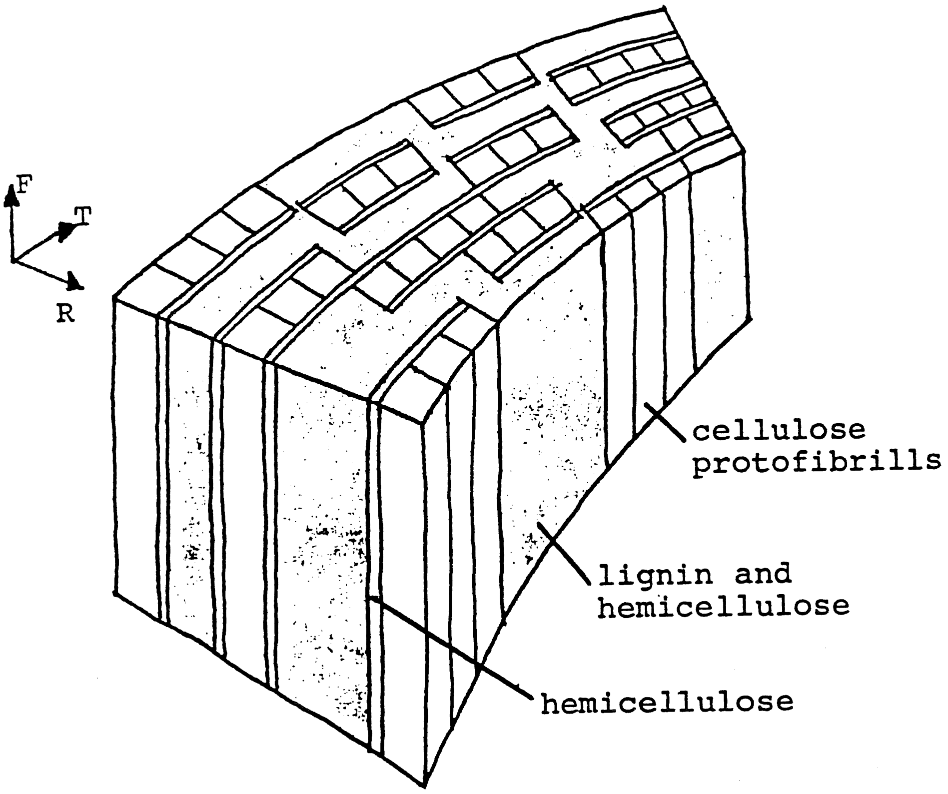
There are no measurements of the diffusion in hemicellulose, but I think it is a good assumption that it is very much the same as for amorphous cellulose. When doing the calculations in chapter 7, I have assumed the same diffusivity for these two substances.

## 3.3 Lignin

Lignin has a very complicated amorphous structure, the main component being an aromatic ring with a propane chain. It does not have nearly as many OH-groups as cellulose and hemicellulose have. Lignin is thermoplastic; it softens as the temperature is raised (Kolseth 1983). It is therefore likely that its permeability to water molecules will increase when the temperature is raised. This permeability is probably low, as lignin has low hygroscopicity and is not swelled by water (Kolseth 1983). However I have not found any measurements of diffusion in lignin. In my calculations I have assumed that it is 1/10 of the diffusion in amorphous cellulose (this might seem too rough an assumption, but the diffusivity value of lignin is not crucial for the calculations).

# 4 THE STRUCTURE OF THE CELL WALL

It is not fully known how the fibre wall is organized, but the model of Kerr and Goring (1975) is probably very near the truth:



The radial (R) and tangential (T) directions are with reference to the fibre, not the tree! I call the surface facing in the radial direction "the radial surface" (I think this is not the convention among wood reserchers, but I think it is more logical). In this model the cell wall consists of three parts:

1. Protofibrills of cellulose. These are 35 nm thick and consist of alternating zones of crystalline and amorphous cellulose.

