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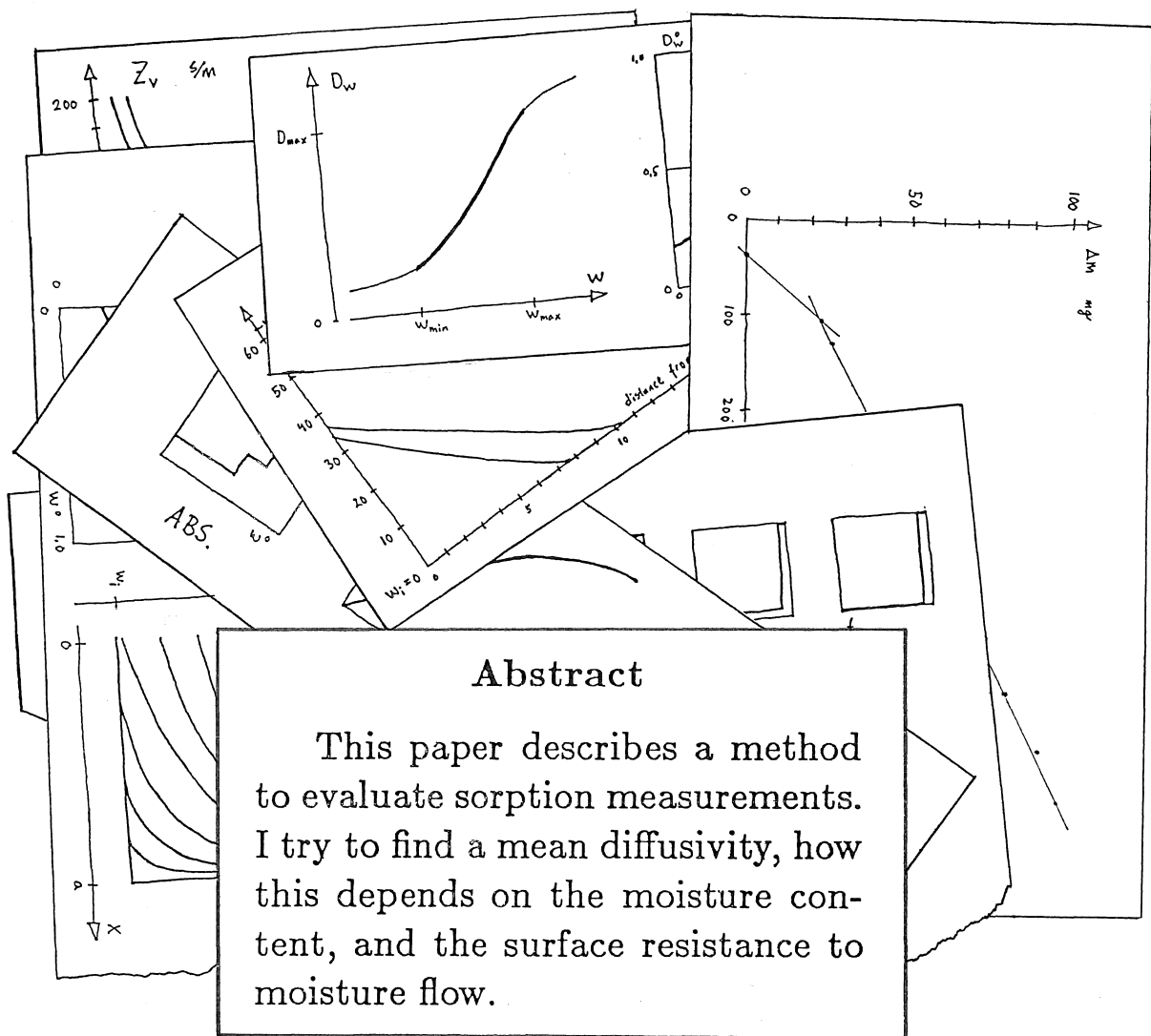
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The sorption method old and new ideas

Lars Wadsö



Abstract

This paper describes a method to evaluate sorption measurements. I try to find a mean diffusivity, how this depends on the moisture content, and the surface resistance to moisture flow.

Division of Building Materials, Lund Institute of Technology

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NOMENCLATURE

a	half sample thickness m
A	area m^2
b	equivalent thickness m
c_p	heat capacity $J/(kg \cdot K)$
d	tube diameter m
$D(w)$	diffusivity as defined by $-g = D_w \cdot \partial w / \partial x$ m^2/s
\tilde{D}	some sort of mean value of $D(w)$ which we get from sorption measurements m^2/s
E	dimensionless sorption
g	mass flow $kg/(m^2 \cdot s)$
L	length m
m	mass kg
r	mean air velocity m/s
S	surface emissivity with w as potential m/s
t	time s
u	moisture content by weight kg/kg
v	moisture content of air kg/m^3
w	moisture content by volume kg/m^3
x	distance m
Z_v	surface resistance with v as potential s/m
Z_w	surface resistance with w as potential s/m
Z_ϕ	surface resistance with ϕ as potential m^2s/kg
α	heat surface emissivity $W/(m^2K)$
β	surface emissivity m/s
ϕ	relative humidity (activity of moist air)
λ	heat conductivity $W/(m \cdot K)$
η	$x/(2\sqrt{t})$ m/\sqrt{s}
ψ	fundamental potential $kg/(m \cdot s)$
ρ	density kg/m^3
τ	dimensionless time $\sqrt{D_w \cdot t}/a$
ξ	moisture differential capacity $dw/d\phi$ kg/m^3

indices

c	convection
f	final
i	initial
max	largest value in an interval
min	smallest value in an interval
s	saturation
th	referring to the analytical solution with constant D_w
o	dimensionless

INTRODUCTION

This is a paper about the sorption method. It describes my work and findings when I introduced myself to this very much used method. Because of this it contains both old and new material.

I use SI-units and the nomenclature of ISO 9346 (1987) as much as possible. This means that I do not use the same symbols as do most wood researchers. I do however not write this paper for wood researchers only, but also for my colleagues who work with moisture transport problems in different building materials. The sorption method is not used so widely among them as among wood scientists.

Most of the diagrams are drawn by free hand from the computer screen output, and are therefore not exact enough to be used quantitatively. Qualitatively they are good enough I think. When I continue this work I will make a catalogue showing the effect of different diffusivities and experimental errors.

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Chapter 1

THEORY

1.1 What is a sorption measurement?

First of all I would like to explain what a sorption measurement or a non steady state measurement is. It is a simple method to measure the moisture diffusivity in a material, but the evaluation of the result is not as simple as I first thought when I began to study this method.

To use the method I take a sample of the material I want to test and seal four surfaces, leaving only two opposite faces open. Then I leave it in a constant climate to equilibrate; this can take several months if the material is wood and the thickness is a few centimeters. When the mass of my sample does not change any more, I change the climate and start to record the changes in mass, which results from the water molecules entering or leaving the wood. This measurement of mass change as a function of time is the result of the experiment. Normally the mass change is plotted as a function of the square root of time, which (according to theory) should give a straight line as long as there is no moisture change in the centre of the sample. After this the mass change will naturally slow down (as the sample gets near equilibrium) and asymptotically approach the final mass change.

This is the sorption method, which has been used by many wood researchers (Stamm 1959, 1960; Choong & Skaar 1969, 1972) and others (Crank & Park 1949; Newns 1956, 1968, 1973, 1974; Stamm 1956; Liu 1987).

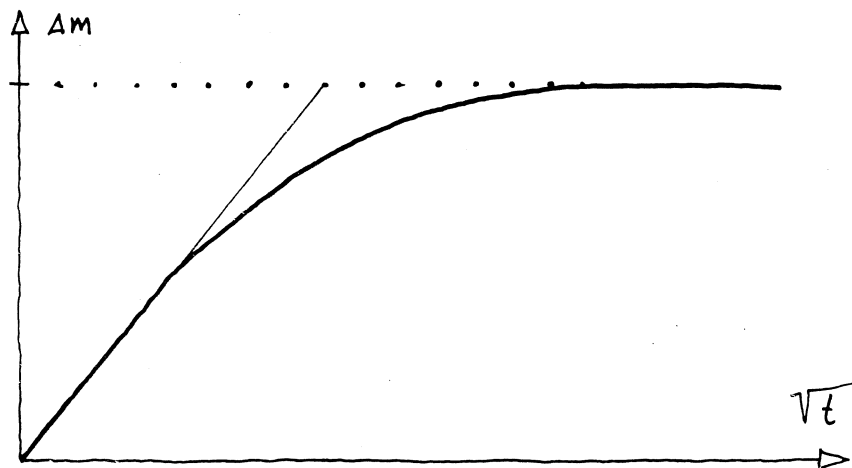


Figure 1.1: The result of an adsorption experiment

1.2 Analytically solvable if D_w is constant

The theory for sorption or drying has been explored by many researchers through the years. I will here give a summary of the most important equations.

The problem is to solve one of the following two equations with the boundary and initial conditions of the sorption problem:

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x} \left(D_w(w) \cdot \frac{\partial w}{\partial x} \right) \quad (1.1)$$

$$\frac{\partial w}{\partial t} = D_w \cdot \frac{\partial^2 w}{\partial x^2} \quad (1.2)$$

initial conditions: $w = w_i$ for all x

boundary conditions: $w = w_f$ for $x = \pm a$

The first equation is for non constant $D_w(w)$ and the second is for a constant D_w . Only the second equation is analytically solvable as the constant D_w then can be moved out from inside the derivations. Newman (1931b) gives the solution to it without showing how it can be derived. He cites Osgood: "a function that satisfies a differential equation is a solution, no matter how obscure its origin; and one that does not satisfy it is not a solution, no matter how illustrious its pedigree may seem to have been". It seems a good idea for a non-matematician like myself to let others give me the solutions, which I can check. Its easy to show that the following equation satisfies the differential equation (Newman 1931b p315-316):

$$w(x, t) = w_f + (w_i - w_f) \cdot \frac{4}{\pi} \cdot \sum_1^{\infty} \frac{(-1)^{n+1}}{2n-1} \cdot \cos \left(\frac{(2n-1) \cdot \pi \cdot x}{2a} \right) \cdot e^{-(2n-1)^2 \cdot D_w \cdot t \cdot \left(\frac{\pi}{2a} \right)^2} \quad (1.3)$$

This solution gives us the concentration at any time and place in a sorption experiment sample. What is more interesting to us is the integrated value of the concentration, as this is what we measure during an experiment as a mass increase or decrease. The integration is performed with the time t constant and distance x as integration variable (Newman 1931b p322-323):

$$E(t) = 1 - \frac{8}{\pi^2} \cdot \sum_1^{\infty} \left(\frac{1}{(2n-1)^2} \cdot e^{-(2n-1)^2 \cdot \frac{D_w \cdot t}{a^2} \cdot \left(\frac{\pi}{2} \right)^2} \right) \quad (1.4)$$

This is the equation which gives us the sorption as a function of time, thickness and a constant diffusivity. E is defined as the dimensionless sorption: zero when we start the sorption, and unity when we have reached a new equilibrium. In this paper this function will be called E_{th} when we refer to the E -value of the theory for constant D_w (equation 1.4).

When I drew the diagram of E in fig 1.1 I drew it as a function of \sqrt{t} . This is because the initial curve in the diagram then becomes a straight line. This can be explained in the following way for all diffusivities (not only constant).

For the first part of a sorption experiment, the concentration in the centre of the sample is still the initial concentration. This is the same as saying that the sorption is effectively a sorption into a half infinite slab.

Boltzmann (1894) was the first to show that the above stated differential equation reduces to an ordinary differential equation if we express the concentration as a function of a new variable $\eta = x/(2\sqrt{t})$. This means that the equation can be solved numerically, the solution being a

function of η and D_w only (Crank & Park 1949 p638). This possible use of the single variable $\eta = x/(2\sqrt{t})$ shows us three things:

- A curve drawn of the concentration in the sample as a function of time, has the same *form* as long as the concentration in the middle has not begun to change. As time goes the only difference is that the concentration curve gets pulled out like an accordion.
- The sorption is proportional to the square root of time. If we want the sorption to extend twice as long into our sample, we have to wait four times as long time.
- As it has the same form, and this form gets pulled out as \sqrt{t} it follows that the mass change in sorption drawn as a function of \sqrt{t} is a straight line.

Remember that this is true for all diffusivities, constant *and* non constant, as long as the sample behaves like a half infinite slab.

1.3 Finding the diffusivity

If we measure the sorption as a function of time, we then want to find the diffusivity D_w . This can be done in many ways, at least if we consider D_w to be constant as there is a solution to this case. As this is an exact solution, it is of course possible to see which D_w that makes the measured curve equal the theoretical.

One way which is used by Crank & Park (1949), Crank & Henry (1949ab), Liu (1987) and others is to equate the measured and the theoretical time to half sorption (when $E = 0,5$). A numerical approximation is (Crank & Park 1949, Crank p239 1986).

$$D_w = 0,04939 \cdot \frac{4a^2}{t} \quad (1.5)$$

A second way is to use the following approximation, which is good if $E > 0,667$ (Liu 1987):

$$D_w = \frac{4a^2}{\pi^2 t} \cdot \ln\left(\frac{8}{\pi^2(1-E)}\right) \quad (1.6)$$

I think a third method is the best. As the initial part of the curve is straight we can use its slope (Crank 1986 p244):

$$D_w = \frac{\pi a^2}{4} \cdot \left(\frac{dE}{d\sqrt{t}}\right)^2 = \frac{\pi a^2}{4} \cdot \frac{E^2}{t} \quad (1.7)$$

This equation can be used as long as the curve is a straight line; as long as the sample can be viewed as half infinite.

An equation that is similar to the last equation above was derived by me to be used when we only have the initial straight line:

$$D_w = \frac{\pi}{4 \cdot w_f - w_i^2 \cdot A^2} \cdot \left(\frac{m(t) - m_i^2}{t}\right) \quad (1.8)$$

Where $m(t) - m_i$ is the mass change at time t , and A the sample area. This equation is good to use when we know the initial sorption into a very thick sample (so thick that we do not want to wait for equilibrium). It can also be used when we only want an approximate value of D or when we want a first approximation when the experiment is still running. The values of $m(t)$ and t should be taken on the initial straight slope. Knowing the initial and the final climates it is easy to get values of w_i and w_f from the sorption isotherm.

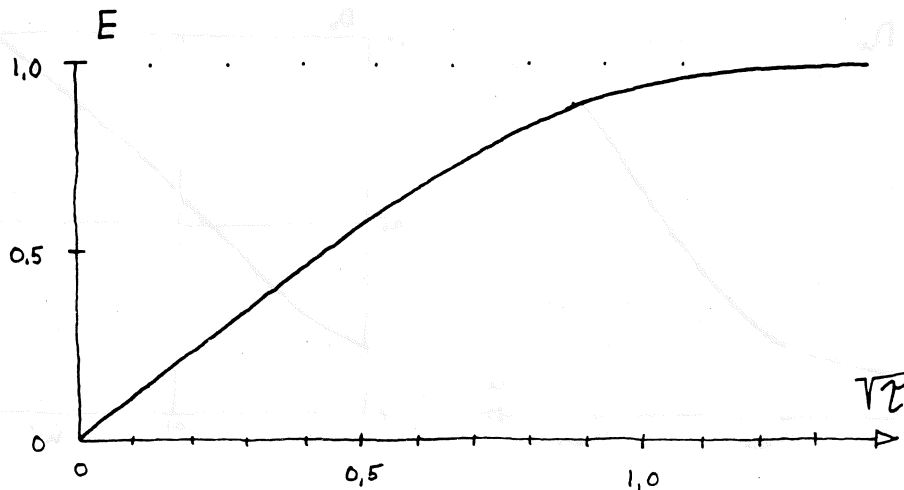


Figure 1.2: A dimensionless sorption curve

The four equations above will give the same results as long as the diffusivity is constant. If it is not, E will not equal E_{th} , and these equations will be different approximations to the diffusivity.

In the following I shall call the calculated diffusivity \tilde{D} to separate it from the real diffusivity and the arithmetic or any other mean value of a non constant diffusivity.

But what is \tilde{D}_w if $D_w(w)$ is not constant? It will be some sort of mean value (not arithmetical mean though). I take a closer look at this in section 3.4.

1.4 It is easier if it is dimensionless

I have shown that it is easier to draw the sorption as a function of the square root of time (fig 1.1). I have also introduced E , which is the dimensionless sorption.

It would be nice if we could draw the diagram totally dimensionless, because then all diagrams (at least with constant D_w) would look exactly the same. This can be done, and the best dimensionless time to use is the Fourier number

$$\tau = \frac{D_w \cdot t}{a^2} \quad (1.9)$$

With this we can plot two standard diagrams, which we will use when we explore different kinds of sorption.

In figure 1.2 it is E_{th} that is drawn against $\sqrt{\tau}$. All sorptions with a constant diffusivity show exactly this behavior. If two measurements from different experiments, both with constant D_w , are drawn in the same diagram, the curves will coincide. The reverse is also true (at least for all cases that I have studied): if a sorption with a non constant $D_w(w)$ is drawn in a diagram like this, it will deviate from E_{th} . This is what I explore in the following chapters.

But first a few words about other dimensionless units. It is also convenient to do like Crank & Henry (1949a), and use dimensionless diffusivity and dimensionless moisture content. I define these in the following way:

$$D^\circ = \frac{D(w)}{D_{max}} \quad (1.10)$$

$$w^\circ = \frac{w - w_{min}}{w_{max} - w_{min}} \quad (1.11)$$

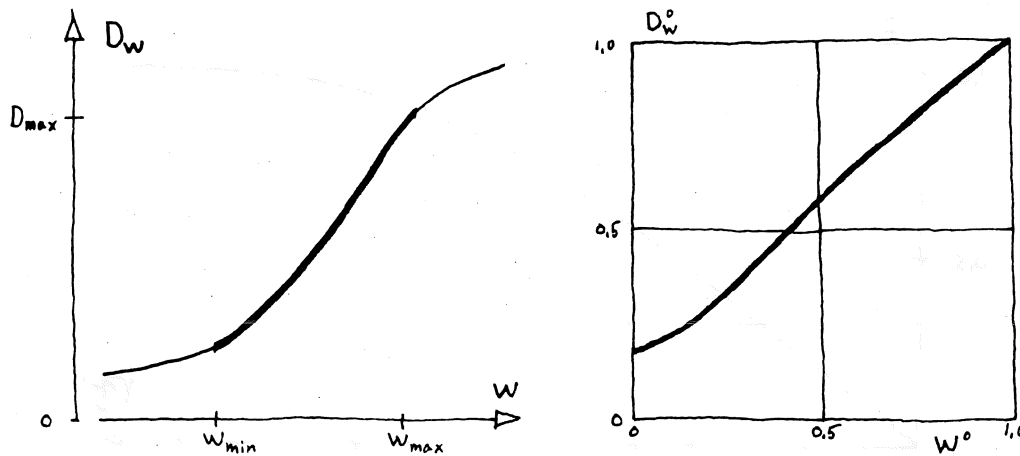


Figure 1.3: The dimensionless diffusivity

By the use of these two new variables I avoid making more calculations than is necessary. In figure 1.3 is an example of a dimensionless diffusivity written in the dimensionless moisture content. The two indices *max* and *min* refers to the highest and the lowest value of D or w in the experiment I am doing or simulating. This range is shown in the left diagram as a thicker drawn line, and is the only thing that is shown in the right dimensionless diagram.

It is very convenient to use dimensionless variables as this will minimize the work I have to do. I can make simulations of sorption experiments with just the curve form of the diffusivity (in the experimental interval) as input. I do not need to take the absolute value of the diffusivity into consideration, nor the actual moisture content range.

Chapter 2

SIMULATION

2.1 Why and why not?

With the help of computers it is possible for any researcher nowadays to make his own calculations of sorption, drying or other transport phenomena. This is a very powerful tool, especially if we want to try new approaches that have not been explored before. Only twenty years ago the calculation of concentration curves in sorption with a variable diffusivity, was a complicated task. Today I can enter a variable diffusivity, check to see if it is ok, and make a simulation of a sorption phenomena; all in less than 15 minutes.

Despite the merits of computer simulations we must not forget the pioneer work done by Newman, Crank & Henry and others. They made simple diagrams or tables of diffusion with different kinds of variable diffusivities (Crank & Henry 1949ab) or different surface resistances (Newman 1931a). In many situations these are still the fastest way to solve our problems, and they are for the variables for which they are made at least as accurate as the computer simulations in this paper. The advantage of using the computer is that we can tailor a solution to exactly the problem we want; we do not need to interpolate as we always can get the values in the points or times we want.

A possible disadvantage of using a computer is that it can be hard to check the accuracy of the results or even see if they are reasonable. It is easy to work as if the computer program was the reality, forgetting it might have its weaknesses and errors. When working with computers there is also a great risk of being caught by the wonders of the computer so that you forget what you originally were going to do. I think it is best for the researcher in transport phenomena if he or she thinks that working with the computer is as fun as doing the old times hand calculations. Then he will get on with his work (which often can be done by brute force on a computer, or with smartness by hand calculations).

In this paper I hope that I have shown that the computer can be used as a tool to evaluate experiments. I am not the first and probably not the last to do this and I do not claim that this is a new dimension in solving moisture problems. Only one more tool in the box.

2.2 How I used the computer

I mainly use the computer to run simulations. I have a library of computer files of different transport properties. Some of these are real measured data, with normal units, which can be used to simulate what happens in a real structure which absorbs water vapour. Most of my computer files are made up by myself. I have for example a series of files with diffusivities that increase in one step, starting with a constant diffusivity and ending with a file containing a diffusivity which increases about a hundred times in one step. These faked material properties

are all presented dimensionlessly. As I show in this paper this is no disadvantage, as it is possible to scale all properties I want to use.

One of the greatest advantages with computers is that it is quite easy for researchers to check the influences of various factors. I have for example looked at or will look at the following factors:

- the influence of an unstable climate
- the influence of surface resistances
- the influence of measuring with the growth rings in parallel or in series (tangential or radial direction)
- the influence of leaks through the sealed surfaces of the samples

2.3 The programs I use

I used two computer programs to do the simulations shown in this paper. First of all I used JAM-1, which is a general program for moisture transport with variable diffusivity. Secondly I used SORP, a version of JAM-1 tailored to run only sorption simulations. Both these programs runs on PC-computers under MS-DOS. The executable code requires a *87 math co-processor, EGA video card and 512 kbytes of RAM.

JAM-1 is a program for the calculation of moisture transport with non constant diffusivities. It is written by Jesper Arfvidsson (Division of Building Physics at Lund Technical University) and is quite easy to run and is ideal for the study of how different $D_w(w)$ affect the moisture situation. As there are possibilities of entering surface resistances, variable boundary conditions etc, it is possible to simulate almost any one dimensional moisture problem. It consists of three parts:

- create material data file
- diagrams of material data
- run transient model.

Moisture transport data for materials can be entered in four ways:

- results from cup measurements
- measured steady state ϕ -profiles and flow
- diffusion coefficient (ϕ as potential) and sorption isotherm
- ϕ , w and ψ

The greek letter ψ is the potential which is used in the calculations. It is defined as the potential with a diffusivity of unity.

SORP is a version of JAM-1 which can simulate only sorption measurements and display the results in the way that is presented in this paper. It has been developed by Jesper Arfvidsson and Lars Wadsö in cooperation. It consists of five parts:

- create material data file
- diagrams of material data

- run sorption simulation
- enter measured data from sorption experiments
- plot measured and simulated data

SORP has the same possibilities of entering measured material data, plus the possibility of entering

- diffusivity (w as potential) and sorption isotherm

Both programs can be ordered from Jesper Arvidsson (Division of Building Physics, Lund Technical University, Box 118, 221 00 Lund, SWEDEN).

NON-CONSTANT

3.1 Dependences on the moisture content

As we draw a diagram of λ as a function of w , the sorption simulation with constant diffusivity we get the curves which I call $\lambda(w)$. This can be calculated for the equations given in chapter 1. If we have not constant diffusivity we will not get the same curves. Why this is so I will explain in this chapter. What is the point of interest here? For example, G and λ (chapter 1.10) show that kind of diffusivities are interesting to study. The answer is that if we have some measurements that show both constant and increasing diffusivity, we can use the curves with a maximum of a minimum. We also need decreasing curves to handle the case with drying experiments or sorption with increasing diffusion coefficient (see section 3.4).