2. A thin layer of hemicellulose on the radial surfaces of the protofibrills.

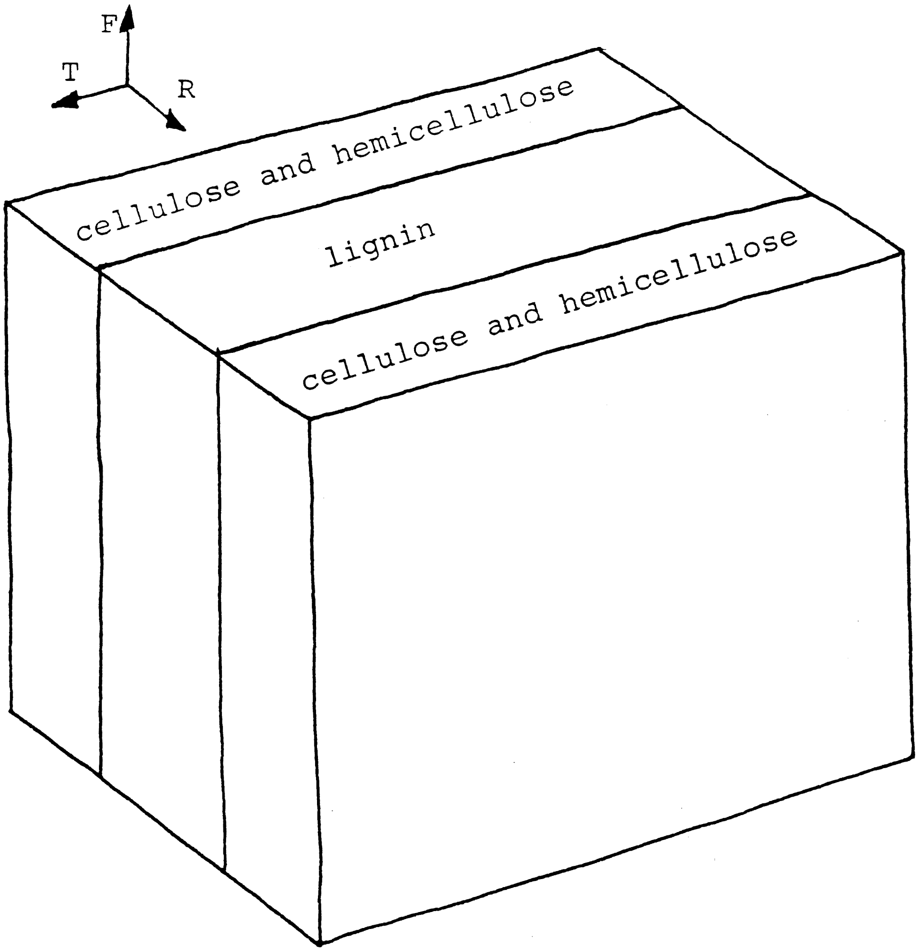
3. An amalgamate of lignin and hemicellulose.

In a softwood (black spruce) the three components have the following percentages (Kerr and Goring 1975):

| | |
|---|---|
| cellulose | 45% |
| hemicellulose | 29% |
| lignin | 26% |

Kerr and Goring try to measure the amount of hemicellulose that is associated with the protofibrills. They get a value of 1/3. This is of course only an approximate figure.

A much simpler model of the cell wall was used by Salmén (1982) for his simulations of the mechanical properties of the fibre. I use it only to see what result a very simple model will give, as the one of Kerr and Goring certainly is much better for diffusion calculations (next page):



In this model the cell wall layers consists of laminae of

1 An amalgamate of cellulose and hemicellulose

2 lignin

In chapter 7, I use these two models of the fibre wall to calculate the coefficient of diffusion in different directions in the fibre.

In none of these calculations I consider the fact that the fibrills of the different secondary layers have different angles to the fibre direction. This might seem strange: to make all these calculations and leaving one of the most important parts out. However, I think that I have to know more about the cell wall layers before making those calculations. It would then be neccesary to include for example the pectinous substances in the middle lamella. I might do this later on if I can find the information that is needed.

I would like to stress that none of these calculations are exact. To get a usable result I need to make calculations that are decisive. A factor of 2 makes no difference, but a factor 100 or 1000 is too much to be accounted for by the methods being rough.

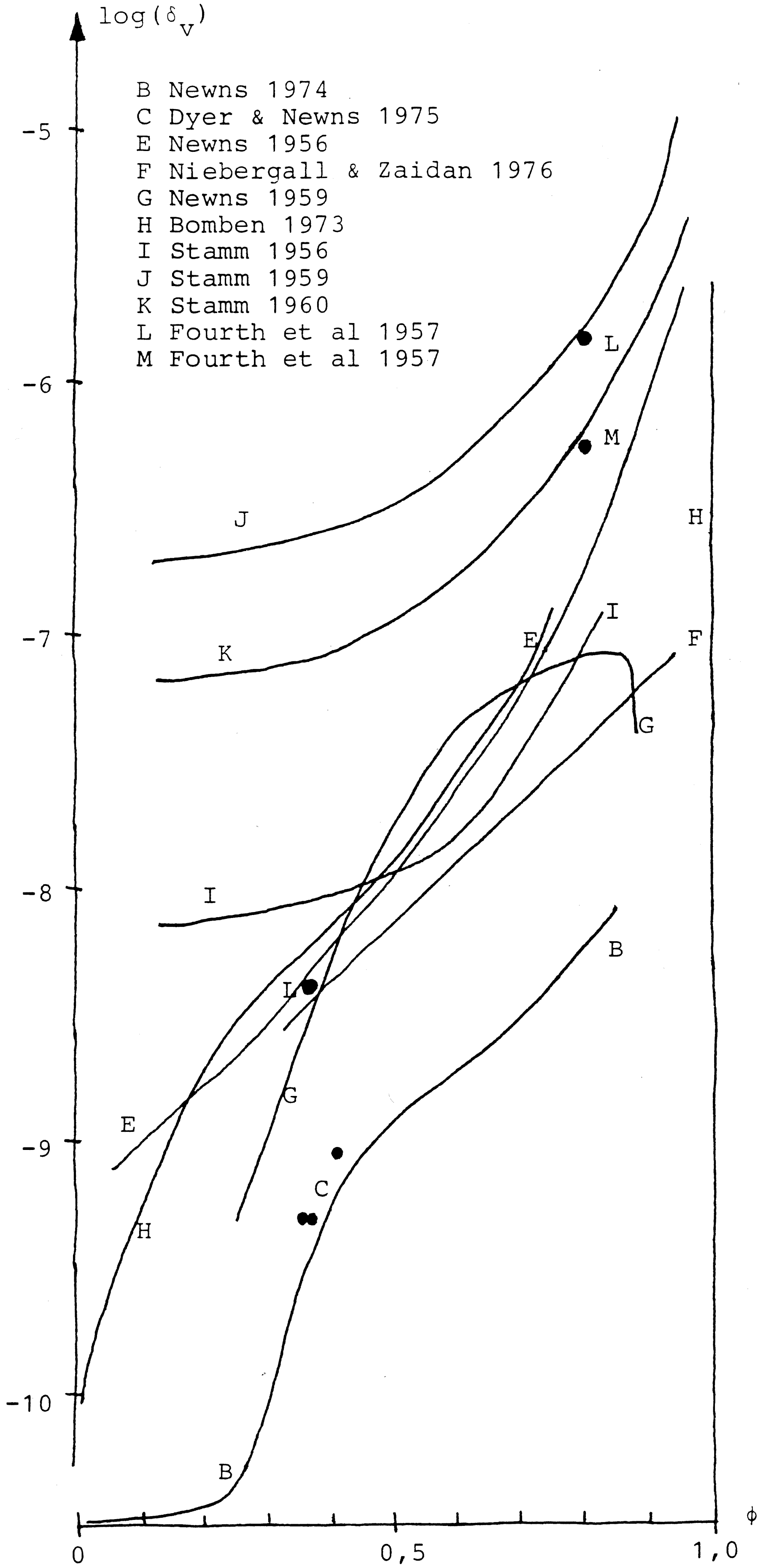
## 5 DIFFUSION IN REGENERATED CELLULOSE

I have made an extensive literature search, but only found eight articles in which measurements of diffusion in cellulose was presented. Nearly all of them concerned regenerated cellulose (cellophane, with and without softener). I thought that there should be many measurements done on cotton and viscose-rayon, but I found only one (Fourth et al 1957).

Below is a list of the articles from which I have taken diffusion coefficients. Details can be found in appendices 1 and 2.

| | |
|---|---|
| Newns (1956) | regenerated cellulose |
| Newns (1959) | regenerated cellulose |
| Newns (1974) | regenerated cellulose |
| Dyer and Newns (1975) | regenerated cellulose |
| Niebergall and Zaidan (1976) | regenerated cellulose |
| Bomben (1973) | different carbohydrates |
| Stamm (1956) | cellophane with softener |
| Fourth et al (1957) | cotton and rayon |
| | |
| Stamm (1959) | softwood cell wall |
| Stamm (1960) | softwood cell wall |

On the next page there is a diagram showing the result of the literature search. The two curves at the top are from Stamm's measurements on metal filled wood (1959,1960). The curve (B) and the three points (C) at the bottom are odd. All the other curves show the same behavior between 40 and 80 % relative humidity (RH). I think they are as assembled as I can expect, being from different authors with different methods and materials.


log(δ_v)
B Newns 1974
C Dyer & Newns 1975
E Newns 1956
F Niebergall & Zaidan 1976
G Newns 1959
H Bomben 1973
I Stamm 1956
J Stamm 1959
K Stamm 1960
L Fourth et al 1957
M Fourth et al 1957
-5
-6
-7
-8
-9
-10
L
M
J
H
K
E
I
F
G
I
B
L
G
E
C
H
B
0
0,5
1,0
φ

One problem with these measurements is that they are made by measuring the flow through a thin membrane, or the sorption of water on a piece of the material. In these methods, if the air is not moving over the surfaces there will be comparatively big surface resistances. Another problem is that the measurements are made between two different RH-levels. In some cases I do not know which one of these are used as the RH of the measurement (maybe the mean value or 2/3-value as Stamm (1959) used).

At low and high relative humidities the curves differ a lot. I think that this has two causes: it is harder to measure at these extremes, and the authors have some prejudices as to what the curves should look like.

Still the curves don't differ very much, so I propose the following approximation of the diffusion coefficient for bound water in regenerated cellulose:

$$\delta_{rc} = 10^{-10+4*\phi}\ m^2/s$$

where $\phi$ is the relative humidity (kg of vapour per $m^3$ of air). This function, a straight line in the diagram, is of course only a very rough approximation which I hope to be able to refine later if I can get more diffusion data.

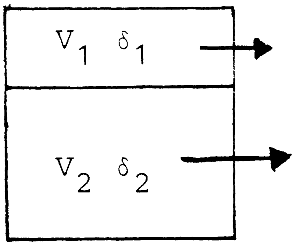
Some authors think that the concentration dependent diffusion coefficient follows an exponential function, but I have only choosen the above mentioned function as it gives a good numerical fit.

## 6 A COMPOSITE-MODEL

There are many ways to find an approximate value of a material property of a composite if you know the properties of the parts. Here I use a very simple one that is a weighted mean of the extreme cases of parallell and series coupling. On the next page I have tried to explain the model.

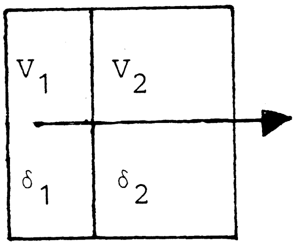
$$\delta = p\ \delta_p + (1-p)\ \delta_s$$

$$\delta_p = V_1\,\delta_1 + V_2\,\delta_2$$



$$\delta_s = \frac{1}{\frac{V_1}{\delta_1} + \frac{V_2}{\delta_2}}$$

$\delta_s=0$ if $\delta_1=0$ or $\delta_2=0$



Here $\delta$, $\delta_1$ and $\delta_2$ are the diffusion coefficients of the composite and its two components, and $V_1$ and $V_2$ are the volumetric parts of the two components ($V_1 + V_2 = 1$).