The program SORP treats the diffusivity curves as piecewise constant functions. This might seem a serious limitation but is not for the following reason. The sorption λ is not a function of w (which gives the flow or stationary conditions) but more like a function of the integral of w . This is the integral of the flow from the evaporated moisture content and the mass change. Thus it is the integral of w that we should use to describe an accurate sorption curve. λ is a function of a process curve and therefore the process is piecewise linear and changes in λ will influence w as well.

For this case I have written a special program to solve the differential equation for w if there have been any new information for the next step in w from some of them.

3.2 How λ have calculated

When I have made a calculation for a certain step in w , I will know for the last equation 1-5-2. If my diffusivity is not constant, I will probably get a new λ for the different sorption. This is because as the sorption process proceeds the moisture content w will increase the sample will be changed. Consider for example a adsorption experiment with an increasing diffusion coefficient (figure 3.1).

During the first part of the process the flow in the moisture content distribution is so changed it is not suited our list of sorptions. During this time we can use the theory for the infinite slab, which tells us that w is proportional to \sqrt{t} . When the moisture content is the centre of the sample starts to raise, we can no longer use the theory for a constant D , so that the diffusion coefficient still is the same in the whole sample. If we have a non constant D , w will not be the same in the whole sample, so there will be some inhomogeneous and their sorption diffusion will be more like a curve.

This will mean the sorption curve for an example the flow w will be a little different from after the first part of the sample. That the reason for this will also result in that the sample for the first part of the sample will be a little different from the rest of the sample. In this case the average value of D will be the same as the value of D at the end of the

Chapter 3

NON-CONSTANT D_w

3.1 Dependencies on the moisture content

As we draw a diagram of E as a function of $\sqrt{\tau}$ for a sorption simulation with constant diffusivity we get the curve which I call $E_{th}(\sqrt{\tau})$. This can be calculated by the equations given in chapter 1. If we have non constant diffusivities we will not get the same curve. Why this is so I will explain in this chapter. Work in this field has already been done by for example Crank & Henry (1949ab).

What kind of diffusivities are interesting to study? The answer is nearly all of them, since researchers have found both constant, slowly increasing, rapidly increasing and curves with a maximum or a minimum. We also need decreasing curves to handle the case with drying experiments on samples with increasing diffusion coefficient (see section 3.4).

The program JAM-1 wants the diffusivities entered as piecewise constant functions. This might seem a serious limitation, but is not for the following reason. The sorption E is not a function of D_w (which gives the flow at stationary conditions), but more like a function of the integral of D_w (as the integral of the flow gives the accumulated moisture content and the mass change). Thus it is the integral of D_w that we should try to describe as accurately as possible, not D_w . If D_w is described by a piecewise constant function the integral is piecewise linear, and changes in D_w will not influence $\int D_w$ as much.

For this work I have worked with about 40 different forms of the diffusivity, but not all of them have given me any new information. In the next chapters I will show some of them.

3.2 How I have calculated \tilde{D}_w

When I have made a simulation I can calculate some sort of mean diffusivities by the four equations 1.5-1.8. If my diffusivity is non constant I will probably get at least three different answers. This is because as the sorption process proceeds the moisture content in the centre of the sample will be changed. Consider for example an adsorption experiment with an increasing diffusion coefficient (figure 3.1).

During the first part of the process the form of the moisture content distribution is unchanged; it is just pulled out like an accordion. During this time we can use the theory for half infinite slab, which tells us that E is proportional to $\sqrt{\tau}$. When the moisture content in the centre of the sample starts to raise, two things can happen: either we have a constant D_w , so that the diffusion coefficient still is the same in the whole sample. Or we have a non constant D_w , in which case the mean value of D_w will have to change as some moisture contents and their associated diffusivities are removed from active service.

This will change the sorption curve. In our example, the lower values of w will disappear one after the other from our sample. Then the respective D_w will also cease to exist in the sample. As they are the lowest values of D_w , only the higher values of D_w will be left. It is then

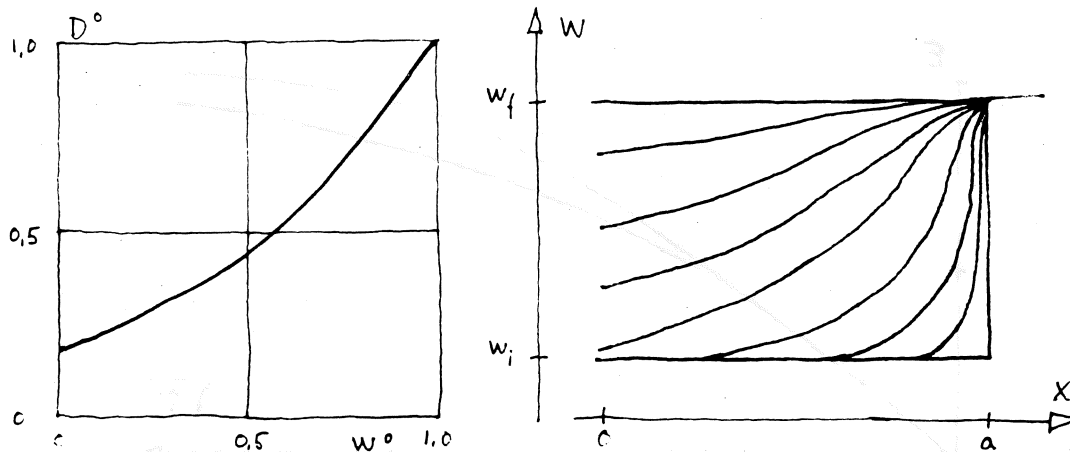


Figure 3.1: An increasing diffusivity and the concentration within a sample during sorption ($x = 0$ is at the centre of the sample and $x = a$ is on the surface). The concentration is shown at different times during the sorption process

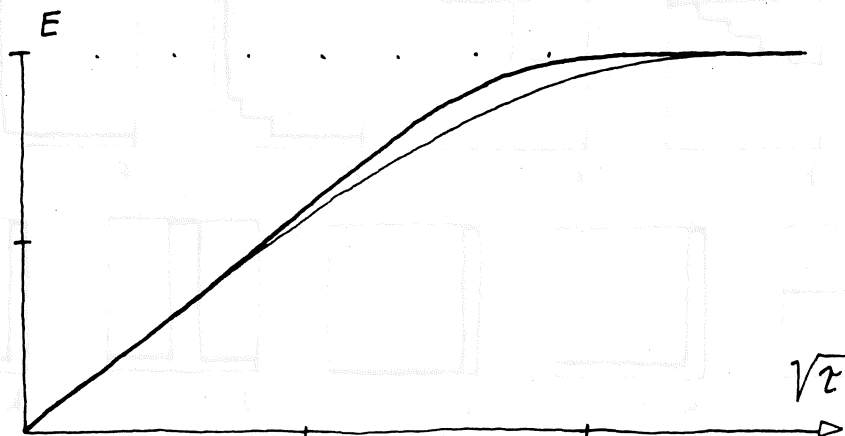


Figure 3.2: A sorption with increasing D_w (thick line) compared to a sorption with constant D_w (thin line)

natural for the sorption to speed up, compared to the sorption with constant diffusivity, if they are both drawn in the same dimensionless diagram.

This will of course effect the values of D_w calculated from the different equations. When we use the dimensionless time τ we have to have a value of \tilde{D}_w , because $\tau = \tilde{D}_w \cdot t/a^2$. Above I have chosen to use the \tilde{D}_w calculated from equation 1.7, which uses the linear part of the curve. Therefore the linear parts of the two curves coincide. It would not have looked the same if I had used a \tilde{D}_w -value calculated from any of the other equations. Especially the second equation, which utilizes the last part of the sorption curve where only the highest $D_w(w)$ -values (in our example above) are active, will give a different result.

I think that it is best to use the slope $dE/d\sqrt{\tau}$ to calculate a value of \tilde{D}_w . Therefore I have used it in this paper (for the method used when there is a surface resistance see chapter 4.7).

In figures 3.1 and 3.2 are shown the effect of different diffusivities.

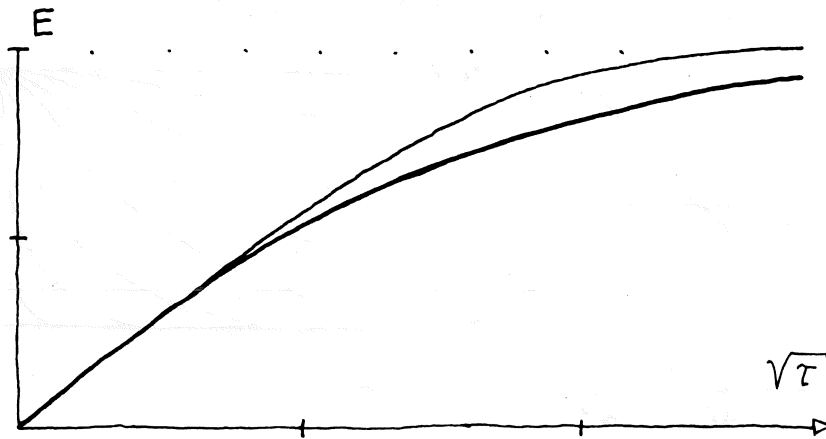


Figure 3.3: A sorption with decreasing D (thick line) compared to a sorption with constant D (thin line)

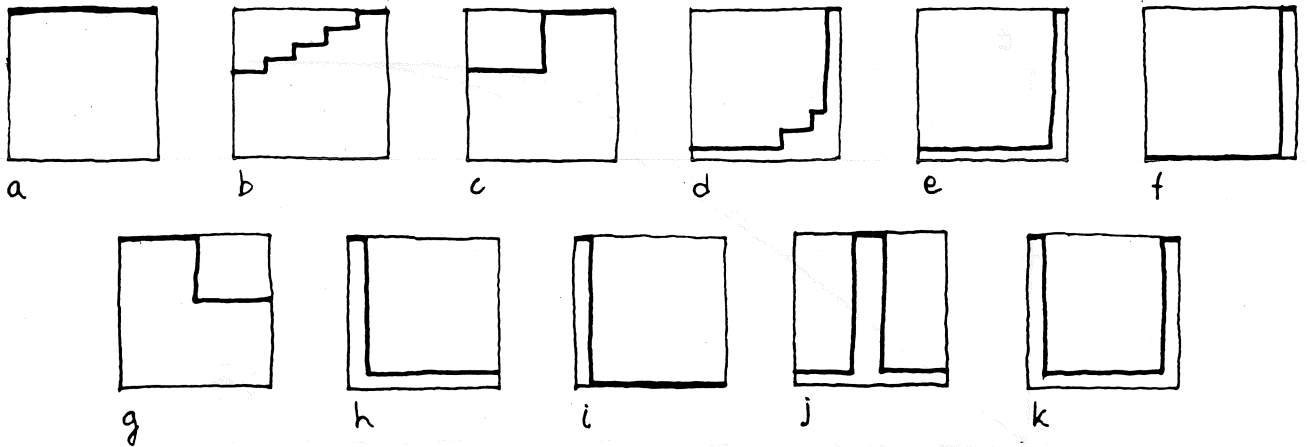


Figure 3.4: Eleven forms of the diffusivity

3.3 How this effects the calculated D_w

The \tilde{D}_w which we calculate is not an arithmetic mean of $D_w(w)$. Instead it is a very complicated mean for which no analytical expression exists as far as I know. It can however be calculated numerically, for example with my sorption program.

In figure 3.4 are shown eleven diffusivities, and in table 3.1 are shown the \tilde{D}_w which is calculated from them by the use of equation 1.7 (in adsorption). As we can see, it seems that the $D_w(w)$ of higher w are weighted more heavily than the ones at lower w (compared with \bar{D}).

3.4 Absorption and desorption

Except for the case with constant diffusivity absorption and desorption in the same interval will not give the same result ($E(\sqrt{t})$ and \tilde{D}_w). This is reasonable as:

- the D at higher w in absorption are weighted most heavily. At desorption we have the opposite situation (which was shown above). Therefore we can usually not get the same \bar{D} from absorption and desorption in the same interval.

	form	\tilde{D}	\bar{D}	\tilde{D}/\bar{D}
a	constant	1,000	1,000	1,00
b	increasing	0,861	0,800	1,08
c	increasing	0,874	0,800	1,09
d	increasing	0,307	0,230	1,33
e	increasing	0,252	0,190	1,33
f	increasing	0,164	0,109	1,50
g	decreasing	0,713	0,800	0,89
h	decreasing	0,117	0,190	0,62
i	decreasing	0,019	0,109	0,17
j	with maxima	0,256	0,280	0,91
k	with minima	0,278	0,280	0,99

Table 3.1: Diffusion coefficients calculated from sorption simulations (\tilde{D}), the arithmetical mean (\bar{D}) and their ratio

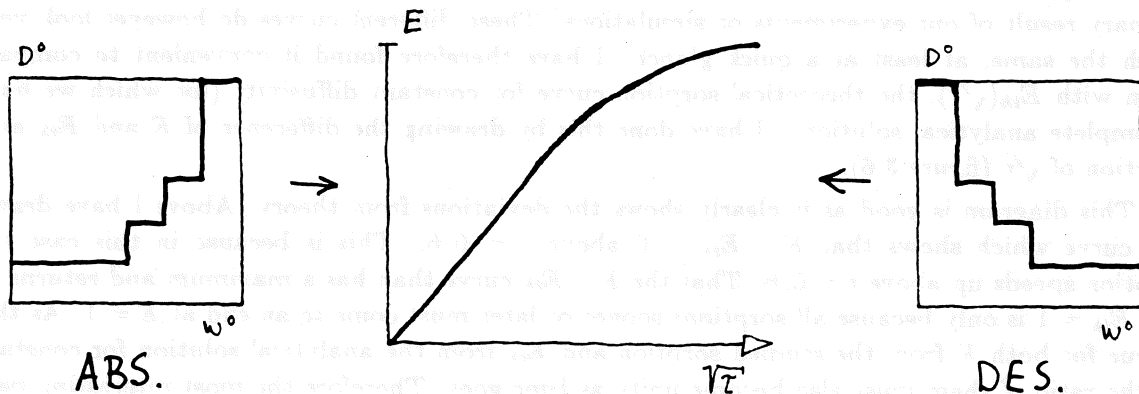


Figure 3.5: A diffusivity in absorption will give the same sorption curve as its mirror image will give for desorption

- the D at the lowest w are first to disappear as w starts to increase in the centre of a sample subjected to absorption. At desorption it is the D at the highest w that disappears first. These different situations will of course effect the later part of the curve in different ways.

Is there then no connection between absorption and desorption? There is one which is shown in figure 3.5.

If we make the transformation $D^\circ(w^\circ) = D^\circ(1 - w^\circ)$ (which is the same as turning the w° -axis the other way) we will get a new D° which will give exactly the same $E(\sqrt{t})$ and \tilde{D} for desorption as the unchanged D° for adsorption (or vice versa). By this I conclude that I need only study one of the two different cases; the other one can then be easily be derived. I have choosen to mostly study absorption (for a discussion of the relation between adsorption and desorption see Crank & Henry 1949a).

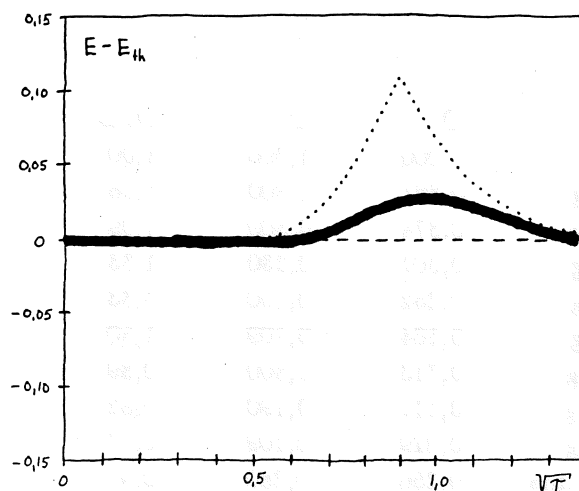


Figure 3.6: The $E - E_{th}$ -diagram, which shows the deviation from the theory for constant D_w

3.5 Expressing deviations from the analytical solution

In this paper I want to study how different factors effect the sorption process. One way of expressing the influence of these different factors is to look at the $E(\sqrt{\tau})$ -curve, which is the primary result of our experiments or simulations. These different curves do however look very much the same, at least at a quick glance. I have therefore found it convenient to compare them with $E_{th}(\sqrt{\tau})$, the theoretical sorption curve for constant diffusivity (for which we have a complete analytical solution). I have done this by drawing the difference of E and E_{th} as a function of $\sqrt{\tau}$ (figure 3.6).

This diagram is good as it clearly shows the deviations from theory. Above I have drawn one curve which shows that $E - E_{th} > 0$ above $\tau = 0,6$. This is because in this case the sorption speeds up above $\tau = 0,6$. That the $E - E_{th}$ -curve than has a maximum and returns to $E - E_{th} = 1$ is only because all sorptions sooner or later must come to an end at $E = 1$. As this is true for both E from the studied sorption and E_{th} from the analytical solution for constant D , the ratio of them must also become unity as time goes. Therefore the most interesting part of the diagram is when $\tau < 1,0$.

In the $E - E_{th}$ -diagram there are two broken lines:

- the left line is the continuation of the initial straight line in the $E(\sqrt{t})$ diagram (see figure 1.1). This is the upper limit to the sorption: it can not be faster than this. If I had not taken equation 1.7 as a definition of \tilde{D} (the slope of the initial straight part of the curve) I would have gotten some problems here (especially with surface resistance). Now there is no possibility of the sorption being faster than the initial straight line (see chapter 4 for a discussion of how this diagram can be used when we have surface resistances).
- the right broken line is for $E_{th} = 1$; in other words is it the value of $1 - E_{th}(\sqrt{\tau})$. This is also a limit for the sorption process as it is impossible for E to become larger than unity.

Both these curves are useful as references when we compare different sorption curves. There are no corresponding curves below $E - E_{th} = 0$, reflecting the fact that the sorption process can slow down very much if the diffusivity is extremely decreasing. The only real limits below $E - E_{th} = 0$ are $\sqrt{\tau} > 0$ and $E - E_{th} > -1$, which not even sorptions with very extreme $D_w(w)$ which I have tested come near.

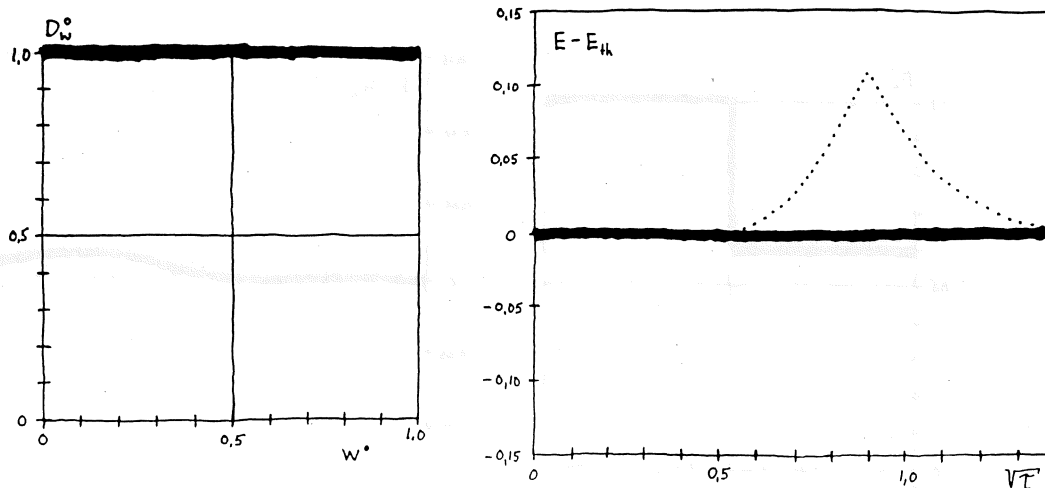


Figure 3.7: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity a

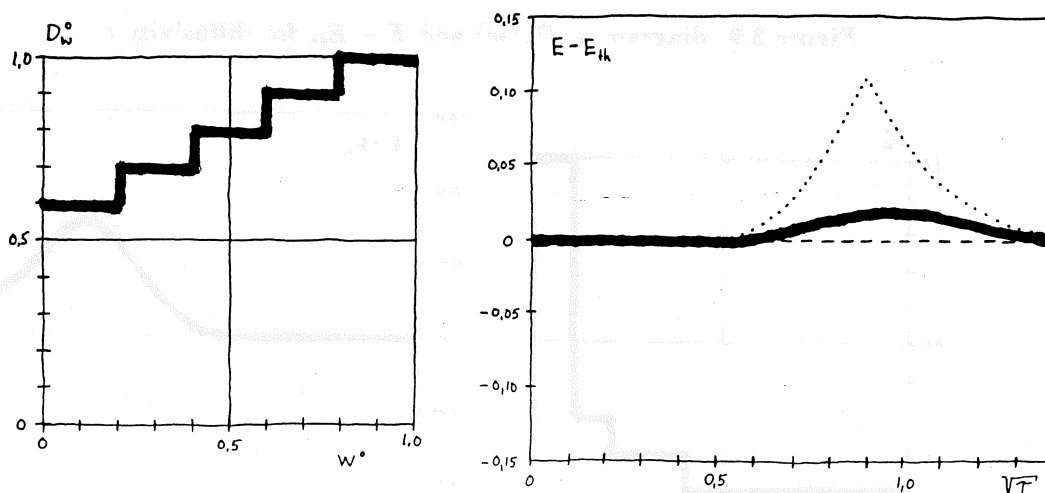


Figure 3.8: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity b

3.6 Diagrams for different $D^o(w^o)$

In this chapter are shown different $D^o(w^o)$ -diagrams for absorption and corresponding $E - E_{th}$ -diagrams. I have chosen to draw the curves in figures 3.7-3.17. I hope they can be a help when interpreting results from simulations or experiments with no or negligible surface resistance.

Studying these curves made me draw the following conclusions:

- If $D(w)$ increases, $E - E_{th}$ for absorption will have a maximum
- If $D(w)$ decreases, $E - E_{th}$ will have a minimum
- Diffusion coefficients which has a minimum or a maximum give $E - E_{th}$ -curves with both a maximum and a minimum.
- It does not give very much more information to divide the $D(w)$ into more steps, to make it look more like a continuous curve (which it of course is in reality). As I mentioned before this is because the mass of the sample which we measure is not a function of the diffusivity, but a function of the integral of the flow, and therefore more like a function of the integral of the diffusivity. Introducing an extra step to make $D(w)$ more realistic does not change the form of $\int D(w)dw$ as much.