Here the indices p and s stand for parallell and series, as shown above. "p" also stands for parallellicity. If p=1, I have the top case above and if p=0, I have the bottom one. If p=0,5 , I have the mean value of the two extremes.

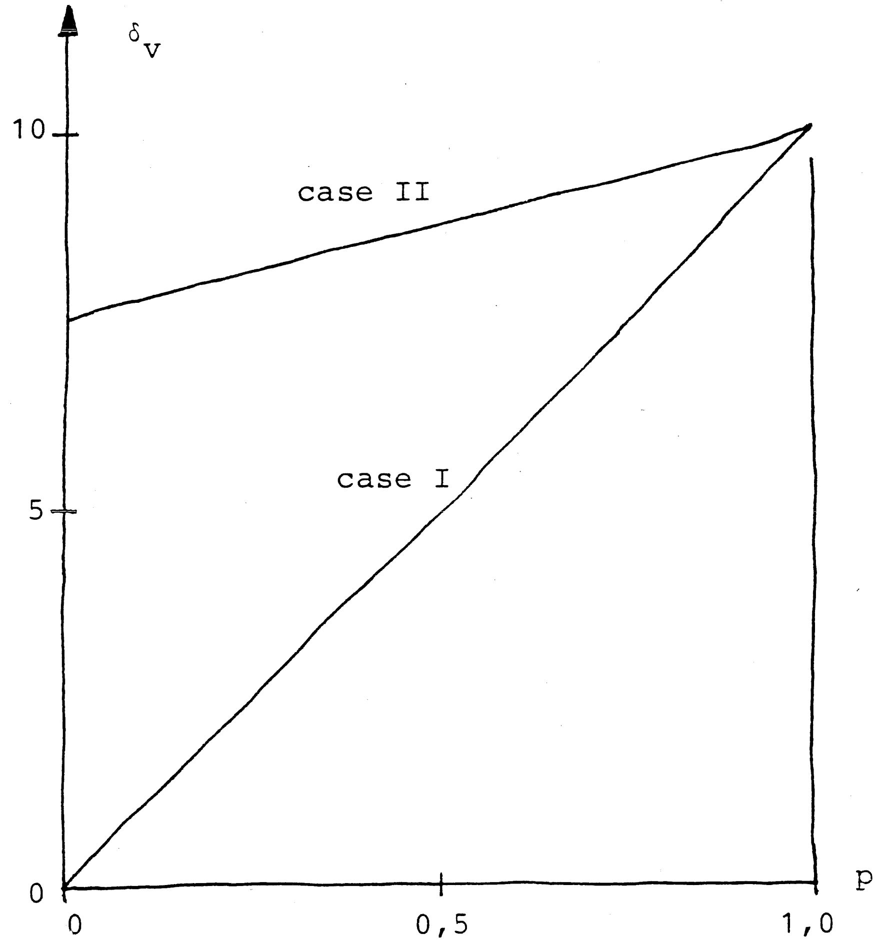
I don't think that there is any use in trying to find better rules for choosing p then these ones:

| | |
|---|---|
| p=0 | coupling in series |
| p=0,25 | more in series than in parallell |
| p=0,5 | neither in series, nor in parallell |
| p=0,75 | more in parallell than in series |
| p=1 | coupling in parallell |

I use these rules in the following chapter.

The above model is maybe not very elegant, but it has an easy geometrical explanation. On the next page I have plotted the resulting coefficient of diffusion as a function of p, in two cases:

case I: $\delta_1=20$, $\delta_2=0$, $V_1=0.5$
case II: $\delta_1=15$, $\delta_2=5$, $V_1=0.5$



## 7 CALCULATIONS

I shall now make two rough, but interesting calculations of the diffusion coefficient of the cell wall. I here assume that the whole cell wall is built in the same way as in the models of Salmén (1982) and Kerr and Goring (1975). This is a simplification, as we know that the cell wall is made up of layers in which the fibrils have different angles to the fibre direction.

In chapter 5, I found that the diffusion coefficient of water in regenerated cellulose could be approximated with the function $\delta_{rc} = 10^{-10+4\phi}$ $m^2/s$. This is the value for regenerated cellulose which has a crystallinity of approximately 35%. As I have explained above, the crystalline parts of the cellulose have very low permeability to water. Therefore it is possible to find the diffusion coefficient of the amorphous cellulose with the composite model.

As I don't know how the crystalline part of the cellulose is distributed I use p=0,5 in the composite model. Then I find that:

$\delta_a = 3\ \delta_{rc}$ (diffusion coefficient of amorphous cellulose)

When writing the results of these calculations I use "=", even if most of the results are rounded and it would be more appropriate to use "≈".

In chapter 4 I described two different models of the cell wall. I shall now calculate the resulting diffusion coefficients in the three directions in the cell wall. I then use the following assumptions (Kerr and Goring 1975; Siau 1984):

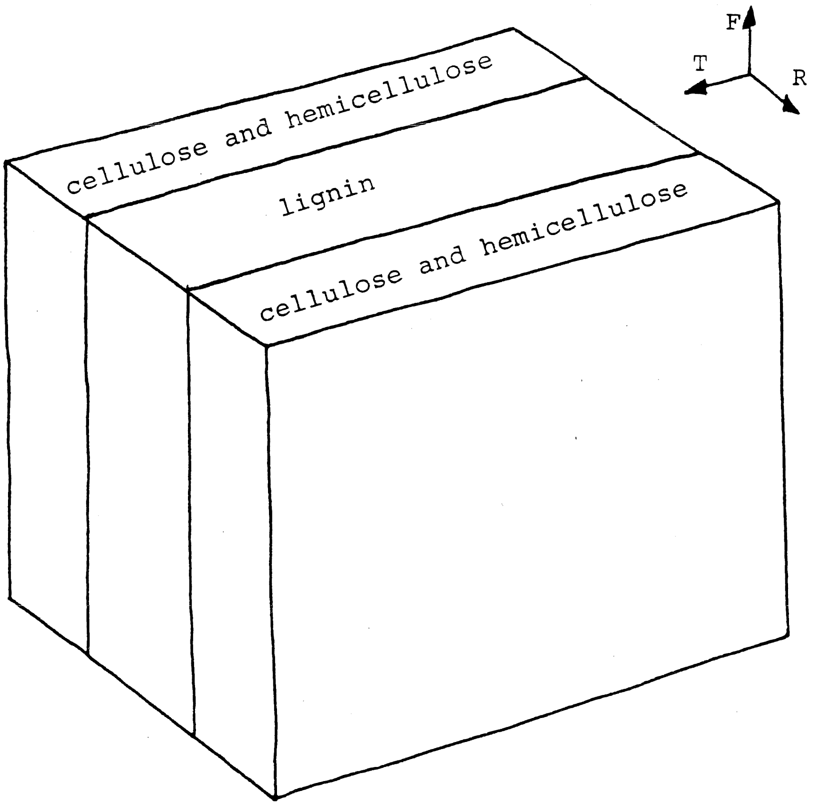
25% crystalline cellulose
20% amorphous cellulose
29% hemicellulose
26% lignin

Diffusion coefficients:

| | |
|---|---|
| crystalline cellulose | 0 |
| amorphous cellulose | $3\ \delta_{rc}$ ($=\delta_a$ in the calculations) |
| hemicellulose | $3\ \delta_{rc}$ |
| lignin | $0,3\ \delta_{rc}$ |

I use the same definitions of the three directions in the fibre as Kerr and Goring: F, R and T with respect to the fibre (not the tree).

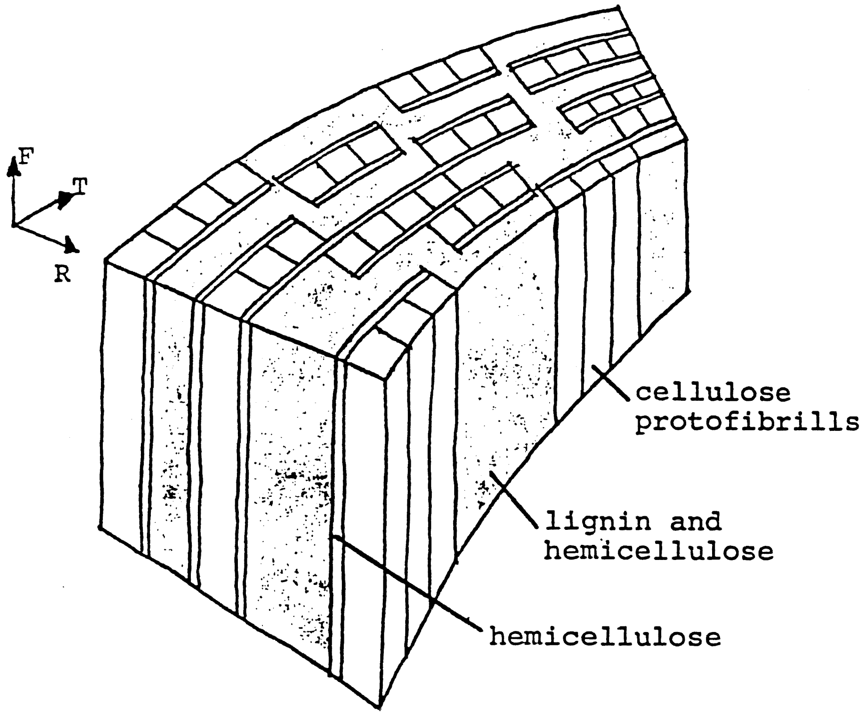
I first make the calculations for the simpler model (Salmén):



It is not neccesary to consider the different layers of the wall (the model is so simple that the result would be the same)

1. The cellulose has a crystallinity of 60%. With the above values and p=0,5 (I don't know anything about the crystalites in this model) I get $\delta = 0{,}2\ \delta_a$.
2. The composite of the cellulose and the hemicellulose contains 39% hemicellulose. With a p=0,5 I get $\delta = 0{,}4\ \delta_a$.
3F. In the fibre direction I use p=1. With $V_{lignin}=0{,}26$ the total diffusion will be $\delta_F = 0{,}32\ \delta_a$.
3T. Same as 3F.
3R. In the radial direction I have to use p=0 to get $\delta_R = 0{,}22\ \delta_a$.