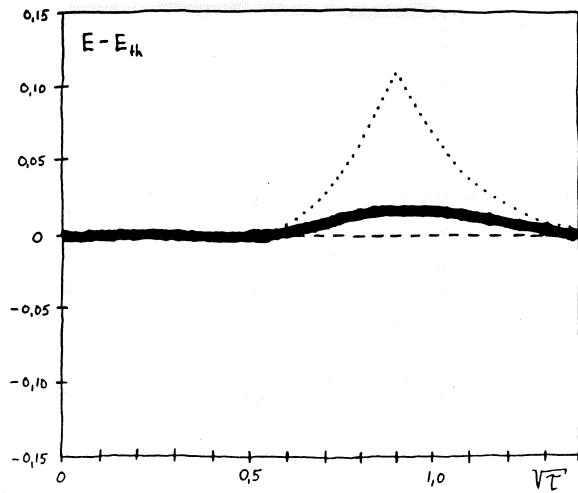
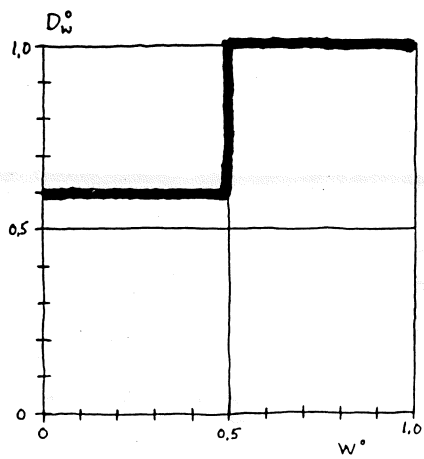


Figure 3.9: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity c

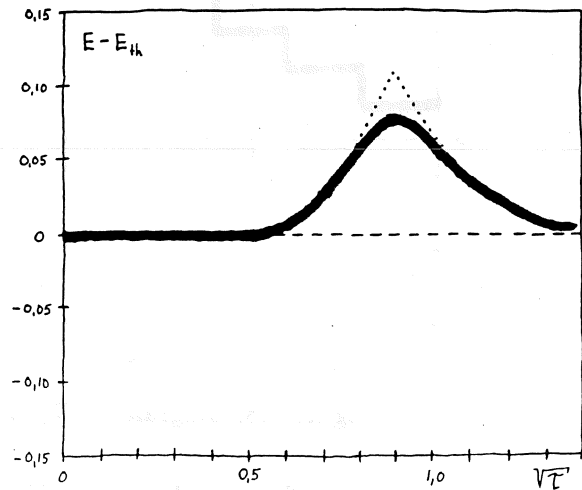
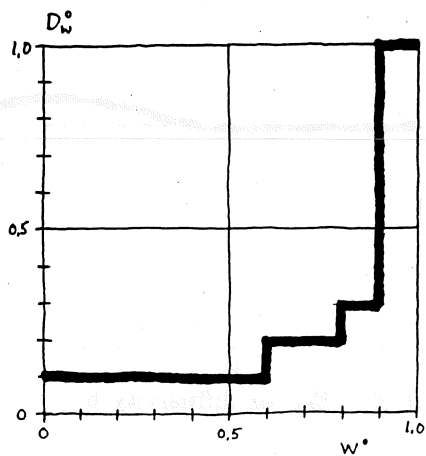


Figure 3.10: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity d

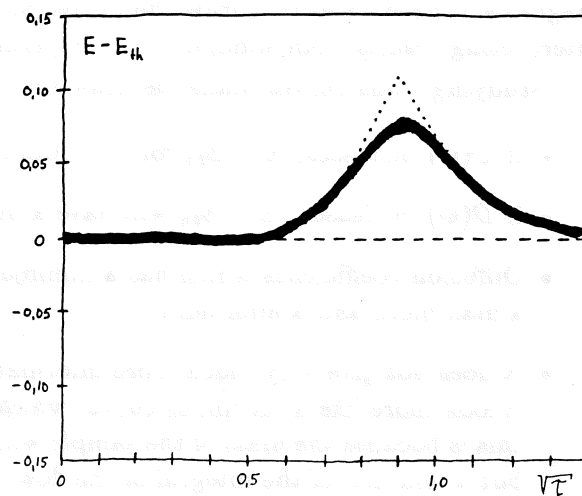
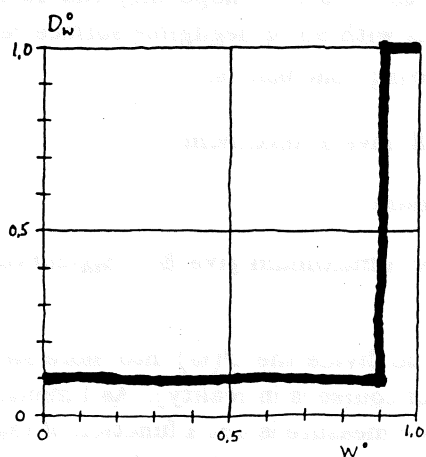


Figure 3.11: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity e

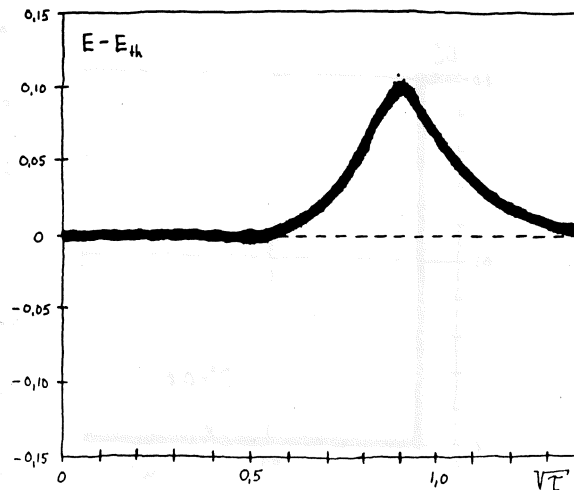
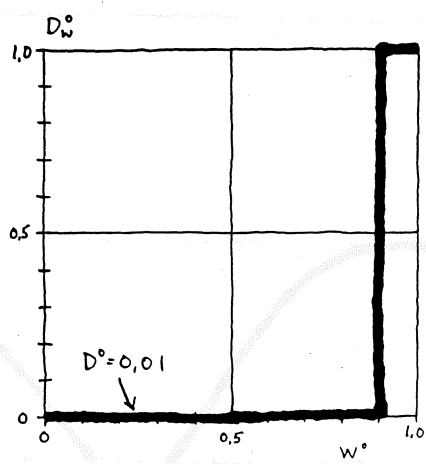


Figure 3.12: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity f

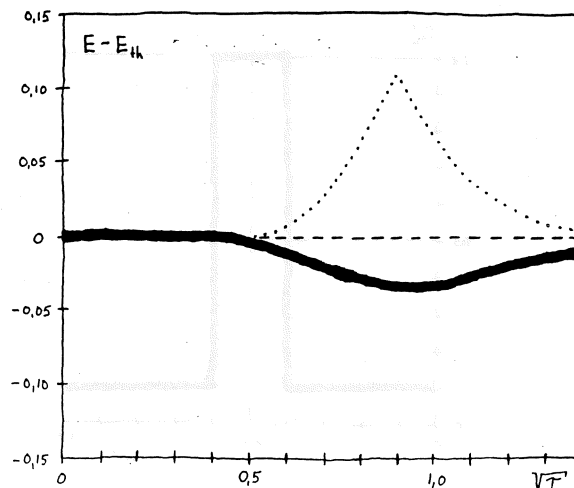
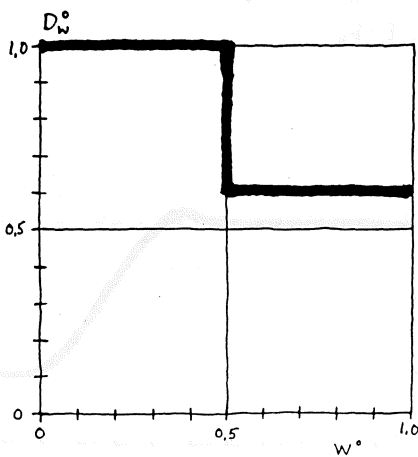


Figure 3.13: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity g

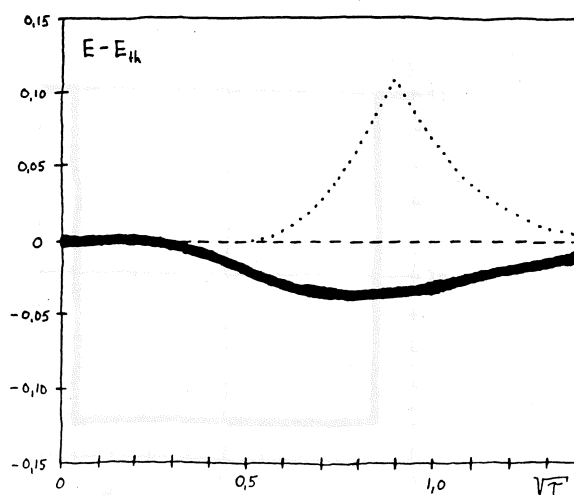
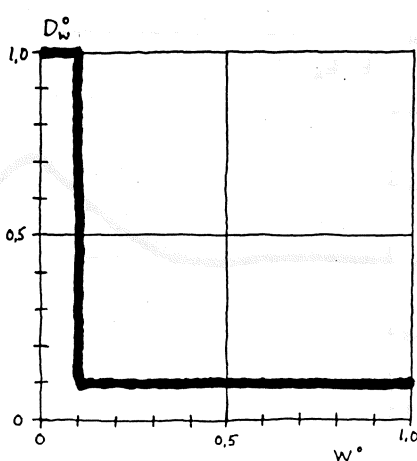


Figure 3.14: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity h

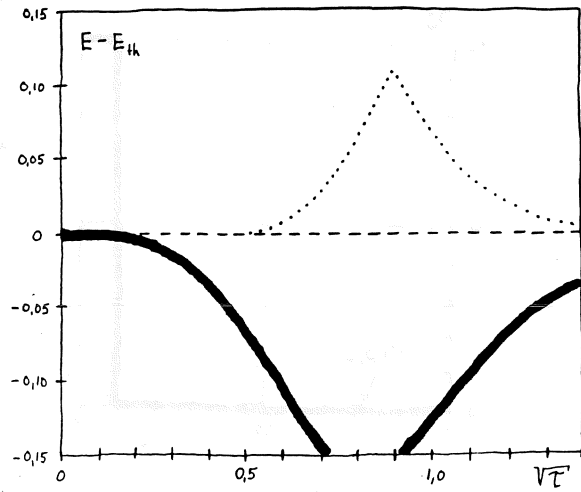
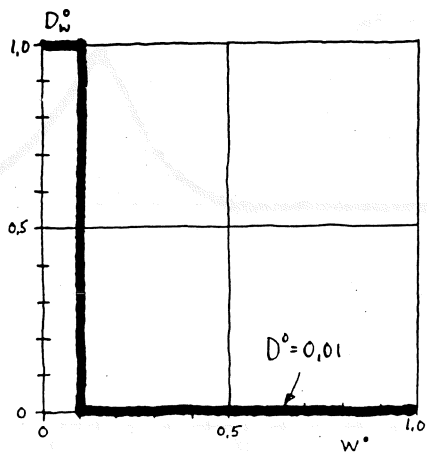


Figure 3.15: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity i

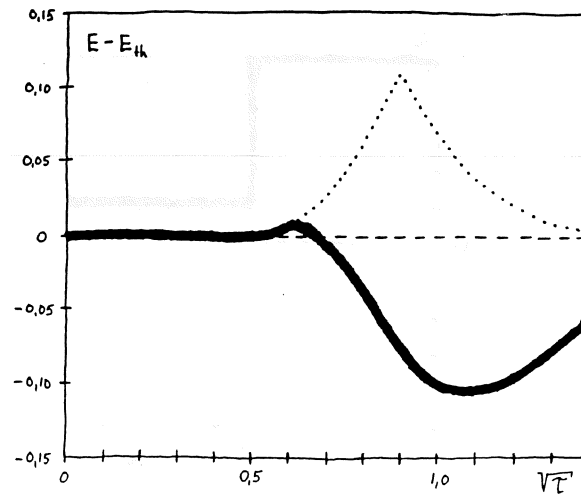
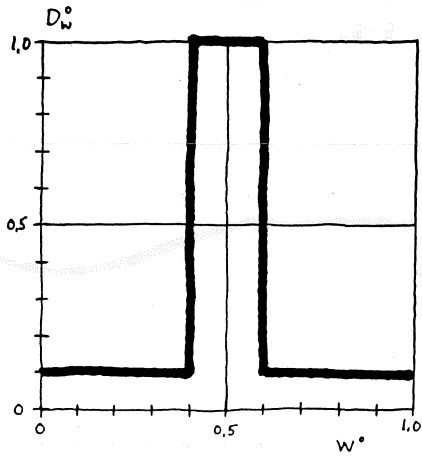


Figure 3.16: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity j

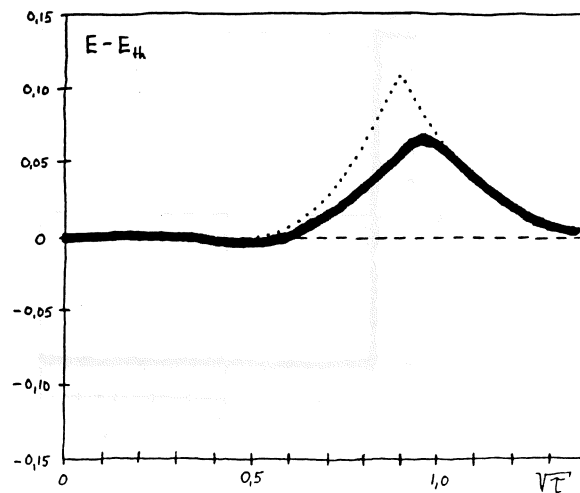
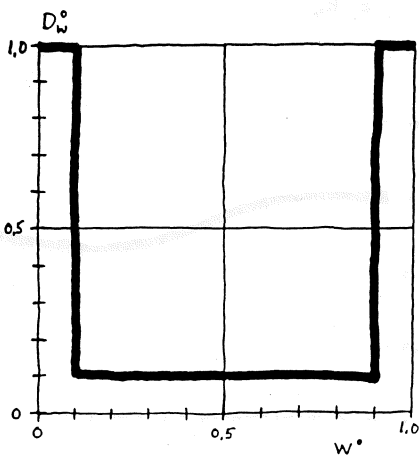


Figure 3.17: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity k

Chapter 4

SURFACE RESISTANCE

4.1 What is it?

A surface resistance is something that makes it harder for the water molecules to transport themselves through the surface of our sample. It is not too clear what is the cause of this, many explanations have been offered:

- As the air near the surface can be still, there is a diffusion resistance through this thin layer which the water molecules have to overcome. In section 4.3 I try to calculate this resistance theoretically by boundary layer theory and arrive at a value of the surface resistance which is much lower than has been measured recently. Another problem with this theory is that it seems to be impossible to remove all of the surface resistance by increasing the air velocity outside the sample (Rosen 1978).
- The possible binding sites for the water molecules on the surface of a sample of wood (and probably extending for some distance into the lumens) have been decreased by other molecules or dirt occupying them; or because they have been destroyed by light or the oxygen in the air. This would give a surface resistance as it would be hard for the water molecules to enter into the wood during absorption or leave it during desorption. As far as I know this theory has not been studied in detail for wood.
- It is of course also possible to imagine that the surface resistance is a thin layer of less conducting material. Given a guess of its thickness it would be easy to calculate its diffusivity. This is called a skin by Crank (1986) and a crust by food engineers.
- It has also been proposed that the heat of sorption, which will increase the temperature of the surface during absorption and decrease it during desorption, would cause this resistance by changing the relative humidity in the (pores of the) surface. Crank & Park (1949), Liu (1987) have shown that this influence is negligible.

An estimation that can be made to check this is to calculate the amount of energy released. If we know the heat conductivities and heat capacities of wood and air, a computer calculation of the temperature build-up at the surface can be made. The heat released is $2260 \cdot 10^3 J/kg$ (the heat of condensation which is a high approximation). The heat conductivity is approximately $0,15 W/(m \cdot K)$ for wood and $0,024 W/(m \cdot K)$ for still air. The respective capacities are $1260 J/(kg \cdot K)$ and $1000 J/(kg \cdot K)$. Using these values and neglecting convection we will certainly get a high guess. I have not done this calculations.

- Another theory is that there is no (or only a very low) surface resistance, and that it is internal mechanical effects that give effects looking like a surface resistance. As far as I know no-one has proved this theory to be correct, but it is of course tempting to use it

symbol	name	defining equation	unit	references
β_v	emissivity	$\beta_v = -g/\Delta v$	m/s	ISO 9346
S	emissivity	$S = -g/\Delta w$	m/s	Newman (1931a), Skaar (1954)
Z_ϕ	resistance	$Z_\phi = -\Delta\phi/g$	m^2s/kg	Arfvidsson (1988)
Z_v	resistance	$Z_v = -\Delta v/g$	s/m	Nevander & Elmarsson (1981)
Z_w	resistance	$Z_w = -\Delta w/g$	s/m	

Table 4.1: Different units for surface resistance

if you are sure that there is no or only a very low resistance at the surface (Liu 1987). I am not convinced that there are any major mechanical effects inside a sample undergoing sorption that can cause a surface resistance looking effect.

4.2 The surface resistance can be expressed in many ways!

The surface resistance can be expressed in many ways, which makes life hard for a researcher. Often one instead talk about surface emissivity, which is the reciprocal of the surface resistance. I prefer to use resistance as I think it is easier to understand, but I am fully aware that surface emissivity is of the same type as is the diffusivity; both have high values when the transport is high. Maybe resistance gives clearer understanding of transport through layers, and diffusion is better for diffusion in volumes.

There are also different ways of expressing the surface resistance depending on which you think is its causes; which gradient it is a function of In table 4.1 I have listed the units that I have found. The last unit of the table, Z_w , is introduced here only because it is the reciprocal of S . The other four units have been used by other researchers.

There is always a problem with using the relative humidity ϕ , and that is that some people prefer to use percent while others let it have values between zero and unity. As I belong to the latter group I do not use percent. If you have a value of Z_ϕ which is calculated using percent, you have to divide the value by 100 to compare it with the values I have. It is possible to run the program JAM-1 in both ways, with percent or with a relative humidity between zero and unity, as long as you are consistent and use the same units all the time (flow, resistances and relative humidities must all be expressed in *one* of these units).

The ϕ which only is a ratio of the actual vapour pressure and the saturation vapour pressure is also called the activity.

It is possible to transform any one of these into any other:

$$Z_w = \frac{1}{S} \quad (4.1)$$

$$Z_v = \frac{v_s}{S \cdot \xi} \quad (4.2)$$

$$\beta = \frac{1}{Z_v} \quad (4.3)$$

$$Z_\phi = \frac{Z_v}{v_s} \quad (4.4)$$

Here $\xi = dw/d\phi$ is the moisture differential capacity which is the slope of the sorption isotherm. As this is a function of the moisture content w , we have to use a mean value if we are

working in an interval. A good approximation is to use the mean value of $dw/d\phi$, which equals $\Delta w/\Delta\phi$.

4.3 A theoretical derivation

It is possible to theoretically derive equations for that part of the surface resistance which is caused by the air layer just outside the surface, the so called boundary air layer. It is important to remember that this theory does not include the effect of a lower diffusivity in the surface layer of the sample. In food engineering one often try to measure the temperature very near the surface as one knows that the material properties are different there, compared to inside the sample. Maybe there is also a crust or skin in wood, especially in weathered wood. We know that the surface properties change when wood is exposed to the sun or to outdoor climate, as it becomes harder to get a paint to adhere to a surface after it has been weathered. It is also advisable to use newly planed wood when gluing, as the joint otherwise will be comparatively weaker. We have to remember this when we now make some short calculations with boundary layer theory.

There is a small but important equation which is called Lewis equation, which relates surface resistance to heat flow, to surface resistance to mass flow (in this case moisture flow). For the case with water vapour in air, the equation looks like this:

$$\beta = \frac{\alpha_c}{\rho \cdot c_p} \quad (4.5)$$

$$\rho \cdot c_p \approx 1200 \text{ at } 20^\circ\text{C}$$

Lewis law is very interesting as it is an relation between transport of heat and transport of mass. It is derived under the presumptions that these to are caused by the same force: forced convection of molecules near a surface. It is therefore that α has an index c (convection), as other possible ways of transport are neglected. Especially for the heat transfer this means that there is no radiation (which of course can not be a way of water molecule transport). It is only for water vapour in air at atmospheric pressure that this simple form of the equation can be used. For other gases or liquids it has to be complemented (see for example Kneule 1975).

Now if we could calculate α_c , we could also find β , the surface emmissivity. I will show two different calculations of α_c . The first is for flow parallel to a thin plate of length L , which is shown in figure 4.1. I have also drawn a picture of my sample to show that the flow around it can not be the same, but I use it as a rough approximation.

I follow Eckert & Drake (1959 p173-178) and let the plate length L be 5 cm and the velocity of the air flow 3 m/s, both are normal values for sorption experiments. The Reynolds number is then 10000 and the Prandtlnumber is 0,7 (tabulated value). From these two values it is possible to calculate the Nusselt number Nu (the ratio of the heat flow by conductivity and convection, and the heat flow by conduction):

$$Nu = 0,332 \cdot (Pr)^{\frac{1}{3}} \cdot \sqrt{Re} = 29 \quad (4.6)$$

This means that the heat flow by convection is much larger then the heat flow by conductivity. The α_c -value decreases from the leading edge to the trailing edge according to $\alpha = (\lambda/x) \cdot Nu$, where λ is the heat conductivity (which is 0,0256 W/(m · K)). This gives us

$$\alpha_{min} = (0,0256/0,05) \cdot 29 \approx 15 \text{ W}/(\text{m}^2 \cdot \text{K}) \quad (4.7)$$

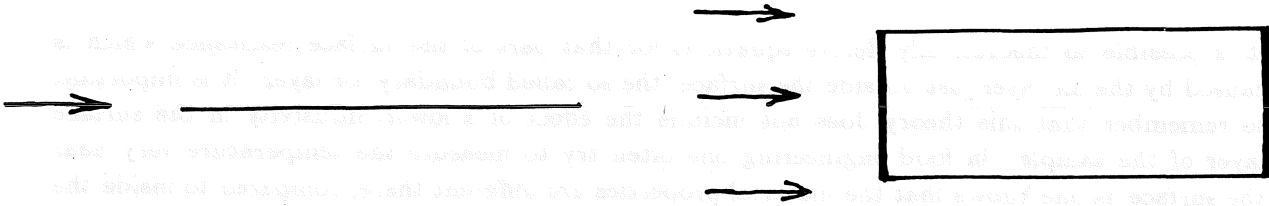


Figure 4.1: A thin plate and a real sorption sample

$$\alpha_{mean} = 2 \cdot \alpha_{min} \approx 30 W/(m^2 \cdot K) \quad (4.8)$$

Another way to calculate an approximation to the real α_c , is to use an equation for the heat transfer from air flowing in a circular tube. This can be said to be a very rough approximation to many samples standing near each others in rows. According to Perry & Chilton (p10/16 1973) we can use this equation:

$$\alpha_c = 3,52 \cdot r^{0,8} / d^{0,2} = 15 W/(m^2 \cdot K) \quad (4.9)$$

Here r is the air flow rate divided by area (mean air velocity) and d is the tube diameter. I have used the same velocity ($3 m/s$) as above and a tube diameter of $5 cm$. As the tube diameter is raised only to the power of two, α is not very sensitive to different values of the diameter (if I double the diameter α will decrease to $13 W/(m^2 \cdot K)$).

I conclude that according to these theories the heat emissivity is in the neighborhood of $15 W/(m^2 \cdot K)$. With Lewis equation we can then calculate a moisture emissivity by dividing 15 with 1200:

$$\beta_v = 0,012 m/s \quad (4.10)$$

$$Z_v = 80 s/m \quad (4.11)$$

$$S = 1,5 \cdot 10^{-6} m/s \quad (4.12)$$

with $\xi = 150 kg/m^3$ and at $20^\circ C$

Remember that this calculation is a calculation of the resistance of the boundary layer only.

This value agrees very well with measurements made by Choong & Skaar (1969, 1972), but are lower (the resistance) than the measurements by Rosen (1978) and Avramides & Siau (1987).

In figure 4.2 is a plot of Z_v as a function of the flow velocity calculated by the two methods.