The same calculations for the model by Kerr and Goring is a little bit longer:



1. The cellulose is in the protofibrills which lies in the fibrill direction. In the three directions T, R and F I use p= 0,25; 0,25 and 0,75. I then get the following diffusion coefficients:

$\delta_T = \delta_R = 0{,}10\ \delta_a \qquad \delta_F = 0{,}30\ \delta_a$

2. On the radial surfaces of these protofibrills there is a layer of hemicellulose. According to Kerr and Goring this layer holds 1/3 of the total amount of hemicellulose. In the three directions T, R and F I use p= 1; 0 and 1:

$\delta_T = 0{,}26\ \delta_a \qquad \delta_R = 0{,}12\ \delta_a \qquad \delta_F = 0{,}43\ \delta_a$

3. The composite of all the lignin and 2/3 of the hemicellulose contains 43% hemicellulose. I use p=0,5 and get $\delta = 0{,}33\ \delta_a$.

4. The cell wall contains 45% of the composite of lignin and hemicellulose. I use the following p-values in the T, R and F-directions: 0,25; 0,75 and 0.

$\delta_T = 0{,}15\ \delta_a \qquad \delta_R = 0{,}11\ \delta_a \qquad \delta_F = 0{,}35\ \delta_a$

The results of the calculations based on the two different models of the cell wall construction is summarized below:

| model | $\delta_T/\delta_a$ | $\delta_R/\delta_a$ | $\delta_F/\delta_a$ |
|---|---|---|---|
| Salmén | 0,32 | 0,22 | 0,32 |
| Kerr & Goring | 0,15 | 0,11 | 0,35 |

It is interesting to compare these figures with a the results of a calculation using only p=0,5, which will be between 0,19 $\delta_a$ and 0,32 $\delta_a$, depending on in the order in which I apply the composite model.

All these calculations are rough, but the one using the model of Kerr and Goring is probably the best. It is therefore interesting to note that I with this model get the same results for the tangential and radial directions, and a value about three times as large in the fibre direction. Stamm also found that the diffusion in the fiber direction was three times as large as in the other directions. In the next chapter I will compare my results with Stamm's experimental values from 1959 and 1960.

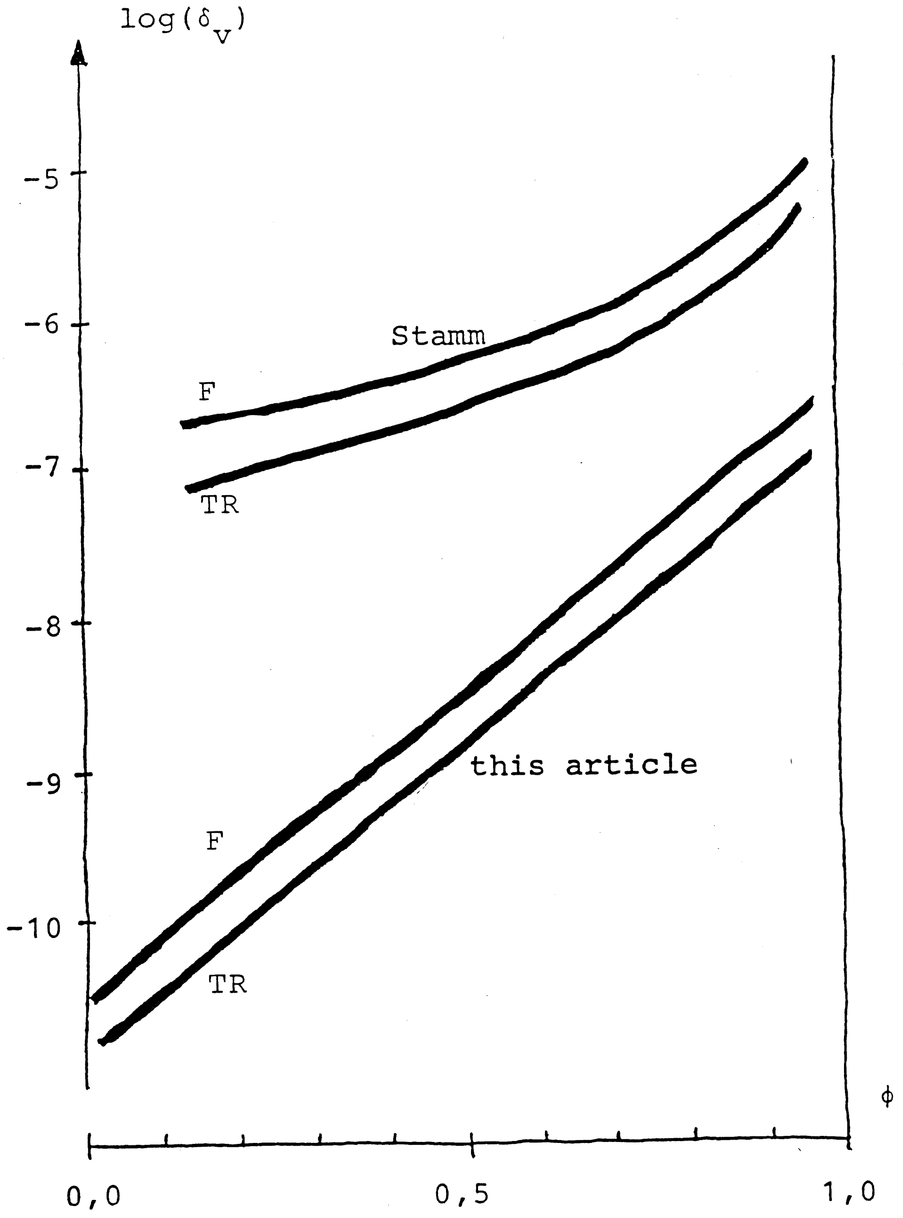
## 8 A COMPARISON WITH STAMM'S MEASUREMENTS

In 1959, Stamm published an article with measurements of the bound water diffusivity in the fibre direction of Sitka spruce. He had filled most of the lumen volume with an alloy of lead, tin and bismuth which has a very low melting point. When he measured the rate of sorption in these metal filled wood specimens he said that he measured only the bound water diffusivity.