4.4 Three experiments to find the surface resistance

I have found three distinctly different methods to measure a value of the surface resistance. The first has been used a lot, the second is comparatively new and the third method is as far as I know not used before:

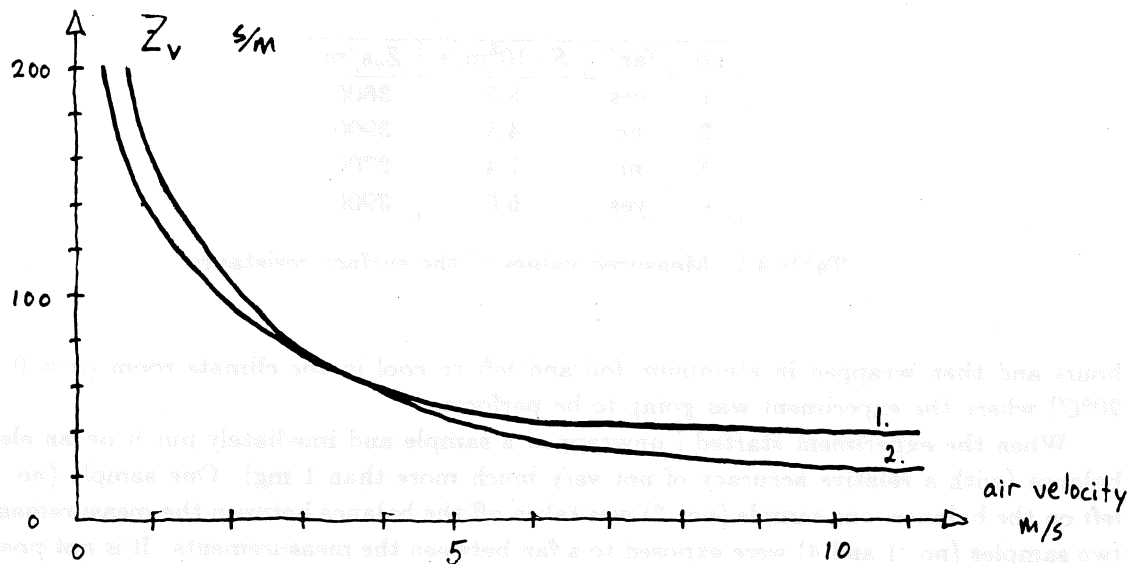


Figure 4.2: Surface resistance as a function of the air flow velocity for the two methods used (1: Eckert & Drake, 2: Perry & Chilton)

Newman (1931a) solved the sorption equation including the surface resistance expressed as a function of the difference in moisture content. Skaar (1954) and Choong & Skaar (1969) used this solution to show that it was possible to calculate the surface resistance from a number of sorption experiments with different sample thicknesses. This method has been used by Choong & Skaar (1969, 1972), Rosen (1978) and Avramides & Siau (1987).

Hart (1977) proposed a different method to find the effective moisture content of the surface as a function of the equilibrium moisture content and the flow during drying. He used a modified psychrometric equation. Knowing the surface moisture content makes it easy to calculate the surface resistance. Rosen (1982) reports that the method of Hart compares favourably with experimental data from Choong & Skaar (1972). Studying all values given by Hart makes the comparison less favourable, but still not bad; possibly indicating that the surface resistance is not a function of the moisture content.

Arne Hillerborg, one of my tutors, has suggested a different method which I have tried to use. In short I measure the surface resistance by studying the initial moisture uptake during a sorption experiment. I have not found any references to a method like this, but it is such a simple method that has probably been used before. I explain my experiments in detail in the next section.

4.5 New measurements of the surface resistance

When a dry sample is put into a wet climate it starts to absorb humidity. During the first seconds the only resistance to sorption is the surface resistance; the flow being from humid air into dry wood through this resistance. It should then be possible to calculate the resistance if we knew the flow of vapour into the sample during the very first instances of the experiment.

To test the idea I have made a simple experiment with four samples of spruce (*Picea abies*), each approximately 300 x 70 x 8 mm. The end grain was hidden with a strip of aluminum tape (I do not think that this was necessary). The samples was dried at about 100°C for about 20

no.	fan?	$S \cdot 10^8 \text{m/s}$	$Z_v \text{s/m}$
1	yes	5,0	3600
2	no	4,5	3900
3	no	7,4	2700
4	yes	5,0	3900

Table 4.2: Measured values of the surface resistance

hours and then wrapped in aluminum foil and left to cool in the climate room ($\phi = 0,65$ and 20°C) where the experiment was going to be performed.

When the experiment started I unwrapped a sample and immediately put it on an electronic balance (with a relative accuracy of not very much more than 1 mg). One sample (no. 3) was left on the balance, one sample (no. 2) was taken off the balance between the measurements, and two samples (no. 1 and 4) were exposed to a fan between the measurements. It is not possible to see any differences between the measured results of the different samples. In table 4.2 is shown the values of the surface resistance evaluated on the basis of the slope of the sample weights from 0 to 60 s.

These values are very much like the values of Rosen (1978) and Avramides & Siau (1987), but very much larger (resistances) than Choong & Skaar (1969, 1972).

The only serious problem with these measurements is that it is hard to know when the initial period is over; when the internal resistances also begin to effect the sorption. I have two ways of investigating for how long time I can measure the effect of the surface resistance only:

1. The initial sorption through the surface resistance should be a function of time, whereas the later sorption is a function of the square root of time. When I have a large surface resistance the sorption will never completely become a function of the square root of time, but one way of judging the length of the initial period is probably to see when the sorption begins to leave the initial straight line.

If I look at my four sorption curves three of them are nearly straight lines from 60 s to 600 s (I have not measured more than 600 s). One of the curves (no. 3) is concave towards the time axis. All four curves have an initial jump between 0 s and 60 s. I do not know the cause of this. If this is the true initial slope of the sorption, then the real value of the surface resistance is lower than in the table.

2. As I know the approximate equilibrium sorption curve it is possible to calculate the moisture content of a layer x mm thick which holds all the humidity which the sample has absorbed during the first 600 s of the experiment (the equilibrium moisture content of spruce at $\phi = 0,65$ is $u = 0,125$). In table 4.3 it is seen that a layer of more than $0,03 \text{ mm} = 30 \mu\text{m}$ must be affected (because the equilibrium moisture content in the outside climate is $u \approx 0,12$). Probably $0,1 \text{ mm}$ or so is affected. so what we are watching is not just a surface effect.

To find out more about this I made a simulation of the situation using a surface resistance $Z_v = 3500 \text{ s/m}$ and a measured diffusivity taken from Bertelsen (1983) and extended down to $w = 0$ (I do not think that the form of the diffusivity is very important in this simulation). The result is shown in figure 4.4.

From 50 s to 250 s the surface moisture content increases from 33 kg/m^3 to 45 kg/m^3 . From this I easily calculate that the moisture content difference decreases from 29 kg/m^3 to 17 kg/m^3 . When I calculated the surface resistances in table 4.2 ($\approx 3500 \text{ s/m}$) I used a moisture content

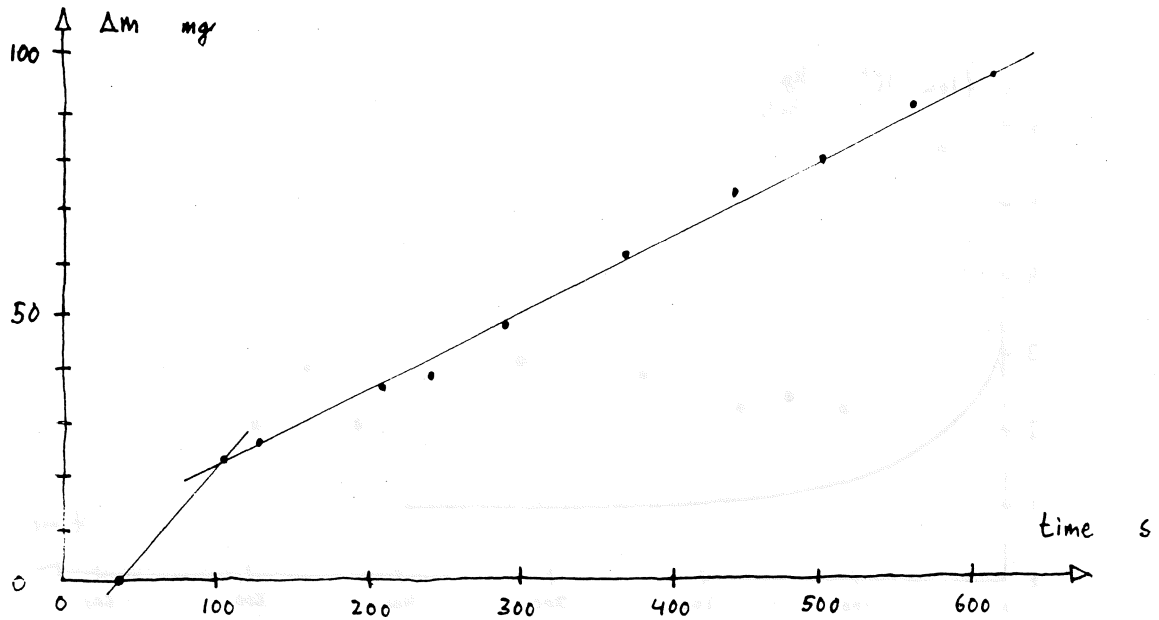


Figure 4.3: Initial sorption by sample no. 4 with first measurement at 30s. Note the linear time scale in this diagram.

thickness x (mm)	moisture content u (kg/kg)
0,001	3,6
0,01	0,36
0,1	0,036
1	0,0036
10	0,00036

Table 4.3: moisture content absorbed during first 600 s of experiment compressed into different thicknesses

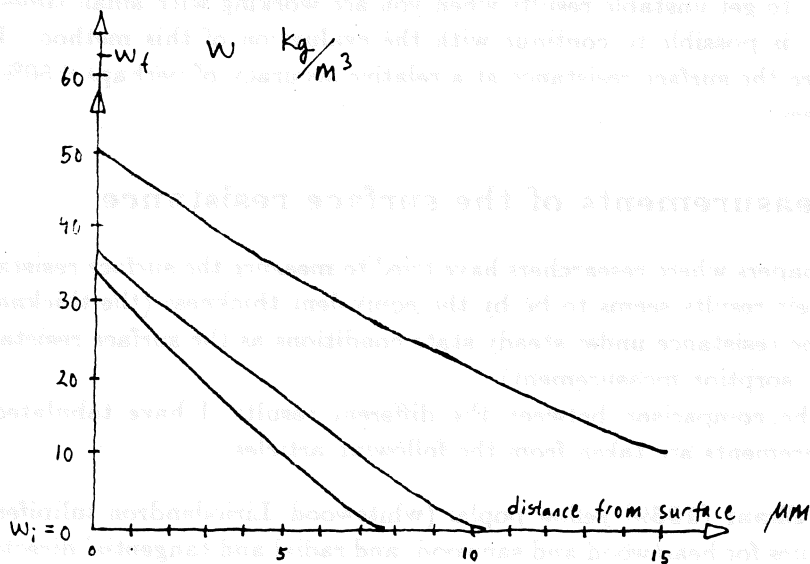


Figure 4.4: Simulated moisture contents near the surface at the beginning of the sorption (the final equilibrium moisture content is $w_f = 62 \text{ kg/m}^3$)

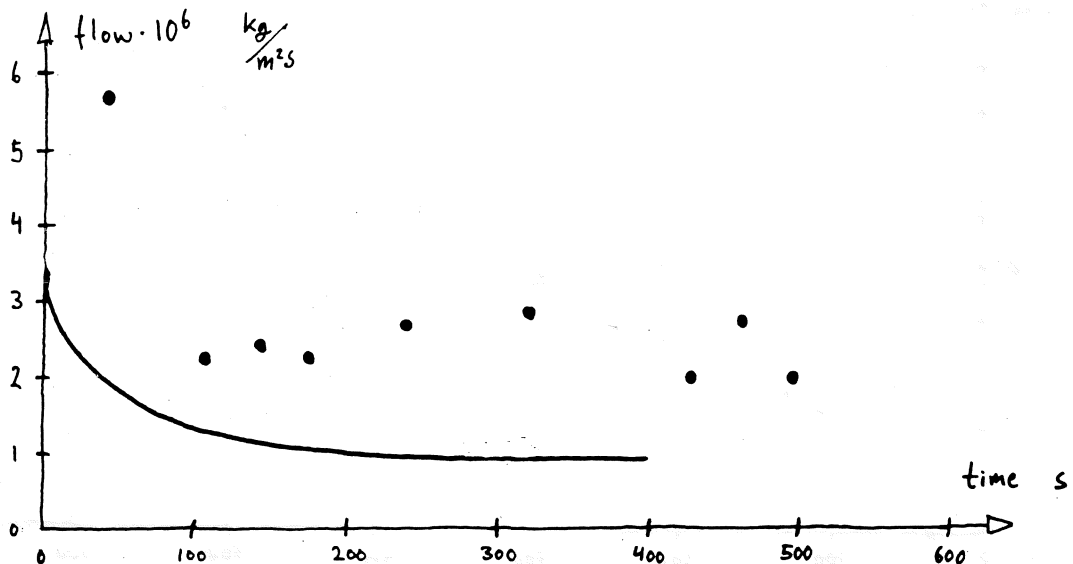


Figure 4.5: Simulated and measured flow (sample no.4)

difference of 62 kg/m^3 . From this I draw the conclusion that the surface resistance is less than half the value I got. Maybe a value of 1500 s/m is a good guess.

In figure 4.5 I have drawn a diagram of the flows from the above mentioned simulation and measurement. The forms of the flow as a function of time agrees quite well, but the measured flow is 2-3 times as large. This is because I have used a surface resistance of 3500 s/m which was calculated from the experimental flow for $t > 100 \text{ s}$. A smaller surface resistance would have given a better result. I plan to continue this work with better experiments and new simulations.

This method of finding the surface resistance seems to be working if I have some knowledge of the diffusivity which I can use in a simulation program. One very important thing about simulations of the moisture content near the surface at the start of the sorption is that there is a relation between the simulation time-step and the simulation cell size. If you do not observe this it is very easy to get unstable results when you are working with small time-steps.

I hope that it is possible to continue with the evaluation of this method. It would seem possible to measure the surface resistance at a relative accuracy of perhaps $\pm 50\%$, which would suffice in most cases.

4.6 Old measurements of the surface resistance

I have read some papers where researchers have tried to measure the surface resistance. The best way to express their results seems to be by the equivalent thickness (the thickness of material which has the same resistance under steady state conditions as the surface resistance has in the initial stage of the sorption measurement).

To simplify the comparison between the different results, I have tabulated them in table 4.4. The measurements are taken from the following articles:

1. Choong & Skaar (1969) yellow poplar (whitewood, *Liriodendron tulipifera*); very much the same values for heartwood and sapwood, and radial and tangential directions. Sorption from $\phi = 0,25$ to $\phi = 0,40$ at 32°C . I have used $\xi = 95 \text{ kg/m}^3$ and $v_s = 0,034 \text{ kg/m}^3$.
2. Choong & Skaar (1972) sweetgum (redgum, *Liquidambar styraciflua*); desorption from near fibre saturation point to $u = 0,18$ ($\phi \approx 0,82$) at 38°C . Air speed $1,5 > \text{ m/s}$. I have

article see page 28	L, T or R direction	Z_v s/m	$D_w \cdot 10^9$ m^2/s	$b \cdot 1000$ mm	
1	T and R	300	0,9	0,8	
2	L	100	2,4	2,1	
	T	130	1,0	1,1	
3	L	70	13	8	
	L	80	7	5	
	T	70	4	4	
	T	70	0,24	0,15	
4		110	0,2	1,5	
5	R	13000	0,07	5	speed of air 0,4
		4000	0,07	2	1,1
		3300	0,07	1,7	1,9
		2300	0,07	1	2,9
		2400	0,07	1,4	3,8
		1800	0,07	0,8	12
6		3300	8	1,2	moisture content 0,032
		6000	9,3	1,7	0,063
		5800	1,4	2,6	0,092
		9700	-	-	0,137

Table 4.4: Surface resistances taken from different articles

used $\xi = 400 \text{ kg/m}^3$ and $v_s = 0,046 \text{ kg/m}^3$.

3. Choong & Skaar (1972) redwood (*Sequoia sempervirens*), otherwise as no. 3.
4. Mackay (1971) *Ceratopetalum apetalum* was used in measurements with the cup method to study the effect of stirring the air in the cup. Berthelsen (1982 p43) has calculated the surface emissivity in the measurements of Mackay as being $0,2 - 0,5 \cdot 10^{-6} \text{ m/s}$. I calculate it as being $0,13 \cdot 10^{-6} \text{ m/s}$. Some values are uncertain in our two calculations.
5. Rosen (1978) black walnut (American walnut, *Juglans nigra*); with different air speeds. Sorption from $u = 0,06$ ($\phi \approx 0,26$) to $\phi = 0,97$ at 25°C . I have used $\xi = 150 \text{ kg/m}^3$ and $v_s = 0,023 \text{ kg/m}^3$.
6. Avramides & Siau (1987) Western White Pine (*Pinus Monticola*). Absorption measurements with the sorption method at 30°C . I have used $\xi = 150 \text{ kg/m}^3$ and $v_s = 0,030 \text{ kg/m}^3$.

The older measurements by Choong & Skaar have much lower values of the surface resistance than have Rosen and Avramides & Siau. The equivalent thickness (b) do however not seem to differ that much, as it is in the range $1 - 5 \text{ mm}$ for most of the measurements.

4.7 Computer simulations with surface resistance

I have made some computer simulations to study the influence of the surface resistance on the sorption curve. The program JAM-1 which I am working with wants the surface resistance expressed as Z_ϕ . This is no problem since I can convert S to Z_ϕ .

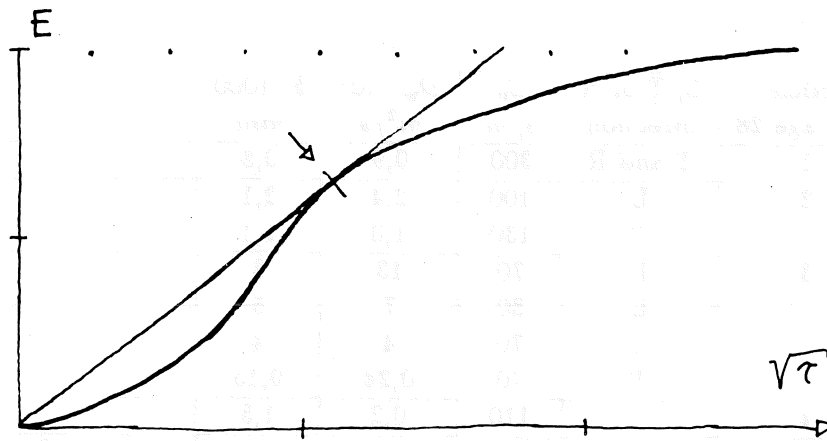


Figure 4.6: My rule to choose a point where to calculate the diffusivity \tilde{D}_w when there is a surface resistance

b/a	surface resistance	legend to figures 4.7-4.9
2,5	high	— — — — —
0,25	normal	- - - - -
0,025	low	· · · · ·
0	no	—————

Table 4.5: Simulated levels of surface resistance

I have chosen to use equation 1.7, and I think this gives certain advantages when I have surface resistances, even if these advantages are quite small. When there is a surface resistance the initial sorption will no longer be proportional to the square root of time, and I will therefore have to have a new rule how to choose the diffusivity. In figure 4.6 is shown how I have done: I calculate the diffusivity with equation 1.7 at the point of largest slope from the origin to any point on the curve.

As I wrote in the first two chapters I have been working with dimensionless variables. This means for example that D° is in the range from zero to unity, which is to be compared with a real value of D_w of around $10^{-9} \text{ m}^2/\text{s}$. If I know the value of a real surface resistance, which value should I then use when working with the dimensionless variables to get the same effect on the sorption?

I have let the equivalent thickness of the surface resistance (b) divided by the actual thickness (a) become an invariable, a variable which does not change its value upon transformation.

$$\text{invariable} \quad \frac{b}{a} = \frac{D_w \cdot Z_w}{a} = \frac{D_w}{S \cdot a} = \frac{D_w \cdot Z_\phi \cdot \xi}{a} \quad (4.13)$$

Knowing b/a it is easy to calculate Z_ϕ if we know $\xi = dw/d\phi$ (which is unity during my simulations).

As I showed in section 4.6 a value of $b = 0,0025 \text{ m}$ is probably quite normal for samples with a half thickness of a centimeter. I have worked with a b/a -value of 0,25 as normal in my simulations. I have also simulated one case with high, one with low, and one with no surface resistance.

In figures 4.7-4.9 are shown the $E - E_{th}$ -diagrams for three different $D^\circ(w^\circ)$.

When looking at these curves, remember that \tilde{D} is taken where it has its maximum value (see chapter 3.4). The diagrams shows therefore not only the effect of the surface resistance,

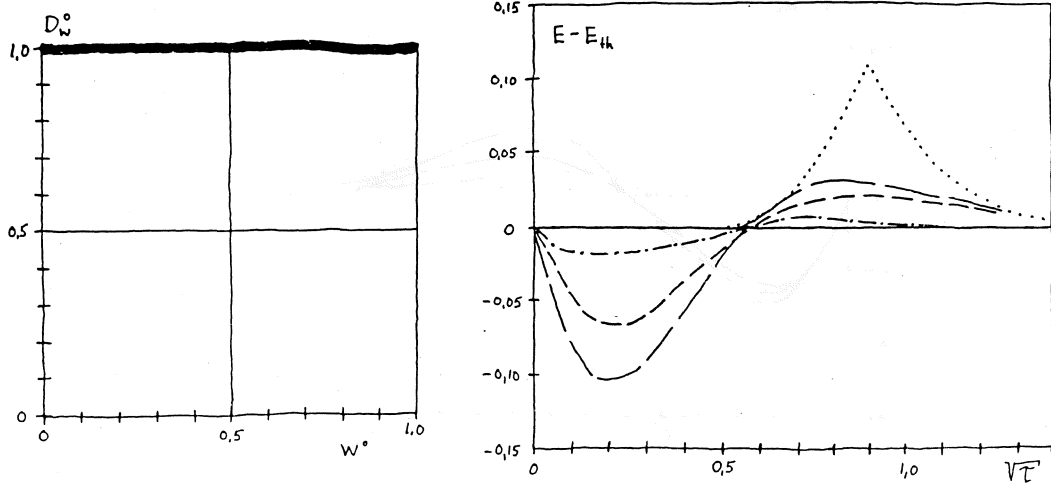


Figure 4.7: The effect of different surface resistances with constant diffusivity

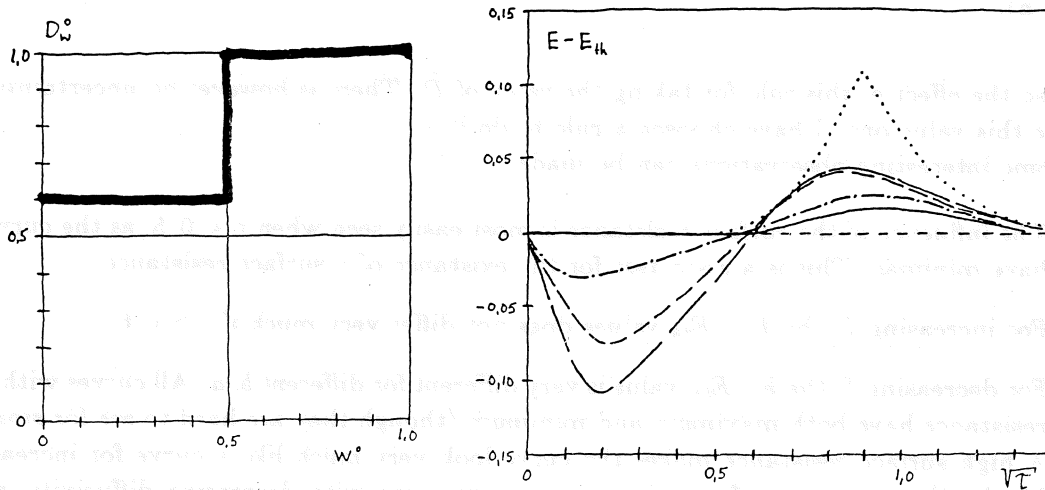


Figure 4.8: The effect of different surface resistances with an increasing diffusivity

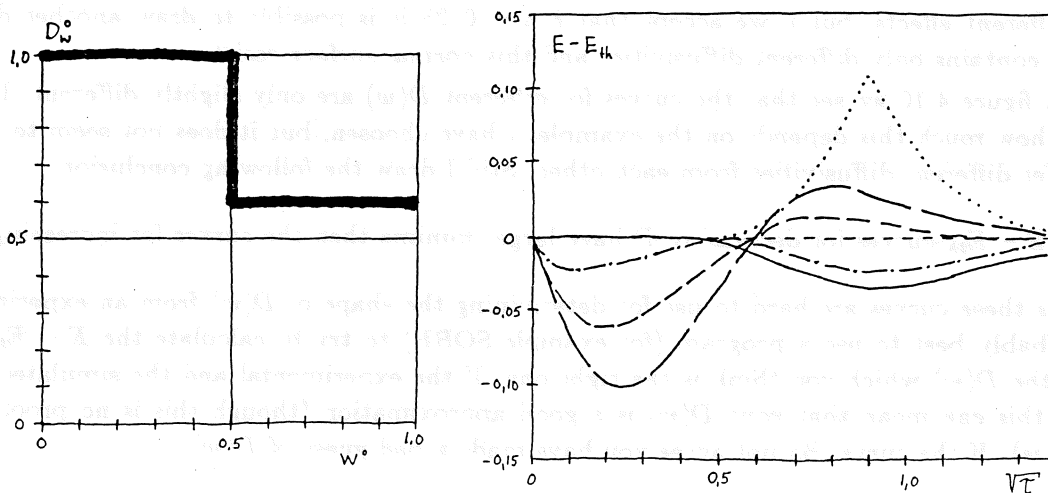


Figure 4.9: The effect of different surface resistances with a decreasing diffusivity

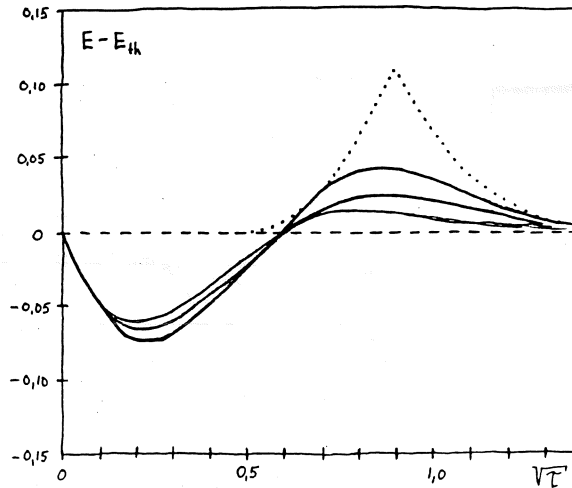


Figure 4.10: The effect of different diffusivities on the $E - E_{th}$ -diagram when the surface resistance is normal ($b/a = 0,25$). The curve with the largest "amplitude" is curve c (with increasing diffusivity). The one with the smallest is g. The middle curve is from the constant diffusivity (curve a).

but also the effect of this rule for taking the value of \tilde{D} . There is however no uncertainty where to take this value once I have chosen a rule to do it.

Some interesting observations can be made:

- The influence of the surface resistance is most easily seen when $\tau < 0,5$, as the curves then have minimas. This is a good test for the existance of a surface resistance.
- For increasing D the $E - E_{th}$ -values does not differ very much if $\tau > 0,6$.
- For decreasing D the $E - E_{th}$ -value is very different for different b/a . All curves with surface resistance have both maximum and minimum (though they are hard to see for small b/a). A high surface resistance makes the curve look very much like a curve for increasing D . Maybe there is more information in a measurement with decreasing diffusivity, as these take much longer time.

These observations makes the curves look confusing. It seems to be impossible to sort out the different effects, but if we accept that $b/a = 0,25$ it is possible to draw another diagram which contains only different diffusivities and this normal surface resistance.

In figure 4.10 we see that the curves for different $D(w)$ are only slightly different. I do not know how much this depends on the examples I have choosen, but it does not seem to be easy to differ different diffusivities from each other. Still I draw the following conclusion:

- $E - E_{th}$ -curves for decreasing D have larger minima then the curves for increasing D

As these curves are hard to use for determining the shape of $D(w)$ from an experiment, it is probably best to use a program (for example SORP) to try to calculate the $E - E_{th}$ -curve from the $D(w)$ which you think is the right one. If the experimental and the simulated curves agree this can mean that your $D(w)$ is a good approximation (though this is no proof that it really is). If the curves do not agree you have made a bad guess of $D(w)$.

Chapter 5

A FEW TEST EXAMPLES

I have taken three sorption curves from articles by Rosen, Crank & Park and Liu. I have measured these curves as exactly as possible with a ruler. This is of course not a method to be encouraged and I will try to remake the calculations with real measured data.

In Rosen (1978) a curve for longitudinal adsorption in a 1,6 cm thick sample of silver maple is shown. The adsorption is from $\phi = 0,26$ to $\phi = 0,97$ and the air velocity was 3,8 m/s. In figure 5.1 we can see that there seems to be an initial delay (because of a surface resistance) and a later slowing up of the sorption process (possibly due to a decreasing diffusion coefficient).

In figure 5.2 I have drawn the $E - E_{th}$ -diagram which shows these two effects more clearly.

Crank & Park (1949) made measurements of adsorption of chloroform by polystyrene at $25^{\circ}C$. I have taken one of their diagrams, showing a sorption up to a percentage regain of 9,5 % (figure 5.3). This looks different from the one from Rosen in figure 5.2. Here it is clear that the diffusivity is increasing.

I have also a third example from Liu (1987) in which two half hard fibreboard samples were equilibrated at $\phi = 0,65$. One of them was then put in a drier climate of $\phi = 0,30$ and the other was put in a climate which was $\phi = 0,80$.

On page 35 a $E - E_{th}$ -diagram is shown, with two sets of data. Even if the number of data points are quite few, especially for the desorption, we can draw some conclusions from them. The data from the absorption experiment indicates that there is a surface resistance and that the diffusivity probably is increasing. The data from desorption shows no surface resistance as there are no data-points in this region, but seems to indicate that the desorption is increasing in this ϕ -interval too (remember that desorption plots are interpreted the other way as I showed

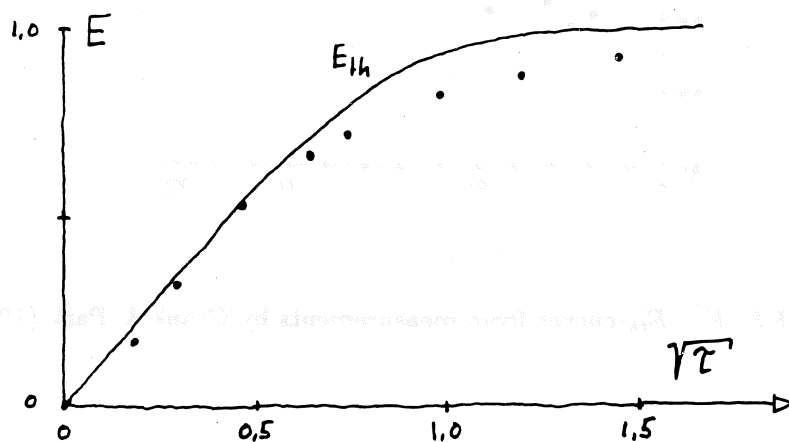


Figure 5.1: Sorption-data taken from Rosen (1978)

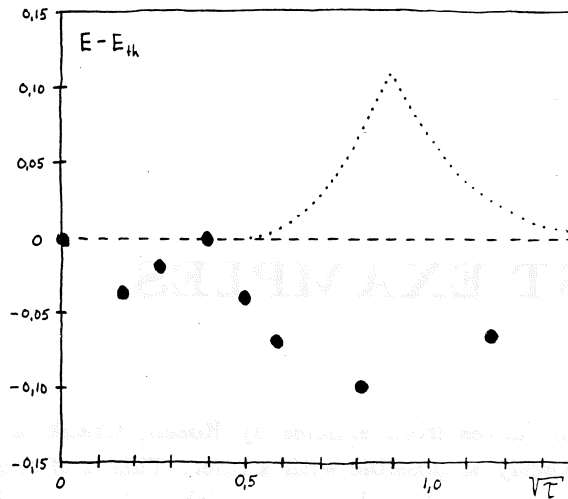


Figure 5.2: $E - E_{th}$ -diagram for data taken from Rosen (1978)

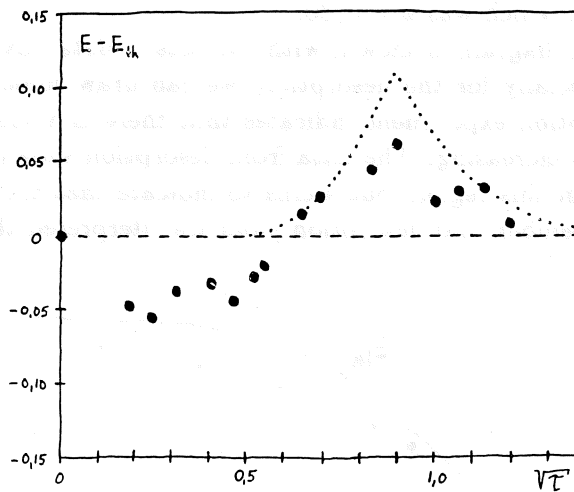


Figure 5.3: $E - E_{th}$ -curves from measurements by Crank & Park (1949)

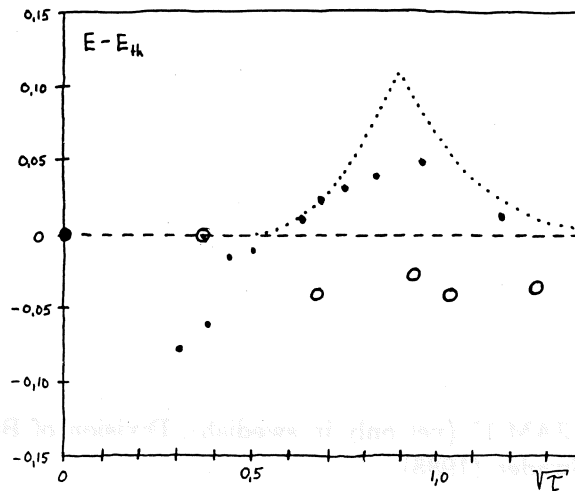


Figure 5.4: $E - E_{th}$ -curves taken from Liu 1987. Filled circles are for absorption and open circles are for desorption

in section 3.4). The diagram seems to indicate that the diffusivity is increasing in the whole ϕ -interval.

I do not know if this theoretical method is reliable or not when it comes to real measurements. Some reasons why it might not be good enough are listed below.

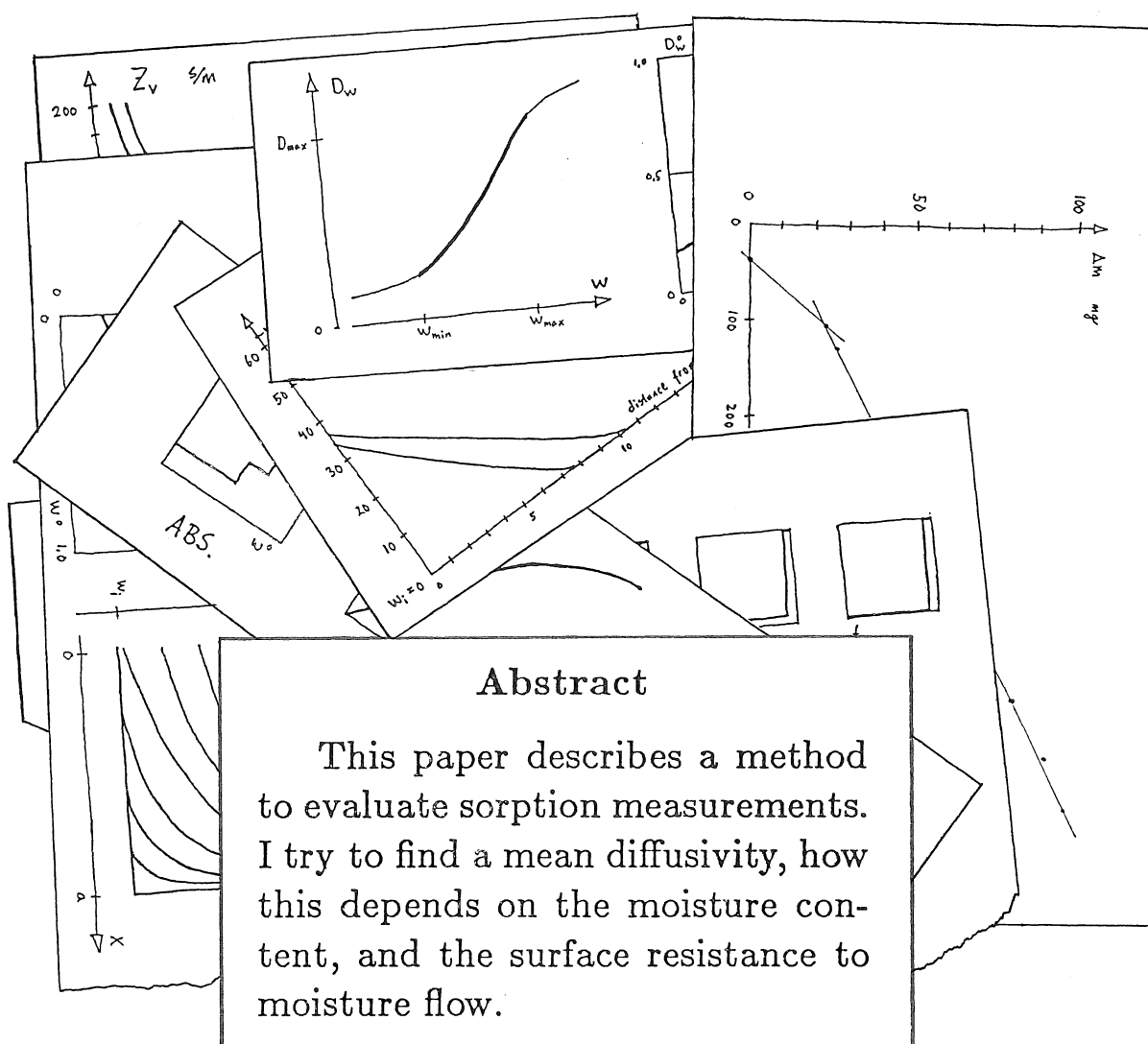
- Unavoidable errors in the measurement:
 - non-constant ϕ
 - leaks in the sealed surfaces
 - fluctuating air velocity
 - etc.
- The material does not fulfill the requirements of the method:
 - cracks
 - late- and earlywood having different properties
- Other effects which are not accounted for:
 - mechanical effects from swelling and shrinking
 - decomposition of the wood
 - non Fickian behavior

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The sorption method old and new ideas

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INTRODUCTION

This is a paper about the sorption method. It describes my work and findings when I introduced myself to this very much used method. Because of this it contains both old and new material.

I use SI-units and the nomenclature of ISO 9346 (1987) as much as possible. This means that I do not use the same symbols as do most wood researchers. I do however not write this paper for wood researchers only, but also for my colleagues who work with moisture transport problems in different building materials. The sorption method is not used so widely among them as among wood scientists.

Most of the diagrams are drawn by free hand from the computer screen output, and are therefore not exact enough to be used quantitatively. Qualitatively they are good enough I think. When I continue this work I will make a catalogue showing the effect of different diffusivities and experimental errors.

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Chapter 1

THEORY

1.1 What is a sorption measurement?

First of all I would like to explain what a sorption measurement or a non steady state measurement is. It is a simple method to measure the moisture diffusivity in a material, but the evaluation of the result is not as simple as I first thought when I began to study this method.

To use the method I take a sample of the material I want to test and seal four surfaces, leaving only two opposite faces open. Then I leave it in a constant climate to equilibrate; this can take several months if the material is wood and the thickness is a few centimeters. When the mass of my sample does not change any more, I change the climate and start to record the changes in mass, which results from the water molecules entering or leaving the wood. This measurement of mass change as a function of time is the result of the experiment. Normally the mass change is plotted as a function of the square root of time, which (according to theory) should give a straight line as long as there is no moisture change in the centre of the sample. After this the mass change will naturally slow down (as the sample gets near equilibrium) and asymptotically approach the final mass change.

This is the sorption method, which has been used by many wood researchers (Stamm 1959, 1960; Choong & Skaar 1969, 1972) and others (Crank & Park 1949; Newns 1956, 1968, 1973, 1974; Stamm 1956; Liu 1987).

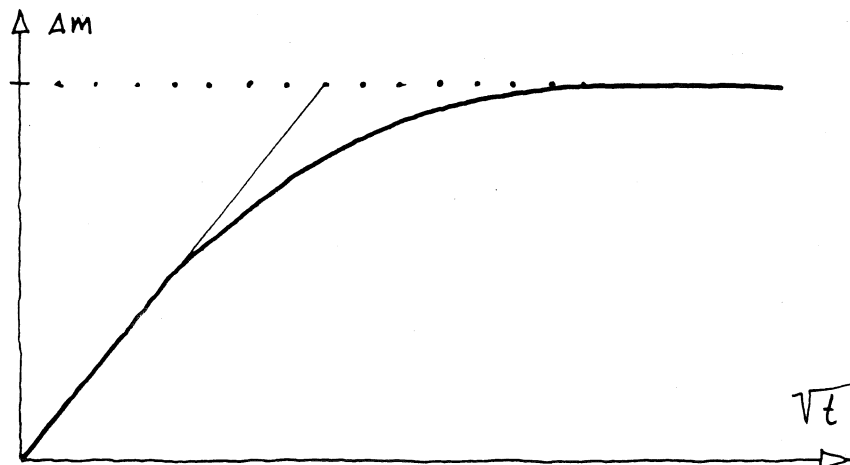


Figure 1.1: The result of an adsorption experiment

1.2 Analytically solvable if D_w is constant

The theory for sorption or drying has been explored by many researchers through the years. I will here give a summary of the most important equations.

The problem is to solve one of the following two equations with the boundary and initial conditions of the sorption problem:

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x} \left(D_w(w) \cdot \frac{\partial w}{\partial x} \right) \quad (1.1)$$

$$\frac{\partial w}{\partial t} = D_w \cdot \frac{\partial^2 w}{\partial x^2} \quad (1.2)$$

initial conditions: $w = w_i$ for all x

boundary conditions: $w = w_f$ for $x = \pm a$

The first equation is for non constant $D_w(w)$ and the second is for a constant D_w . Only the second equation is analytically solvable as the constant D_w then can be moved out from inside the derivations. Newman (1931b) gives the solution to it without showing how it can be derived. He cites Osgood: "a function that satisfies a differential equation is a solution, no matter how obscure its origin; and one that does not satisfy it is not a solution, no matter how illustrious its pedigree may seem to have been". It seems a good idea for a non-matematician like myself to let others give me the solutions, which I can check. Its easy to show that the following equation satisfies the differential equation (Newman 1931b p315-316):

$$w(x, t) = w_f + (w_i - w_f) \cdot \frac{4}{\pi} \cdot \sum_1^{\infty} \frac{(-1)^{n+1}}{2n-1} \cdot \cos\left(\frac{(2n-1) \cdot \pi \cdot x}{2a}\right) \cdot e^{-(2n-1)^2 \cdot D_w \cdot t \cdot \left(\frac{\pi}{2a}\right)^2} \quad (1.3)$$

This solution gives us the concentration at any time and place in a sorption experiment sample. What is more interesting to us is the integrated value of the concentration, as this is what we measure during an experiment as a mass increase or decrease. The integration is performed with the time t constant and distance x as integration variable (Newman 1931b p322-323):

$$E(t) = 1 - \frac{8}{\pi^2} \cdot \sum_1^{\infty} \left(\frac{1}{(2n-1)^2} \cdot e^{-(2n-1)^2 \cdot \frac{D_w \cdot t}{a^2} \cdot \left(\frac{\pi}{2}\right)^2} \right) \quad (1.4)$$

This is the equation which gives us the sorption as a function of time, thickness and a constant diffusivity. E is defined as the dimensionless sorption: zero when we start the sorption, and unity when we have reached a new equilibrium. In this paper this function will be called E_{th} when we refer to the E -value of the theory for constant D_w (equation 1.4).

When I drew the diagram of E in fig 1.1 I drew it as a function of \sqrt{t} . This is because the initial curve in the diagram then becomes a straight line. This can be explained in the following way for all diffusivities (not only constant).

For the first part of a sorption experiment, the concentration in the centre of the sample is still the initial concentration. This is the same as saying that the sorption is effectively a sorption into a half infinite slab.

Boltzmann (1894) was the first to show that the above stated differential equation reduces to an ordinary differential equation if we express the concentration as a function of a new variable $\eta = x/(2\sqrt{t})$. This means that the equation can be solved numerically, the solution being a

function of η and D_w only (Crank & Park 1949 p638). This possible use of the single variable $\eta = x/(2\sqrt{t})$ shows us three things:

- A curve drawn of the concentration in the sample as a function of time, has the same *form* as long as the concentration in the middle has not begun to change. As time goes the only difference is that the concentration curve gets pulled out like an accordion.
- The sorption is proportional to the square root of time. If we want the sorption to extend twice as long into our sample, we have to wait four times as long time.
- As it has the same form, and this form gets pulled out as \sqrt{t} it follows that the mass change in sorption drawn as a function of \sqrt{t} is a straight line.

Remember that this is true for all diffusivities, constant *and* non constant, as long as the sample behaves like a half infinite slab.

1.3 Finding the diffusivity

If we measure the sorption as a function of time, we then want to find the diffusivity D_w . This can be done in many ways, at least if we consider D_w to be constant as there is a solution to this case. As this is an exact solution, it is of course possible to see which D_w that makes the measured curve equal the theoretical.

One way which is used by Crank & Park (1949), Crank & Henry (1949ab), Liu (1987) and others is to equate the measured and the theoretical time to half sorption (when $E = 0,5$). A numerical approximation is (Crank & Park 1949, Crank p239 1986).

$$D_w = 0,04939 \cdot \frac{4a^2}{t} \quad (1.5)$$

A second way is to use the following approximation, which is good if $E > 0,667$ (Liu 1987):

$$D_w = \frac{4a^2}{\pi^2 t} \cdot \ln\left(\frac{8}{\pi^2(1-E)}\right) \quad (1.6)$$

I think a third method is the best. As the initial part of the curve is straight we can use its slope (Crank 1986 p244):

$$D_w = \frac{\pi a^2}{4} \cdot \left(\frac{dE}{d\sqrt{t}}\right)^2 = \frac{\pi a^2}{4} \cdot \frac{E^2}{t} \quad (1.7)$$

This equation can be used as long as the curve is a straight line; as long as the sample can be viewed as half infinite.

An equation that is similar to the last equation above was derived by me to be used when we only have the initial straight line:

$$D_w = \frac{\pi}{4 \cdot w_f - w_i^2 \cdot A^2} \cdot \left(\frac{m(t) - m_i^2}{t}\right) \quad (1.8)$$

Where $m(t) - m_i$ is the mass change at time t , and A the sample area. This equation is good to use when we know the initial sorption into a very thick sample (so thick that we do not want to wait for equilibrium). It can also be used when we only want an approximate value of D or when we want a first approximation when the experiment is still running. The values of $m(t)$ and t should be taken on the initial straight slope. Knowing the initial and the final climates it is easy to get values of w_i and w_f from the sorption isotherm.

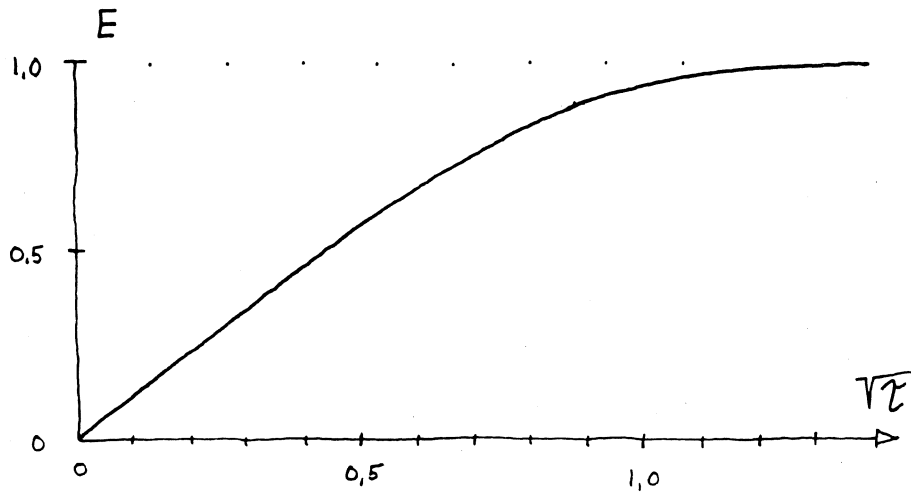


Figure 1.2: A dimensionless sorption curve

The four equations above will give the same results as long as the diffusivity is constant. If it is not, E will not equal E_{th} , and these equations will at be different approximations to the diffusivity.