In a later article (1960) he calculated the bound water diffusivity in the transversal (tangential and radial) directions by using his old measurements in the fibre direction and an electrical analogy.

These two articles are mentioned in the reference lists of almost every article on wood drying since they were published, but it seems to me that few other wood researchers have tried to repeat his measurements. Palin and Petty (1981) have made some measurements above the fibre saturation point with an osmotic method, but their results can't be used in calculations below the fibre saturation point. Yokota (1959) measured bound water diffusion in parafine filled wood and got even higher diffusion values than Stamm.

Below is a diagram of Stamm's result together with my calculations. The difference is large: more than a factor 100. I think this is too much to be accounted for by my models and calculations being crude.



What can cause this large difference? First of all I like to mention some weaknesses in my arguments:

- The experimental values are mostly from hydrolyzed cellulose acetate films (Newns). It would have been better if I had found more values on cotton and vicose-rayon.
- All measurements are made on very thin films (Newns (1956, 1959, 1974 and 1975 (with Dyer)), Stamm (1956) and Niebergall and Zaidan (1976a and 1976b) or on thin fibres embedded in resin (Fourth et al 1957). With these methods I can think of a number of experimental errors that can ruin the experiments: surface resistance, porosity of membrane (or worse: passages through the film), error in measurement of film thickness etc.
- When I make my calculations I assume that there is zero porosity of the cellwall. I think that most researchers would agree on this, but if there are passages through the cell wall, my calculations will be of little value. This is because of the free air vapour diffusion being between 10 and 100 000 times larger than the bound water diffusion. Especially at lower relative humidities, even minute passages will transport much more water than the cell wall.

I would also like to point out some things I find questionable in Stamm's articles (Stamm 1959 and 1960):

- I think it is a doubtful method of simulating 100% relative humidity with liquid water. I know that is is possible to argue that if we could get exactly 100% RH, we would have liquid water. Despite this I think it is much safer to try to get as high RH in the air as possible, e.g. be satisfied with 98% RH.
- It seems strange that he got as small errors as he did with only 90% of the void volume filled with metal (see fig 4 in Stamm 1959). As mentioned above, water penetrates a capillary much more easily as liquid water or vapour, than a non porous cell wall is penetrated by bound water.

# APPENDIX 1 UNIT CONVERSIONS

Different authors use different units and different gradients. Below I have summarized the ones I found in the eight articles on measurements of diffusion coefficients of cellulose.

In all articles by Newns (1956, 1959, 1974 and 1975 (with Dyer)) concentration is used as the gradient. To convert $\delta_c$ to $\delta_v$ I use:

$$\delta_c\ dc = \delta_v\ dv \qquad \delta_c\ dc/dv = \delta_c\ dc/du\ du/d\phi\ d\phi/dv = \delta_v$$

Here u is the moisture content (kg of water per kg of dry material), dc/du is the density (1520 kg/m$^3$) for cellulose and $d\phi/dv$ equals the invers of the saturation vapour content. I calculated the derivative of the sorption isotherm, $du/d\phi$, numerically, from a sorption isotherm given by Newns.

Niebergall and Zaidan (1976) give the diffusion coefficients on a vapour pressure basis which is very common in polymer technology. The unit they use is (g cm)/(cm$^2$ s bar) which equals $10^{-6}$(kg m)/( m$^2$ s Pa). To convert the vapour pressure to vapour content I use the ideal gas law, and find that at 20$^o$C $p=140000v$. From that I get $\delta_p\ dp/dv = \delta_p\ 140000 = \delta_v$.

Bomben (1973) uses the same units as Newns and Stamm (1956), and Fourth et al (1957) give their measurements directly on a vapour contents basis that I only have to change from cm$^2$/s to m$^2$/s.

In Stamm's two articles on cell wall permeability (1959,1960) his results are given on a concentration basis. They are therefore converted in the same way as Newns' data.