In the following I shall call the calculated diffusivity \tilde{D} to separate it from the real diffusivity and the arithmetic or any other mean value of a non constant diffusivity.

But what is \tilde{D}_w if $D_w(w)$ is not constant? It will be some sort of mean value (not arithmetical mean though). I take a closer look at this in section 3.4.

1.4 It is easier if it is dimensionless

I have shown that it is easier to draw the sorption as a function of the square root of time (fig 1.1). I have also introduced E , which is the dimensionless sorption.

It would be nice if we could draw the diagram totally dimensionless, because then all diagrams (at least with constant D_w) would look exactly the same. This can be done, and the best dimensionless time to use is the Fourier number

$$\tau = \frac{D_w \cdot t}{a^2} \quad (1.9)$$

With this we can plot two standard diagrams, which we will use when we explore different kinds of sorption.

In figure 1.2 it is E_{th} that is drawn against $\sqrt{\tau}$. All sorptions with a constant diffusivity show exactly this behavior. If two measurements from different experiments, both with constant D_w , are drawn in the same diagram, the curves will coincide. The reverse is also true (at least for all cases that I have studied): if a sorption with a non constant $D_w(w)$ is drawn in a diagram like this, it will deviate from E_{th} . This is what I explore in the following chapters.

But first a few words about other dimensionless units. It is also convenient to do like Crank & Henry (1949a), and use dimensionless diffusivity and dimensionless moisture content. I define these in the following way:

$$D^\circ = \frac{D(w)}{D_{max}} \quad (1.10)$$

$$w^\circ = \frac{w - w_{min}}{w_{max} - w_{min}} \quad (1.11)$$

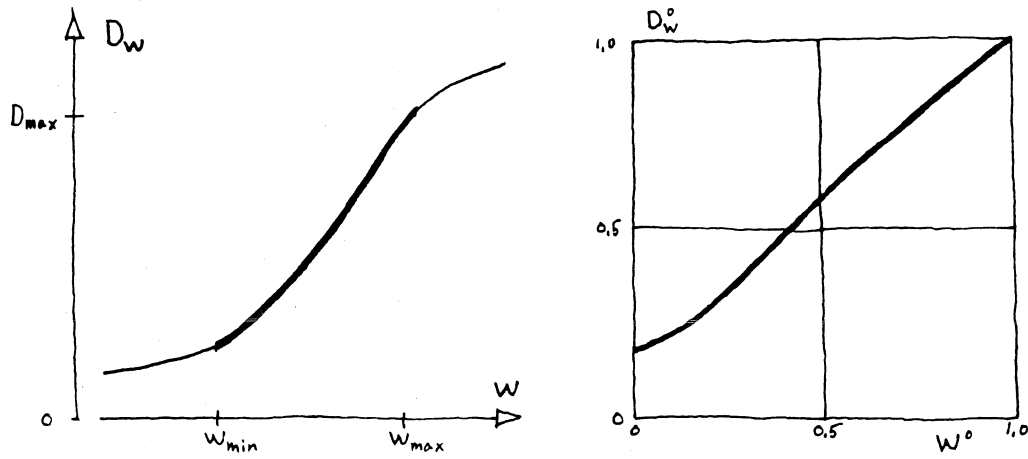


Figure 1.3: The dimensionless diffusivity

By the use of these two new variables I avoid making more calculations than is necessary. In figure 1.3 is an example of a dimensionless diffusivity written in the dimensionless moisture content. The two indices *max* and *min* refers to the highest and the lowest value of D or w in the experiment I am doing or simulating. This range is shown in the left diagram as a thicker drawn line, and is the only thing that is shown in the right dimensionless diagram.

It is very convenient to use dimensionless variables as this will minimize the work I have to do. I can make simulations of sorption experiments with just the curve *form* of the diffusivity (in the experimental interval) as input. I do not need to take the absolute value of the diffusivity into consideration, nor the actual moisture content range.

Chapter 2

SIMULATION

2.1 Why and why not?

With the help of computers it is possible for any researcher nowadays to make his own calculations of sorption, drying or other transport phenomena. This is a very powerful tool, especially if we want to try new approaches that have not been explored before. Only twenty years ago the calculation of concentration curves in sorption with a variable diffusivity, was a complicated task. Today I can enter a variable diffusivity, check to see if it is ok, and make a simulation of a sorption phenomena; all in less than 15 minutes.

Despite the merits of computer simulations we must not forget the pioneer work done by Newman, Crank & Henry and others. They made simple diagrams or tables of diffusion with different kinds of variable diffusivities (Crank & Henry 1949ab) or different surface resistances (Newman 1931a). In many situations these are still the fastest way to solve our problems, and they are for the variables for which they are made at least as accurate as the computer simulations in this paper. The advantage of using the computer is that we can tailor a solution to exactly the problem we want; we do not need to interpolate as we always can get the values in the points or times we want.

A possible disadvantage of using a computer is that it can be hard to check the accuracy of the results or even see if they are reasonable. It is easy to work as if the computer program was the reality, forgetting it might have its weaknesses and errors. When working with computers there is also a great risk of being caught by the wonders of the computer so that you forget what you originally were going to do. I think it is best for the researcher in transport phenomena if he or she thinks that working with the computer is as fun as doing the old times hand calculations. Then he will get on with his work (which often can be done by brute force on a computer, or with smartness by hand calculations).

In this paper I hope that I have shown that the computer can be used as a tool to evaluate experiments. I am not the first and probably not the last to do this and I do not claim that this is a new dimension in solving moisture problems. Only one more tool in the box.

2.2 How I used the computer

I mainly use the computer to run simulations. I have a library of computer files of different transport properties. Some of these are real measured data, with normal units, which can be used to simulate what happens in a real structure which absorbs water vapour. Most of my computer files are made up by myself. I have for example a series of files with diffusivities that increase in one step, starting with a constant diffusivity and ending with a file containing a diffusivity which increases about a hundred times in one step. These faked material properties

are all presented dimensionlessly. As I show in this paper this is no disadvantage, as it is possible to scale all properties I want to use.

One of the greatest advantages with computers is that it is quite easy for researchers to check the influences of various factors. I have for example looked at or will look at the following factors:

- the influence of an unstable climate
- the influence of surface resistances
- the influence of measuring with the growth rings in parallel or in series (tangential or radial direction)
- the influence of leaks through the sealed surfaces of the samples

2.3 The programs I use

I used two computer programs to do the simulations shown in this paper. First of all I used JAM-1, which is a general program for moisture transport with variable diffusivity. Secondly I used SORP, a version of JAM-1 tailored to run only sorption simulations. Both these programs runs on PC-computers under MS-DOS. The executable code requires a *87 math co-processor, EGA video card and 512 kbytes of RAM.

JAM-1 is a program for the calculation of moisture transport with non constant diffusivities. It is written by Jesper Arfvidsson (Division of Building Physics at Lund Technical University) and is quite easy to run and is ideal for the study of how different $D_w(w)$ affect the moisture situation. As there are possibilities of entering surface resistances, variable boundary conditions etc, it is possible to simulate almost any one dimensional moisture problem. It consists of three parts:

- create material data file
- diagrams of material data
- run transient model.

Moisture transport data for materials can be entered in four ways:

- results from cup measurements
- measured steady state ϕ -profiles and flow
- diffusion coefficient (ϕ as potential) and sorption isotherm
- ϕ , w and ψ

The greek letter ψ is the potential which is used in the calculations. It is defined as the potential with a diffusivity of unity.

SORP is a version of JAM-1 which can simulate only sorption measurements and display the results in the way that is presented in this paper. It has been developed by Jesper Arfvidsson and Lars Wadsö in cooperation. It consists of five parts:

- create material data file
- diagrams of material data

- run sorption simulation
- enter measured data from sorption experiments
- plot measured and simulated data

SORP has the same possibilities of entering measured material data, plus the possibility of entering

- diffusivity (w as potential) and sorption isotherm

Both programs can be ordered from Jesper Arfvidsson (Division of Building Physics, Lund Technical University, Box 118, 221 00 Lund, SWEDEN).

Chapter 3

NON-CONSTANT D_w

3.1 Dependencies on the moisture content

As we draw a diagram of E as a function of $\sqrt{\tau}$ for a sorption simulation with constant diffusivity we get the curve which I call $E_{th}(\sqrt{\tau})$. This can be calculated by the equations given in chapter 1. If we have non constant diffusivities we will not get the same curve. Why this is so I will explain in this chapter. Work in this field has already been done by for example Crank & Henry (1949ab).

What kind of diffusivities are interesting to study? The answer is nearly all of them, since researchers have found both constant, slowly increasing, rapidly increasing and curves with a maximum or a minimum. We also need decreasing curves to handle the case with drying experiments on samples with increasing diffusion coefficient (see section 3.4).

The program JAM-1 wants the diffusivities entered as piecewise constant functions. This might seem a serious limitation, but is not for the following reason. The sorption E is not a function of D_w (which gives the flow at stationary conditions), but more like a function of the integral of D_w (as the integral of the flow gives the accumulated moisture content and the mass change). Thus it is the integral of D_w that we should try to describe as accurately as possible, not D_w . If D_w is described by a piecewise constant function the integral is piecewise linear, and changes in D_w will not influence $\int D_w$ as much.

For this work I have worked with about 40 different forms of the diffusivity, but not all of them have given me any new information. In the next chapters I will show some of them.

3.2 How I have calculated \tilde{D}_w

When I have made a simulation I can calculate some sort of mean diffusivities by the four equations 1.5-1.8 . If my diffusivity is non constant I will probably get at least three different answers. This is because as the sorption process proceeds the moisture content in the centre of the sample will be changed. Consider for example an adsorption experiment with an increasing diffusion coefficient (figure 3.1).

During the first part of the process the form of the moisture content distribution is unchanged; it is just pulled out like an accordion. During this time we can use the theory for half infinite slab, which tells us that E is proportional to $\sqrt{\tau}$. When the moisture content in the centre of the sample starts to raise, two things can happen: either we have a constant D_w , so that the diffusion coefficient still is the same in the whole sample. Or we have a non constant D_w , in which case the mean value of D_w will have to change as some moisture contents and their associated diffusivities are removed from active service.

This will change the sorption curve. In our example, the lower values of w will disappear one after the other from our sample. Then the respective D_w will also cease to exist in the sample. As they are the lowest values of D_w , only the higher values of D_w will be left. It is then

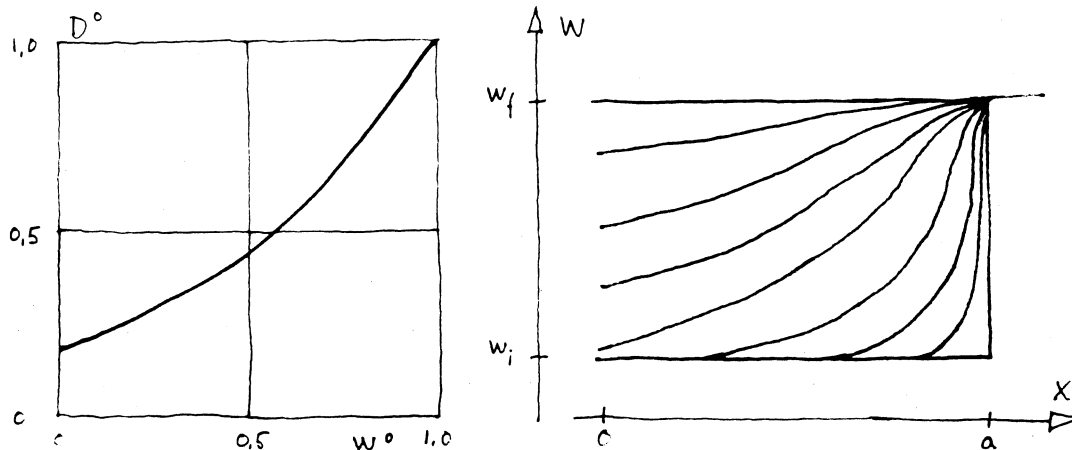


Figure 3.1: An increasing diffusivity and the concentration within a sample during sorption ($x = 0$ is at the centre of the sample and $x = a$ is on the surface). The concentration is shown at different times during the sorption process

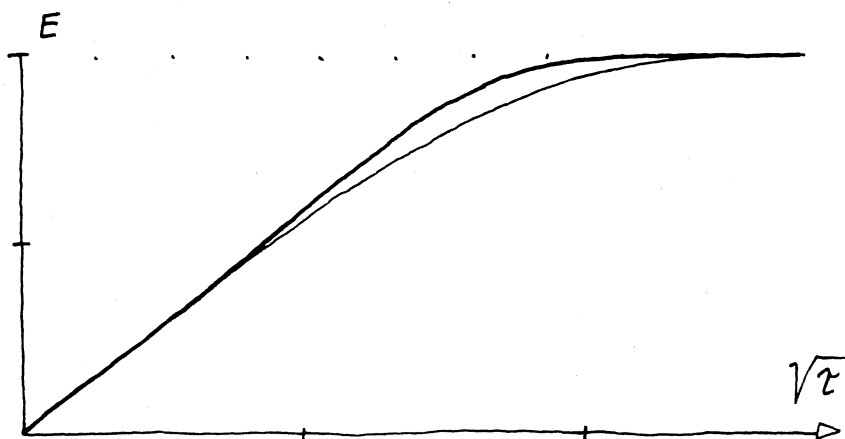


Figure 3.2: A sorption with increasing D_w (thick line) compared to a a sorption with constant D_w (thin line)

natural for the sorption to speed up, compared to the sorption with constant diffusivity, if they are both drawn in the same dimensionless diagram.

This will of course effect the values of D_w calculated from the different equations. When we use the dimensionless time τ we have to have a value of \tilde{D}_w , because $\tau = \tilde{D}_w \cdot t/a^2$. Above I have chosen to use the \tilde{D}_w calculated from equation 1.7, which uses the linear part of the curve. Therefore the linear parts of the two curves coincide. It would not have looked the same if I had used a \tilde{D}_w -value calculated from any of the other equations. Especially the second equation, which utilizes the last part of the sorption curve where only the highest $D_w(w)$ -values (in our example above) are active, will give a different result.

I think that it is best to use the slope $dE/d\sqrt{\tau}$ to calculate a value of \tilde{D}_w . Therefore I have used it in this paper (for the method used when there is a surface resistance see chapter 4.7).

In figures 3.1 and 3.2 are shown the effect of different diffusivities.

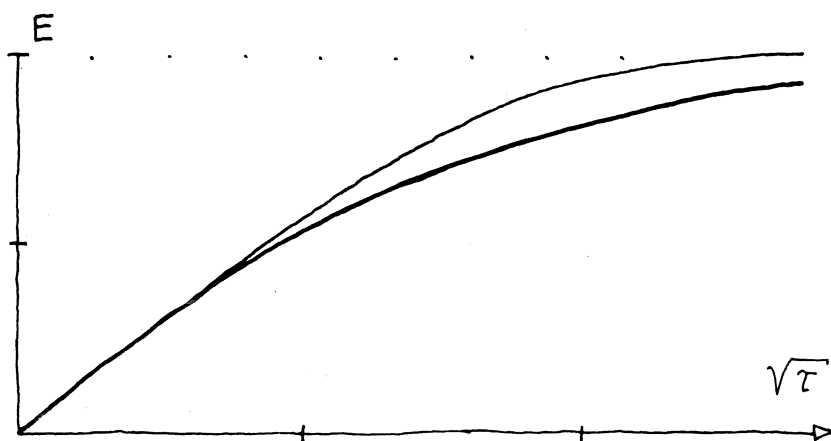


Figure 3.3: A sorption with decreasing D (thick line) compared to a sorption with constant D (thin line)

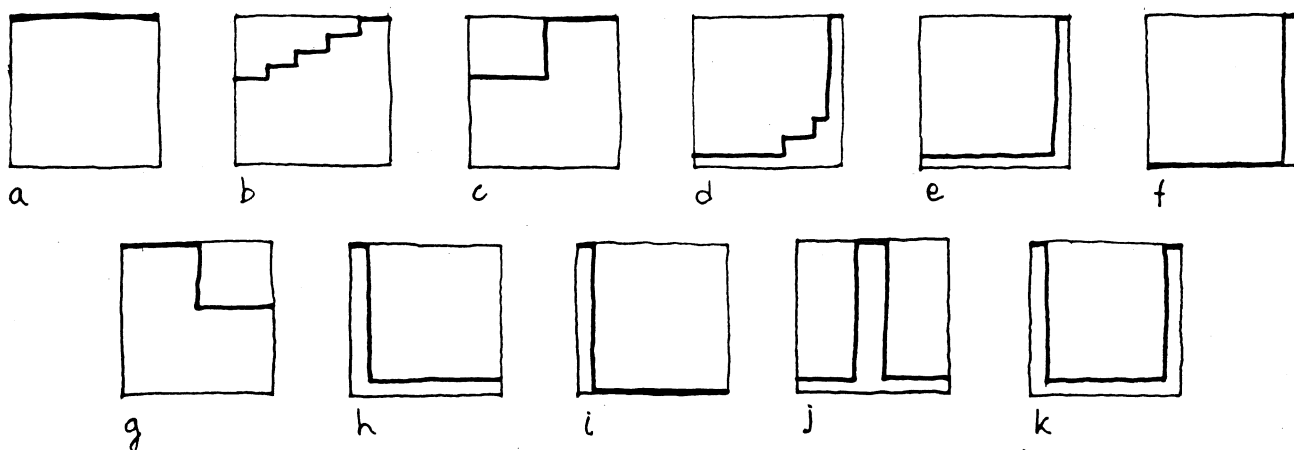


Figure 3.4: Eleven forms of the diffusivity

3.3 How this effects the calculated D_w

The \tilde{D}_w which we calculate is not an arithmetic mean of $D_w(w)$. Instead it is a very complicated mean for which no analytical expression exists as far as I know. It can however be calculated numerically, for example with my sorption program.

In figure 3.4 are shown eleven diffusivities, and in table 3.1 are shown the \tilde{D}_w which is calculated from them by the use of equation 1.7 (in adsorption). As we can see, it seems that the $D_w(w)$ of higher w are weighted more heavily than the ones at lower w (compared with \bar{D}).

3.4 Absorption and desorption

Except for the case with constant diffusivity absorption and desorption in the same interval will not give the same result ($E(\sqrt{t})$ and \tilde{D}_w). This is reasonable as:

- the D at higher w in absorption are weighted most heavily. At desorption we have the opposite situation (which was shown above). Therefore we can usually not get the same \tilde{D} from absorption and desorption in the same interval.

	form	\tilde{D}	\bar{D}	\tilde{D}/\bar{D}
a	constant	1,000	1,000	1,00
b	increasing	0,861	0,800	1,08
c	increasing	0,874	0,800	1,09
d	increasing	0,307	0,230	1,33
e	increasing	0,252	0,190	1,33
f	increasing	0,164	0,109	1,50
g	decreasing	0,713	0,800	0,89
h	decreasing	0,117	0,190	0,62
i	decreasing	0,019	0,109	0,17
j	with maxima	0,256	0,280	0,91
k	with minima	0,278	0,280	0,99

Table 3.1: Diffusion coefficients calculated from sorption simulations (\tilde{D}), the arithmetical mean (\bar{D}) and their ratio

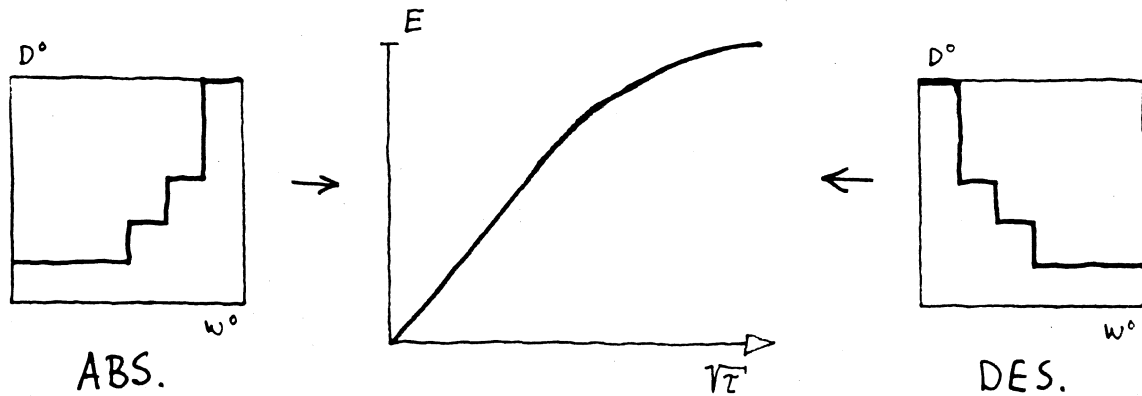


Figure 3.5: A diffusivity in absorption will give the same sorption curve as its mirror image will give for desorption

- the D at the lowest w are first to disappear as w starts to increase in the centre of a sample subjected to absorption. At desorption it is the D at the highest w that disappears first. These different situations will of course effect the later part of the curve in different ways.

Is there then no connection between absorption and desorption? There is one which is shown in figure 3.5.

If we make the transformation $D^\circ(w^\circ) = D^\circ(1 - w^\circ)$ (which is the same as turning the w° -axis the other way) we will get a new D° which will give exactly the same $E(\sqrt{\tau})$ and \tilde{D} for desorption as the unchanged D° for adsorption (or vice versa). By this I conclude that I need only study one of the two different cases; the other one can then be easily be derived. I have choosen to mostly study absorption (for a discussion of the relation between adsorption and desorption see Crank & Henry 1949a).

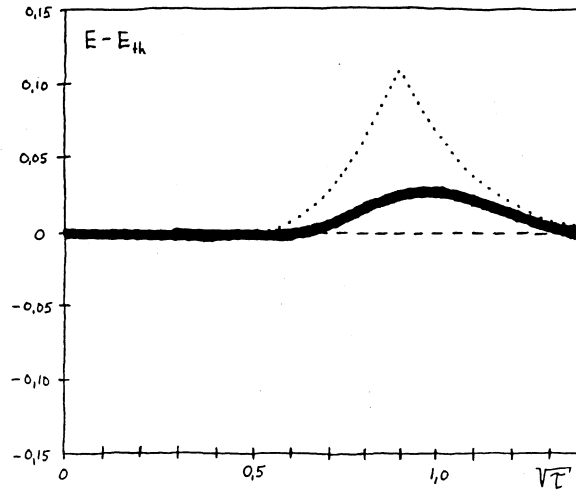


Figure 3.6: The $E - E_{th}$ -diagram, which shows the deviation from the theory for constant D_w

3.5 Expressing deviations from the analytical solution

In this paper I want to study how different factors effect the sorption process. One way of expressing the influence of these different factors is to look at the $E(\sqrt{\tau})$ -curve, which is the primary result of our experiments or simulations. These different curves do however look very much the same, at least at a quick glance. I have therefore found it convenient to compare them with $E_{th}(\sqrt{\tau})$, the theoretical sorption curve for constant diffusivity (for which we have a complete analytical solution). I have done this by drawing the difference of E and E_{th} as a function of $\sqrt{\tau}$ (figure 3.6).

This diagram is good as it clearly shows the deviations from theory. Above I have drawn one curve which shows that $E - E_{th} > 0$ above $\tau = 0,6$. This is because in this case the sorption speeds up above $\tau = 0,6$. That the $E - E_{th}$ -curve than has a maximum and returns to $E - E_{th} = 1$ is only because all sorptions sooner or later must come to an end at $E = 1$. As this is true for both E from the studied sorption and E_{th} from the analytical solution for constant D , the ratio of them must also become unity as time goes. Therefore the most interesting part of the diagram is when $\tau < 1,0$.

In the $E - E_{th}$ -diagram there are two broken lines:

- the left line is the continuation of the initial straight line in the $E(\sqrt{t})$ diagram (see figure 1.1). This is the upper limit to the sorption: it can not be faster than this. If I had not taken equation 1.7 as a definition of \tilde{D} (the slope of the initial straight part of the curve) I would have gotten some problems here (especially with surface resistance). Now there is no possibility of the sorption being faster than the initial straight line (see chapter 4 for a discussion of how this diagram can be used when we have surface resistances).
- the right broken line is for $E_{th} = 1$; in other words is it the value of $1 - E_{th}(\sqrt{\tau})$. This is also a limit for the sorption process as it is impossible for E to become larger than unity.

Both these curves are useful as references when we compare different sorption curves. There are no corresponding curves below $E - E_{th} = 0$, reflecting the fact that the sorption process can slow down very much if the diffusivity is extremely decreasing. The only real limits below $E - E_{th} = 0$ are $\sqrt{\tau} > 0$ and $E - E_{th} > -1$, which not even sorptions with very extreme $D_w(w)$ which I have tested come near.

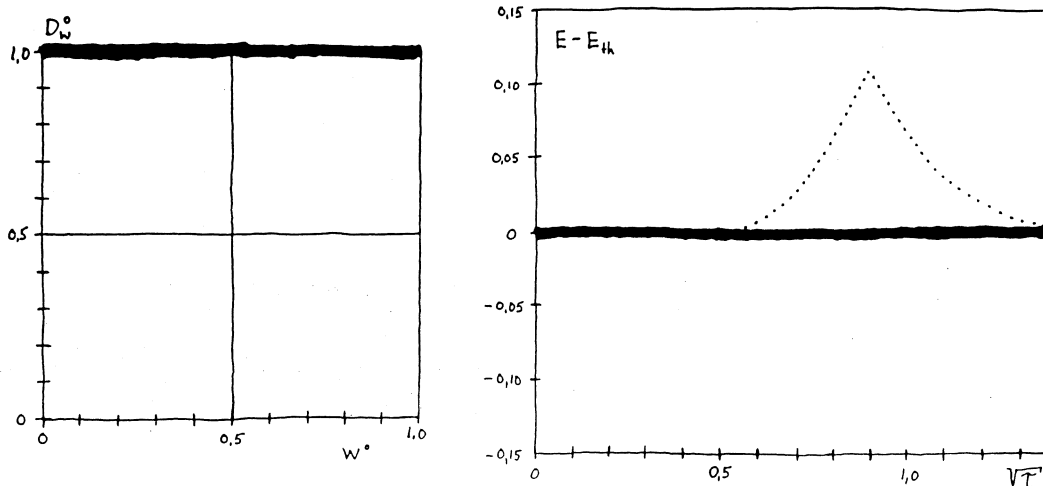


Figure 3.7: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity a

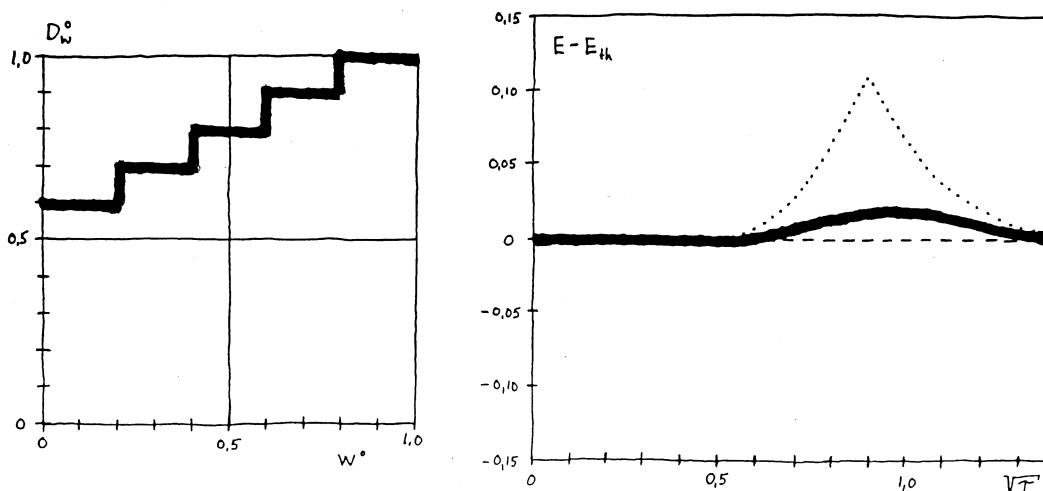


Figure 3.8: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity b

3.6 Diagrams for different $D^\circ(w^\circ)$

In this chapter are shown different $D^\circ(w^\circ)$ -diagrams for absorption and corresponding $E - E_{th}$ -diagrams. I have chosen to draw the curves in figures 3.7-3.17. I hope they can be a help when interpreting results from simulations or experiments with no or negligible surface resistance.

Studying these curves made me draw the following conclusions:

- If $D(w)$ increases, $E - E_{th}$ for absorption will have a maximum
- If $D(w)$ decreases, $E - E_{th}$ will have a minimum
- Diffusion coefficients which has a minimum or a maximum give $E - E_{th}$ -curves with both a maximum and a minimum.
- It does not give very much more information to divide the $D(w)$ into more steps, to make it look more like a continuous curve (which it of course is in reality). As I mentioned before this is because the mass of the sample which we measure is not a function of the diffusivity, but a function of the integral of the flow, and therefore more like a function of the integral of the diffusivity. Introducing an extra step to make $D(w)$ more realistic does not change the form of $\int D(w)dw$ as much.

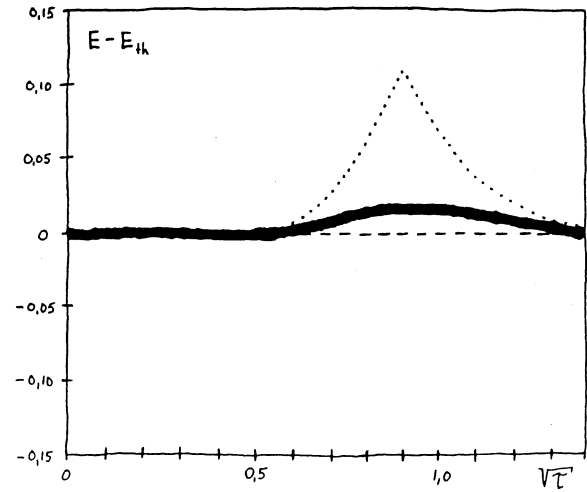
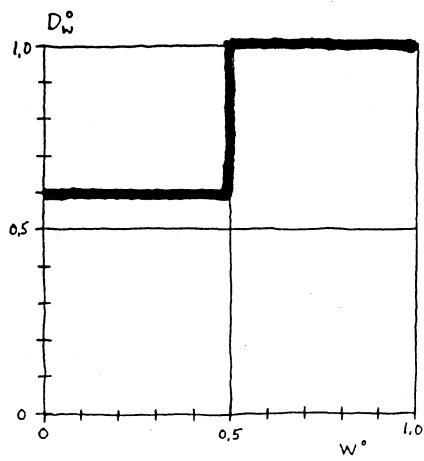


Figure 3.9: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity c

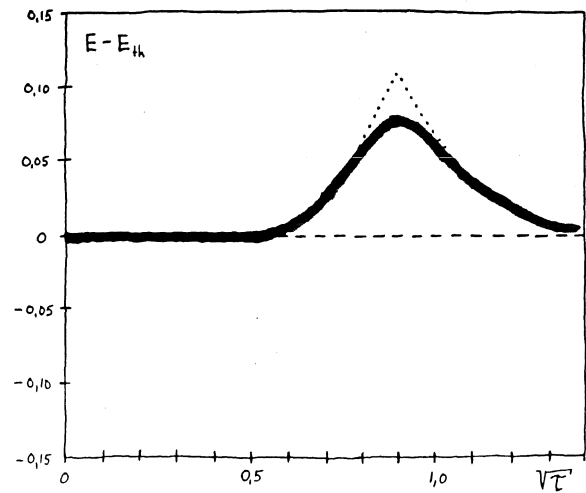
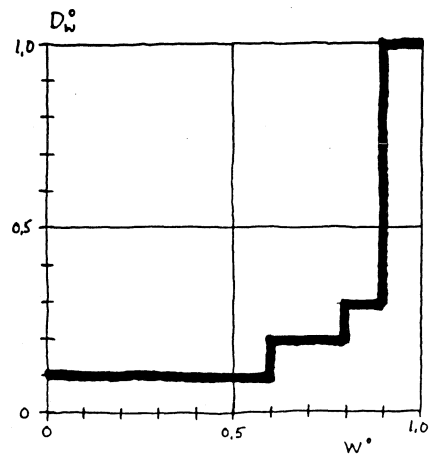


Figure 3.10: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity d

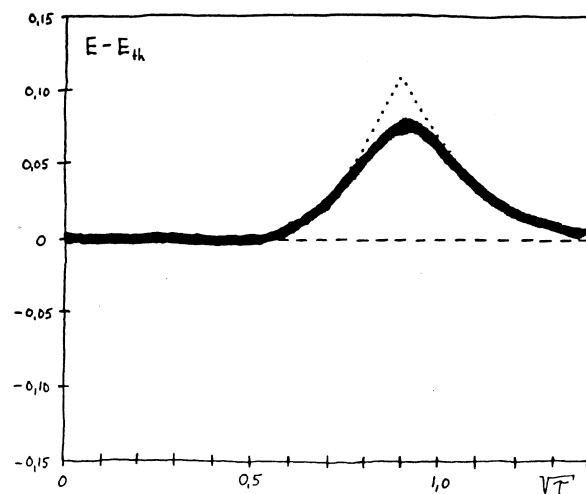
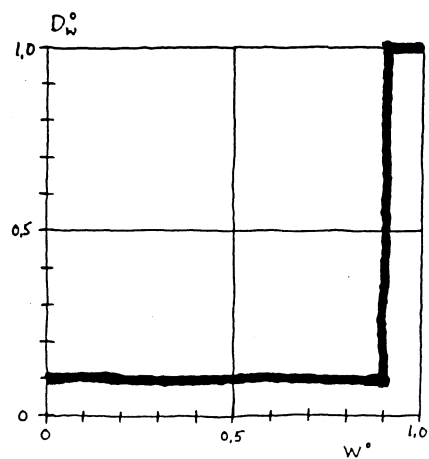


Figure 3.11: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity e

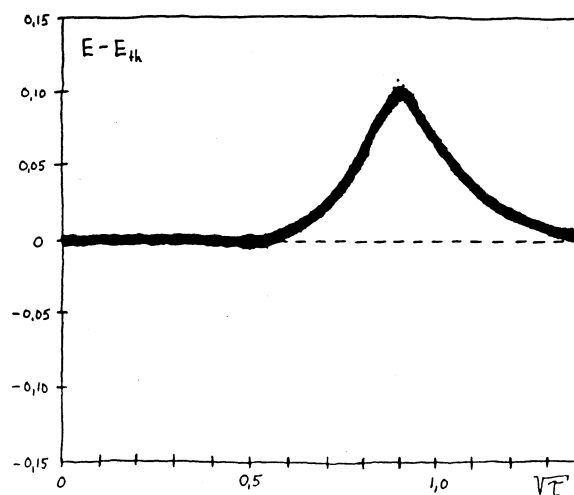
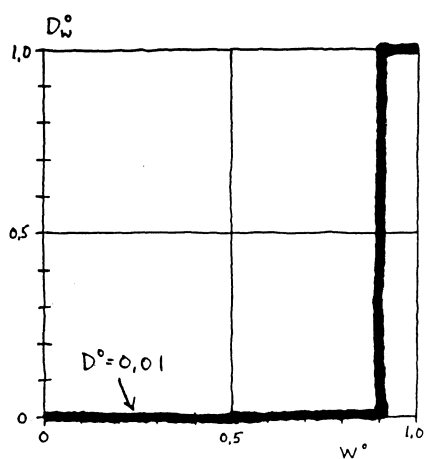


Figure 3.12: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity f

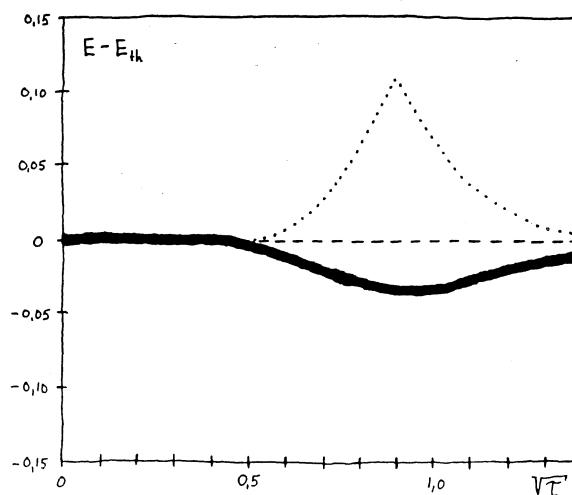
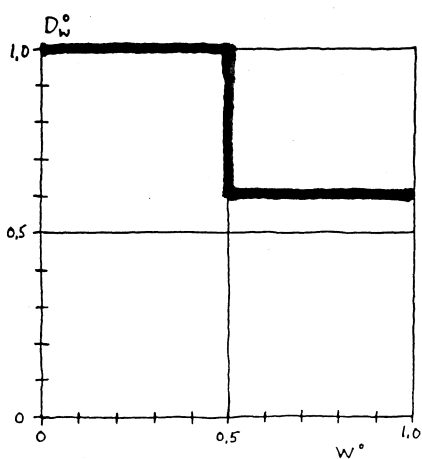


Figure 3.13: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity g

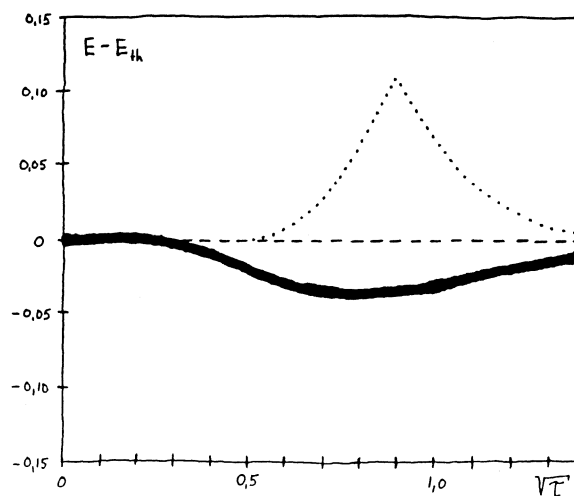
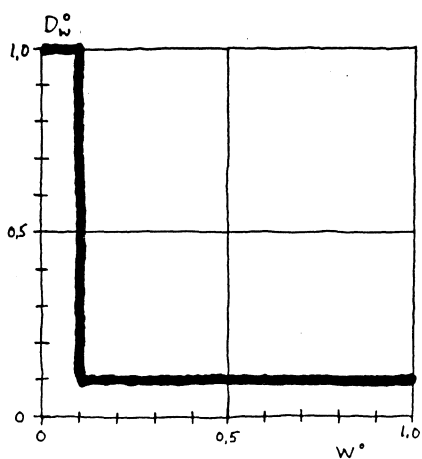


Figure 3.14: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity h

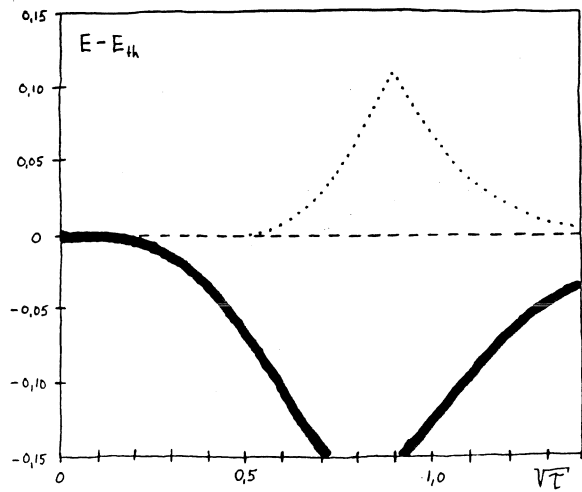
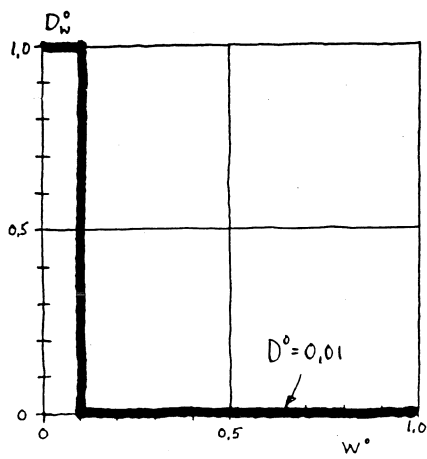


Figure 3.15: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity i

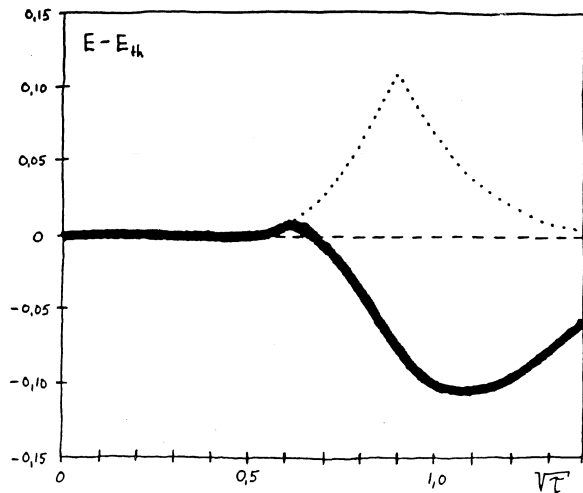
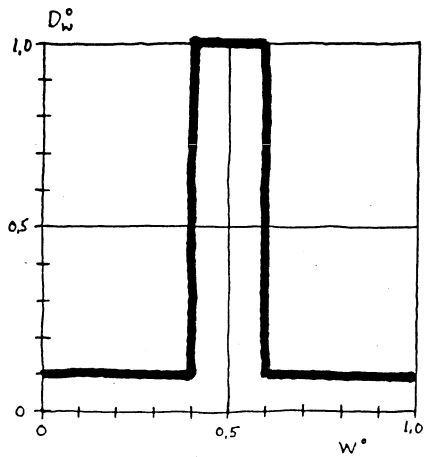


Figure 3.16: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity j

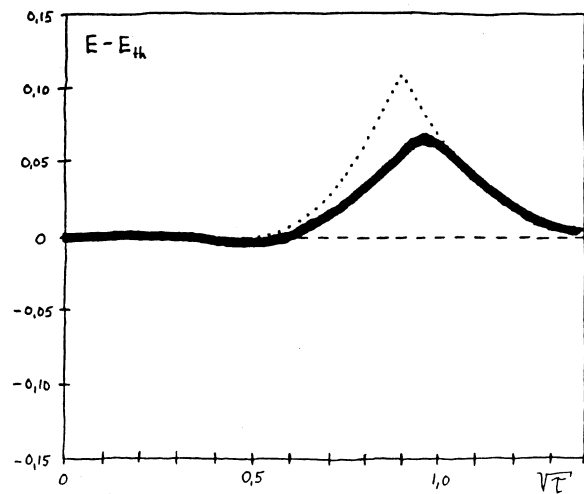
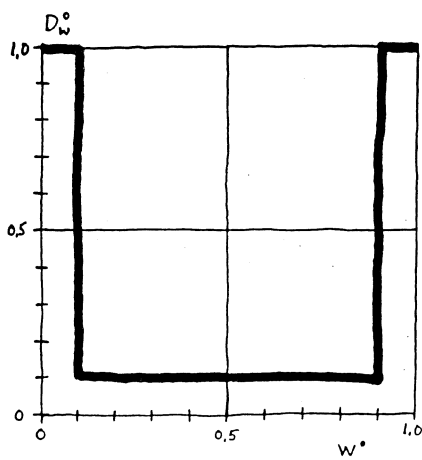


Figure 3.17: diagram of $D_w(w)$ and $E - E_{th}$ for diffusivity k

Chapter 4

SURFACE RESISTANCE

4.1 What is it?

A surface resistance is something that makes it harder for the water molecules to transport themselves through the surface of our sample. It is not too clear what is the cause of this, many explanations have been offered:

- As the air near the surface can be still, there is a diffusion resistance through this thin layer which the water molecules have to overcome. In section 4.3 I try to calculate this resistance theoretically by boundary layer theory and arrive at a value of the surface resistance which is much lower than has been measured recently. Another problem with this theory is that it seems to be impossible to remove all of the surface resistance by increasing the air velocity outside the sample (Rosen 1978).
- The possible binding sites for the water molecules on the surface of a sample of wood (and probably extending for some distance into the lumens) have been decreased by other molecules or dirt occupying them; or because they have been destroyed by light or the oxygen in the air. This would give a surface resistance as it would be hard for the water molecules to enter into the wood during absorption or leave it during desorption. As far as I know this theory has not been studied in detail for wood.
- It is of course also possible to imagine that the surface resistance is a thin layer of less conducting material. Given a guess of its thickness it would be easy to calculate its diffusivity. This is called a skin by Crank (1986) and a crust by food engineers.
- It has also been proposed that the heat of sorption, which will increase the temperature of the surface during absorption and decrease it during desorption, would cause this resistance by changing the relative humidity in the (pores of the) surface. Crank & Park (1949), Liu (1987) have shown that this influence is negligible.

An estimation that can be made to check this is to calculate the amount of energy released. If we know the heat conductivities and heat capacities of wood and air, a computer calculation of the temperature build-up at the surface can be made. The heat released is $2260 \cdot 10^3 J/kg$ (the heat of condensation which is a high approximation). The heat conductivity is approximately $0,15 W/(m \cdot K)$ for wood and $0,024 W/(m \cdot K)$ for still air. The respective capacities are $1260 J/(kg \cdot K)$ and $1000 J/(kg \cdot K)$. Using these values and neglecting convection we will certainly get a high guess. I have not done this calculations.

- Another theory is that there is no (or only a very low) surface resistance, and that it is internal mechanical effects that give effects looking like a surface resistance. As far as I know no-one has proved this theory to be correct, but it is of course tempting to use it

symbol	name	defining equation	unit	references
β_v	emissivity	$\beta_v = -g/\Delta v$	m/s	ISO 9346
S	emissivity	$S = -g/\Delta w$	m/s	Newman (1931a), Skaar (1954)
Z_ϕ	resistance	$Z_\phi = -\Delta\phi/g$	m^2s/kg	Arfvidsson (1988)
Z_v	resistance	$Z_v = -\Delta v/g$	s/m	Nevander & Elmarsson (1981)
Z_w	resistance	$Z_w = -\Delta w/g$	s/m	

Table 4.1: Different units for surface resistance

if you are sure that there is no or only a very low resistance at the surface (Liu 1987). I am not convinced that there are any major mechanical effects inside a sample undergoing sorption that can cause a surface resistance looking effect.

4.2 The surface resistance can be expressed in many ways!

The surface resistance can be expressed in many ways, which makes life hard for a researcher. Often one instead talk about surface emissivity, which is the reciprocal of the surface resistance. I prefer to use resistance as I think it is easier to understand, but I am fully aware that surface emissivity is of the same type as is the diffusivity; both have high values when the transport is high. Maybe resistance gives clearer understanding of transport through layers, and diffusion is better for diffusion in volumes.

There are also different ways of expressing the surface resistance depending on which you think is its causes; which gradient it is a function of In table 4.1 I have listed the units that I have found. The last unit of the table, Z_w , is introduced here only because it is the reciprocal of S . The other four units have been used by other researchers.