## APPENDIX 2 MEASUREMENTS OF DIFFUSION IN CELLULOSE

Below is a table of all the data I have used. In the second column I have indicated if the authors have given numerical values (N) or if I have measured in a diagram (D).

| author | N/D | $\phi$ | $\delta_c$ $m^2/s$ | $\delta_v$ $m_2/s$ |
|---|---|---|---|---|
| Newns (1956) | D | 0,05 | $1\ 10^{-14}$ | $700\ 10^{-12}$ |
| | | 0,25 | $8{,}8\ 10^{-14}$ | $2{,}1\ 10^{-9}$ |
| | | 0,47 | $4{,}3\ 10^{-13}$ | $10\ 10^{-9}$ |
| | | 0,70 | $1{,}5\ 10^{-12}$ | $61\ 10^{-9}$ |
| | | 0,75 | $2{,}7\ 10^{-12}$ | $130\ 10^{-9}$ |

According to the author, these values are not very accurate

| author | N/D | $\phi$ | $\delta_c$ $m^2/s$ | $\delta_v$ $m^2/s$ |
|---|---|---|---|---|
| Newns (1959) | N | 0,25 | $2\ 10^{-14}$ | $490\ 10^{-12}$ |
| | | 0,36 | $14\ 10^{-14}$ | $3{,}4\ 10^{-9}$ |
| | | 0,47 | $55\ 10^{-14}$ | $14\ 10^{-9}$ |
| | | 0,57 | $116\ 10^{-14}$ | $34\ 10^{-9}$ |
| | | 0,66 | $171\ 10^{-14}$ | $58\ 10^{-9}$ |
| | | 0,70 | $125\ 10^{-14}$ | $48\ 10^{-9}$ |
| | | 0,79 | $134\ 10^{-14}$ | $78\ 10^{-9}$ |
| | | 0,84 | $108\ 10^{-14}$ | $88\ 10^{-9}$ |
| | | 0,88 | $38\ 10^{-14}$ | $35\ 10^{-9}$ |
| Newns (1974) | D | 0,00 | $3{,}4\ 10^{-16}$ | $30\ 10^{-12}$ |
| | | 0,25 | $1{,}7\ 10^{-15}$ | $41\ 10^{-12}$ |
| | | 0,50 | $4{,}7\ 10^{-14}$ | $1{,}2\ 10^{-9}$ |
| | | 0,75 | $8{,}7\ 10^{-14}$ | $4{,}1\ 10^{-9}$ |
| | | 0,85 | $8{,}7\ 10^{-14}$ | $8{,}2\ 10^{-9}$ |
| Dyer and Newns (1975) | N | 0,37 | $20\ 10^{-15}$ | $490\ 10^{-12}$ |
| | | 0,41 | $37\ 10^{-15}$ | $900\ 10^{-12}$ |
| | | 0,36 | $20\ 10^{-15}$ | $490\ 19^{-12}$ |

| author | N/D | $\phi$ | $D_c$ $m^2/s$ | $D_v$ $m^2/s$ |
|---|---|---|---|---|
| Niebergall and Zaidan | N | 0,32 * | | $2{,}7\ 10^{-9}$ |
| | | 0,64 * | | $17\ 10^{-9}$ |
| | | 0,85 * | | $53\ 10^{-9}$ |
| | | 0,94 * | | $82\ 10^{-9}$ |
| Bomben (1973) | D | 0,00 | $10^{-15}$ | $63\ 10^{-12}$ |
| | | 0,13 | $3{,}5\ 10^{-14}$ | $810\ 10^{-12}$ |
| | | 0,43 | $5{,}8\ 10^{-13}$ | $8{,}7\ 10^{-9}$ |
| | | 0,74 | $3{,}0\ 10^{-12}$ | $91\ 10^{-9}$ |
| | | 0,88 | $8{,}7\ 10^{-12}$ | $500\ 10^{-9}$ |
| | | 0,95 | $1{,}9\ 10^{-11}$ | $1{,}9\ 10^{-6}$ |
| | | 1,00 | $5{,}1\ 10^{-11}$ | $7{,}5\ 10^{-6}$ |
| Stamm (1956) | D | 0,13 | | $7{,}7\ 10^{-9}$ |
| | | 0,56 | | $13\ 10^{-9}$ |
| | | 0,68 | | $28\ 10^{-9}$ |
| | | 0,72 | | $43\ 10^{-9}$ |
| | | 0,83 | | $120\ 10^{-9}$ |
| | | 0,76 | | $53\ 10^{-9}$ |
| | | 0,75 | | $48\ 10^{-9}$ |
| Fourth et al | N | 0,80 * | cotton | $1{,}54\ 10^{-6}$ |
| | | 0,36 * | cotton | $4\ 10^{-9}$ |
| | | 0,80 * | rayon | $550\ 10^{-9}$ |

The $\phi$-values marked with a star are calculated as the lowest value plus 2/3 of the distance to the greater value. This is a method that Stamm (1959) has used with data from sorption measurements. I have also used it for data from cup experiments. This might not be the best way of treating those relative humidity values.

When Stamm gives his experimental results he gives them as diffusion coefficients for his metal filled wooden specimens. In this paper I compare my results with his values for the diffusion in the cell wall. I have therefore calculated the cell wall diffusivity by assuming that the cellular structure of Sitka spruce is the same as of Scots pine (Pinus sylvestris), which I have more data on. I have then made different calculations in the three directions, taking care to imitate the actual structure. This calculation is quite simple as the wood structure easily can be modelled as couplings in series and parallell.

Below are Stamm's values for the cell wall

| author | D/N | $\phi$ | $D_v$ $m^2/s$ |
|---|---|---|---|
| Stamm (1959) | D | 0,12 | 0,2 $10^{-6}$ |
| | | 0,47 | 0,3 $10^{-6}$ |
| | | 0,70 | 0,88 $10^{-6}$ |
| | | 0,88 | 3,4 $10^{-6}$ |
| | | 0,95 | 10,5 $10^{-6}$ |
| | | 0,98 | 28 $10^{-6}$ |

This is in the fibre direction. The flow is three times less in the transversal directions.

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