There is always a problem with using the relative humidity ϕ , and that is that some people prefer to use percent while others let it have values between zero and unity. As I belong to the latter group I do not use percent. If you have a value of Z_ϕ which is calculated using percent, you have to divide the value by 100 to compare it with the values I have. It is possible to run the program JAM-1 in both ways, with percent or with a relative humidity between zero and unity, as long as you are consistent and use the same units all the time (flow, resistances and relative humidities must all be expressed in *one* of these units).

The ϕ which only is a ratio of the actual vapour pressure and the saturation vapour pressure is also called the activity.

It is possible to transform any one of these into any other:

$$Z_w = \frac{1}{S} \quad (4.1)$$

$$Z_v = \frac{v_s}{S \cdot \xi} \quad (4.2)$$

$$\beta = \frac{1}{Z_v} \quad (4.3)$$

$$Z_\phi = \frac{Z_v}{v_s} \quad (4.4)$$

Here $\xi = dw/d\phi$ is the moisture differential capacity which is the slope of the sorption isotherm. As this is a function of the moisture content w , we have to use a mean value if we are

working in an interval. A good approximation is to use the mean value of $dw/d\phi$, which equals $\Delta w/\Delta\phi$.

4.3 A theoretical derivation

It is possible to theoretically derive equations for that part of the surface resistance which is caused by the air layer just outside the surface, the so called boundary air layer. It is important to remember that this theory does not include the effect of a lower diffusivity in the surface layer of the sample. In food engineering one often try to measure the temperature very near the surface as one knows that the material properties are different there, compared to inside the sample. Maybe there is also a crust or skin in wood, especially in weathered wood. We know that the surface properties change when wood is exposed to the sun or to outdoor climate, as it becomes harder to get a paint to adhere to a surface after it has been weathered. It is also advisable to use newly planed wood when gluing, as the joint otherwise will be comparatively weaker. We have to remember this when we now make some short calculations with boundary layer theory.

There is a small but important equation which is called Lewis equation, which relates surface resistance to heat flow, to surface resistance to mass flow (in this case moisture flow). For the case with water vapour in air, the equation looks like this:

$$\beta = \frac{\alpha_c}{\rho \cdot c_p} \quad (4.5)$$

$$\rho \cdot c_p \approx 1200 \text{ at } 20^\circ\text{C}$$

Lewis law is very interesting as it is an relation between transport of heat and transport of mass. It is derived under the presumptions that these to are caused by the same force: forced convection of molecules near a surface. It is therefore that α has an index c (convection), as other possible ways of transport are neglected. Especially for the heat transfer this means that there is no radiation (which of course can not be a way of water molecule transport). It is only for water vapour in air at atmospheric pressure that this simple form of the equation can be used. For other gases or liquids it has to be complemented (see for example Kneule 1975).

Now if we could calculate α_c , we could also find β , the surface emmissivity. I will show two different calculations of α_c . The first is for flow parallel to a thin plate of length L , which is shown in figure 4.1. I have also drawn a picture of my sample to show that the flow around it can not be the same, but I use it as a rough approximation.

I follow Eckert & Drake (1959 p173-178) and let the plate length L be 5 cm and the velocity of the air flow 3 m/s, both are normal values for sorption experiments. The Reynolds number is then 10000 and the Prandtlnumber is 0,7 (tabulated value). From these two values it is possible to calculate the Nusselt number Nu (the ratio of the heat flow by conductivity and convection, and the heat flow by conduction):

$$Nu = 0,332 \cdot (Pr)^{\frac{1}{3}} \cdot \sqrt{Re} = 29 \quad (4.6)$$

This means that the heat flow by convection is much larger then the heat flow by conductivity. The α_c -value decreases from the leading edge to the trailing edge according to $\alpha = (\lambda/x) \cdot Nu$, where λ is the heat conductivity (which is 0,0256 W/(m · K). This gives us

$$\alpha_{min} = (0,0256/0,05) \cdot 29 \approx 15 \text{ W}/(\text{m}^2 \cdot \text{K}) \quad (4.7)$$

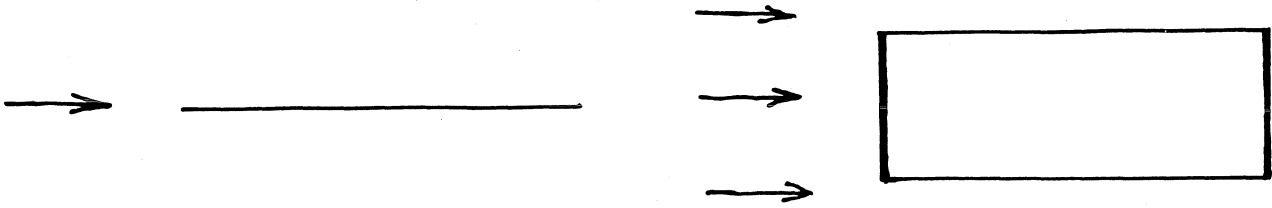


Figure 4.1: A thin plate and a real sorption sample

$$\alpha_{mean} = 2 \cdot \alpha_{min} \approx 30 W/(m^2 \cdot K) \quad (4.8)$$

Another way to calculate an approximation to the real α_c , is to use an equation for the heat transfer from air flowing in a circular tube. This can be said to be a very rough approximation to many samples standing near each others in rows. According to Perry & Chilton (p10/16 1973) we can use this equation:

$$\alpha_c = 3,52 \cdot r^{0,8} / d^{0,2} = 15 W/(m^2 \cdot K) \quad (4.9)$$

Here r is the air flow rate divided by area (mean air velocity) and d is the tube diameter. I have used the same velocity ($3 m/s$) as above and a tube diameter of $5 cm$. As the tube diameter is raised only to the power of two, α is not very sensitive to different values of the diameter (if I double the diameter α will decrease to $13 W/(m^2 \cdot K)$).

I conclude that according to these theories the heat emissivity is in the neighborhood of $15 W/(m^2 \cdot K)$. With Lewis equation we can then calculate a moisture emissivity by dividing 15 with 1200:

$$\beta_v = 0,012 m/s \quad (4.10)$$

$$Z_v = 80 s/m \quad (4.11)$$

$$S = 1,5 \cdot 10^{-6} m/s \quad (4.12)$$

with $\xi = 150 kg/m^3$ and at $20^\circ C$

Remember that this calculation is a calculation of the resistance of the boundary layer only.

This value agrees very well with measurements made by Choong & Skaar (1969, 1972), but are lower (the resistance) than the measurements by Rosen (1978) and Avramides & Siau (1987).

In figure 4.2 is a plot of Z_v as a function of the flow velocity calculated by the two methods.

4.4 Three experiments to find the surface resistance

I have found three distinctly different methods to measure a value of the surface resistance. The first has been used a lot, the second is comparatively new and the third method is as far as I know not used before:

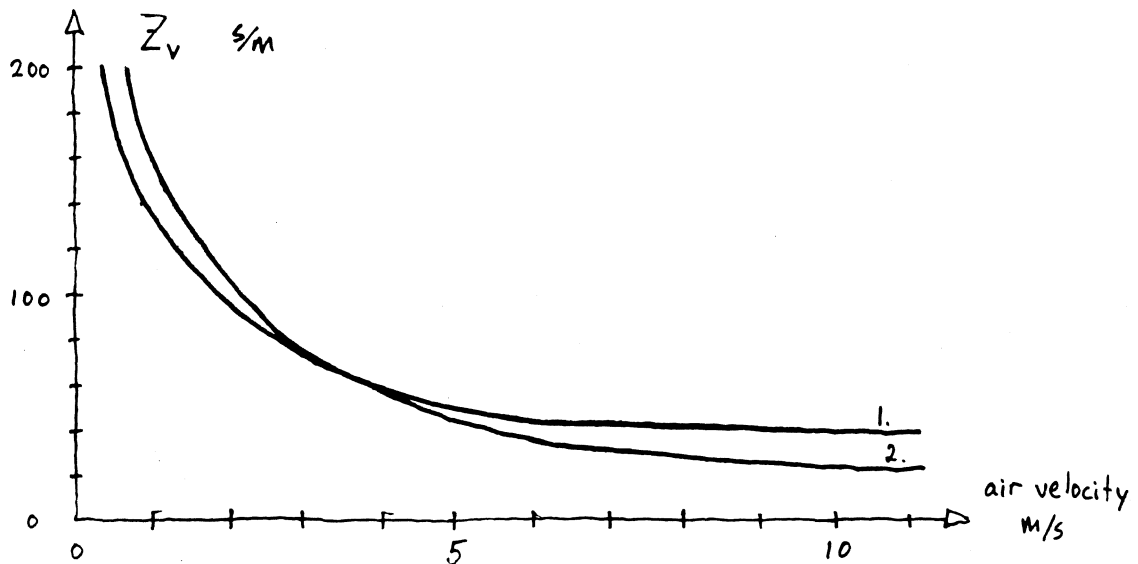


Figure 4.2: Surface resistance as a function of the air flow velocity for the two methods used (1: Eckert & Drake, 2: Perry & Chilton)

Newman (1931a) solved the sorption equation including the surface resistance expressed as a function of the difference in moisture content. Skaar (1954) and Choong & Skaar (1969) used this solution to show that it was possible to calculate the surface resistance from a number of sorption experiments with different sample thicknesses. This method has been used by Choong & Skaar (1969, 1972), Rosen (1978) and Avramides & Siau (1987).

Hart (1977) proposed a different method to find the effective moisture content of the surface as a function of the equilibrium moisture content and the flow during drying. He used a modified psychrometric equation. Knowing the surface moisture content makes it easy to calculate the surface resistance. Rosen (1982) reports that the method of Hart compares favourably with experimental data from Choong & Skaar (1972). Studying all values given by Hart makes the comparison less favourable, but still not bad; possibly indicating that the surface resistance is not a function of the moisture content.

Arne Hillerborg, one of my tutors, has suggested a different method which I have tried to use. In short I measure the surface resistance by studying the initial moisture uptake during a sorption experiment. I have not found any references to a method like this, but it is such a simple method that has probably been used before. I explain my experiments in detail in the next section.

4.5 New measurements of the surface resistance

When a dry sample is put into a wet climate it starts to absorb humidity. During the first seconds the only resistance to sorption is the surface resistance; the flow being from humid air into dry wood through this resistance. It should then be possible to calculate the resistance if we knew the flow of vapour into the sample during the very first instances of the experiment.

To test the idea I have made a simple experiment with four samples of spruce (*Picea abies*), each approximately 300 x 70 x 8 mm. The end grain was hidden with a strip of aluminum tape (I do not think that this was necessary). The samples was dried at about 100°C for about 20

no.	fan?	$S \cdot 10^8 \text{m/s}$	$Z_v \text{s/m}$
1	yes	5,0	3600
2	no	4,5	3900
3	no	7,4	2700
4	yes	5,0	3900

Table 4.2: Measured values of the surface resistance

hours and then wrapped in aluminum foil and left to cool in the climate room ($\phi = 0,65$ and 20°C) where the experiment was going to be performed.

When the experiment started I unwrapped a sample and immediately put it on an electronic balance (with a relative accuracy of not very much more than 1 mg). One sample (no. 3) was left on the balance, one sample (no. 2) was taken off the balance between the measurements, and two samples (no. 1 and 4) were exposed to a fan between the measurements. It is not possible to see any differences between the measured results of the different samples. In table 4.2 is shown the values of the surface resistance evaluated on the basis of the slope of the sample weights from 0 to 60 s.

These values are very much like the values of Rosen (1978) and Avramides & Siau (1987), but very much larger (resistances) than Choong & Skaar (1969, 1972).

The only serious problem with these measurements is that it is hard to know when the initial period is over; when the internal resistances also begin to effect the sorption. I have two ways of investigating for how long time I can measure the effect of the surface resistance only:

1. The initial sorption through the surface resistance should be a function of time, whereas the later sorption is a function of the square root of time. When I have a large surface resistance the sorption will never completely become a function of the square root of time, but one way of judging the length of the initial period is probably to see when the sorption begins to leave the initial straight line.

If I look at my four sorption curves three of them are nearly straight lines from 60 s to 600 s (I have not measured more than 600 s). One of the curves (no. 3) is concave towards the time axis. All four curves have an initial jump between 0 s and 60 s. I do not know the cause of this. If this is the true initial slope of the sorption, then the real value of the surface resistance is lower than in the table.

2. As I know the approximate equilibrium sorption curve it is possible to calculate the moisture content of a layer x mm thick which holds all the humidity which the sample has absorbed during the first 600 s of the experiment (the equilibrium moisture content of spruce at $\phi = 0,65$ is $u = 0,125$). In table 4.3 it is seen that a layer of more than $0,03 \text{ mm} = 30 \mu\text{m}$ must be affected (because the equilibrium moisture content in the outside climate is $u \approx 0,12$). Probably $0,1 \text{ mm}$ or so is affected. so what we are watching is not just a surface effect.

To find out more about this I made a simulation of the situation using a surface resistance $Z_v = 3500 \text{ s/m}$ and a measured diffusivity taken from Bertelsen (1983) and extended down to $w = 0$ (I do not think that the form of the diffusivity is very important in this simulation). The result is shown in figure 4.4.

From 50 s to 250 s the surface moisture content increases from 33 kg/m^3 to 45 kg/m^3 . From this I easily calculate that the moisture content difference decreases from 29 kg/m^3 to 17 kg/m^3 . When I calculated the surface resistances in table 4.2 ($\approx 3500 \text{ s/m}$) I used a moisture content

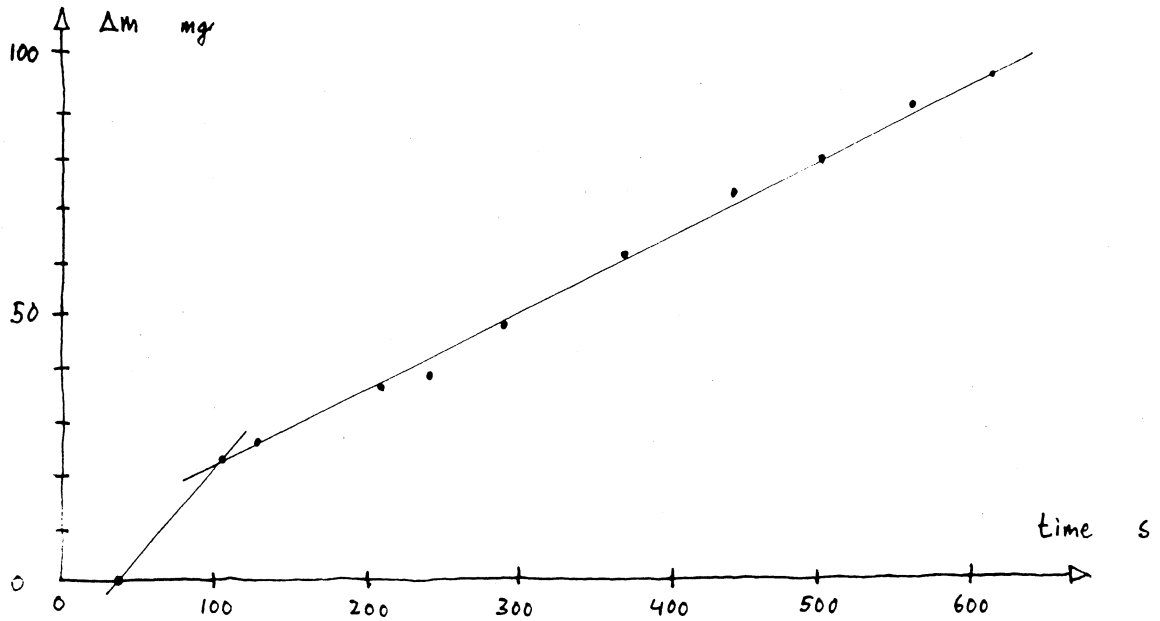


Figure 4.3: Initial sorption by sample no. 4 with first measurement at 30s. Note the linear time scale in this diagram.

thickness x (mm)	moisture content u (kg/kg)
0,001	3,6
0,01	0,36
0,1	0,036
1	0,0036
10	0,00036

Table 4.3: moisture content absorbed during first 600 s of experiment compressed into different thicknesses

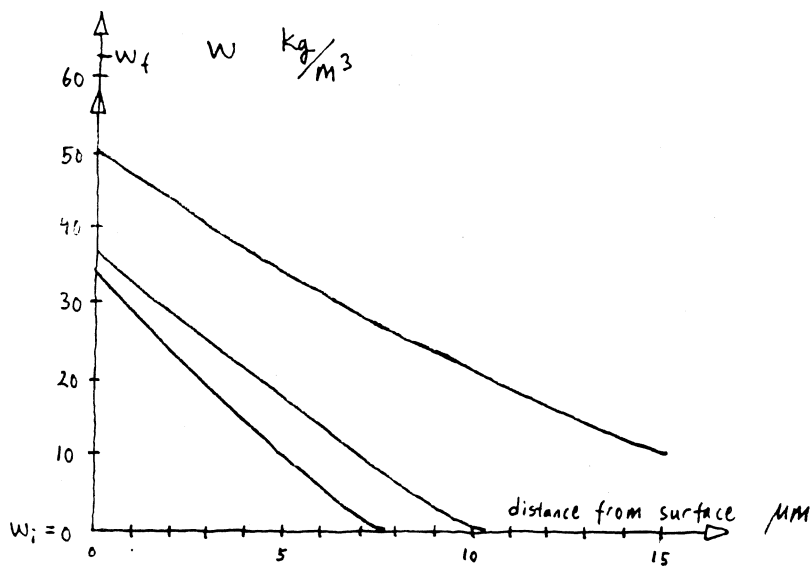


Figure 4.4: Simulated moisture contents near the surface at the beginning of the sorption (the final equilibrium moisture content is $w_f = 62 \text{ kg/m}^3$)

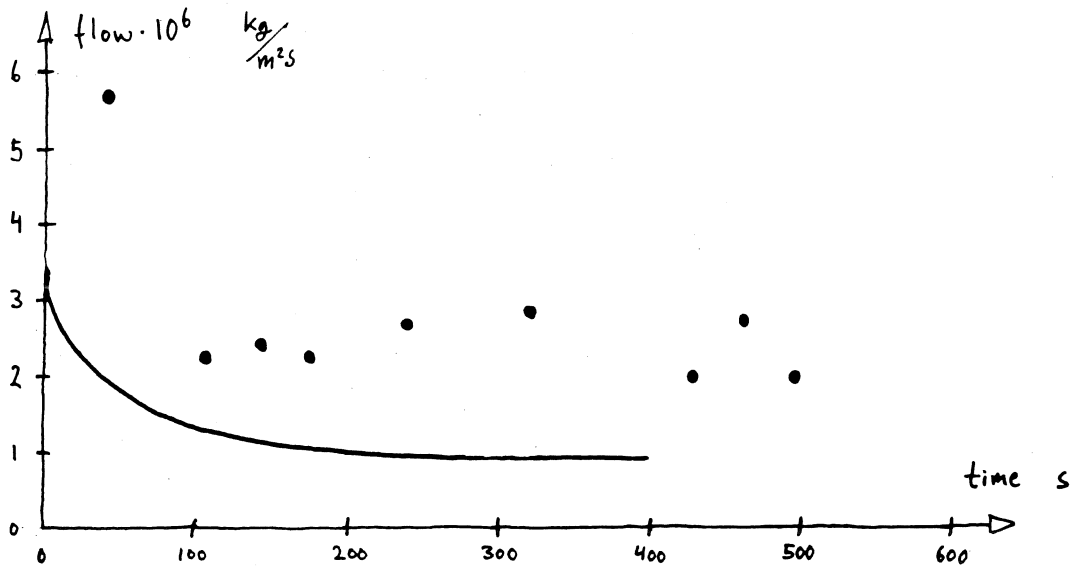


Figure 4.5: Simulated and measured flow (sample no.4)

difference of 62 kg/m^3 . From this I draw the conclusion that the surface resistance is less than half the value I got. Maybe a value of 1500 s/m is a good guess.

In figure 4.5 I have drawn a diagram of the flows from the above mentioned simulation and measurement. The forms of the flow as a function of time agrees quite well, but the measured flow is 2-3 times as large. This is because I have used a surface resistance of 3500 s/m which was calculated from the experimental flow for $t > 100 \text{ s}$. A smaller surface resistance would have given a better result. I plan to continue this work with better experiments and new simulations.

This method of finding the surface resistance seems to be working if I have some knowledge of the diffusivity which I can use in a simulation program. One very important thing about simulations of the moisture content near the surface at the start of the sorption is that there is a relation between the simulation time-step and the simulation cell size. If you do not observe this it is very easy to get unstable results when you are working with small time-steps.

I hope that it is possible to continue with the evaluation of this method. It would seem possible to measure the surface resistance at a relative accuracy of perhaps $\pm 50\%$, which would suffice in most cases.

4.6 Old measurements of the surface resistance

I have read some papers where researchers have tried to measure the surface resistance. The best way to express their results seems to be by the equivalent thickness (the thickness of material which has the same resistance under steady state conditions as the surface resistance has in the initial stage of the sorption measurement).

To simplify the comparison between the different results, I have tabulated them in table 4.4. The measurements are taken from the following articles:

1. Choong & Skaar (1969) yellow poplar (whitewood, *Liriodendron tulipifera*); very much the same values for heartwood and sapwood, and radial and tangential directions. Sorption from $\phi = 0,25$ to $\phi = 0,40$ at 32°C . I have used $\xi = 95 \text{ kg/m}^3$ and $v_s = 0,034 \text{ kg/m}^3$.
2. Choong & Skaar (1972) sweetgum (redgum, *Liquidambar styraciflua*); desorption from near fibre saturation point to $u = 0,18$ ($\phi \approx 0,82$) at 38°C . Air speed $1,5 > \text{ m/s}$. I have

article see page 28	L, T or R direction	Z_v s/m	$D_w \cdot 10^9$ m^2/s	$b \cdot 1000$ mm	
1	T and R	300	0,9	0,8	
2	L	100	2,4	2,1	
	T	130	1,0	1,1	
3	L	70	13	8	
	L	80	7	5	
	T	70	4	4	
	T	70	0,24	0,15	
4		110	0,2	1,5	
5	R	13000	0,07	5	speed of air 0,4
		4000	0,07	2	1,1
		3300	0,07	1,7	1,9
		2300	0,07	1	2,9
		2400	0,07	1,4	3,8
		1800	0,07	0,8	12
6		3300	8	1,2	moisture content 0,032
		6000	9,3	1,7	0,063
		5800	1,4	2,6	0,092
		9700	-	-	0,137

Table 4.4: Surface resistances taken from different articles

used $\xi = 400 \text{ kg/m}^3$ and $v_s = 0,046 \text{ kg/m}^3$.

3. Choong & Skaar (1972) redwood (*Sequoia sempervirens*), otherwise as no. 3.
4. Mackay (1971) *Ceratopetalum apetalum* was used in measurements with the cup method to study the effect of stirring the air in the cup. Berthelsen (1982 p43) has calculated the surface emissivity in the measurements of Mackay as being $0,2 - 0,5 \cdot 10^{-6} \text{ m/s}$. I calculate it as being $0,13 \cdot 10^{-6} \text{ m/s}$. Some values are uncertain in our two calculations.
5. Rosen (1978) black walnut (American walnut, *Juglans nigra*); with different air speeds. Sorption from $u = 0,06$ ($\phi \approx 0,26$) to $\phi = 0,97$ at 25°C . I have used $\xi = 150 \text{ kg/m}^3$ and $v_s = 0,023 \text{ kg/m}^3$.
6. Avramides & Siau (1987) Western White Pine (*Pinus Monticola*). Absorption measurements with the sorption method at 30°C . I have used $\xi = 150 \text{ kg/m}^3$ and $v_s = 0,030 \text{ kg/m}^3$.

The older measurements by Choong & Skaar have much lower values of the surface resistance than have Rosen and Avramides & Siau. The equivalent thickness (b) do however not seem to differ that much, as it is in the range $1 - 5 \text{ mm}$ for most of the measurements.

4.7 Computer simulations with surface resistance

I have made some computer simulations to study the influence of the surface resistance on the sorption curve. The program JAM-1 which I am working with wants the surface resistance expressed as Z_ϕ . This is no problem since I can convert S to Z_ϕ .

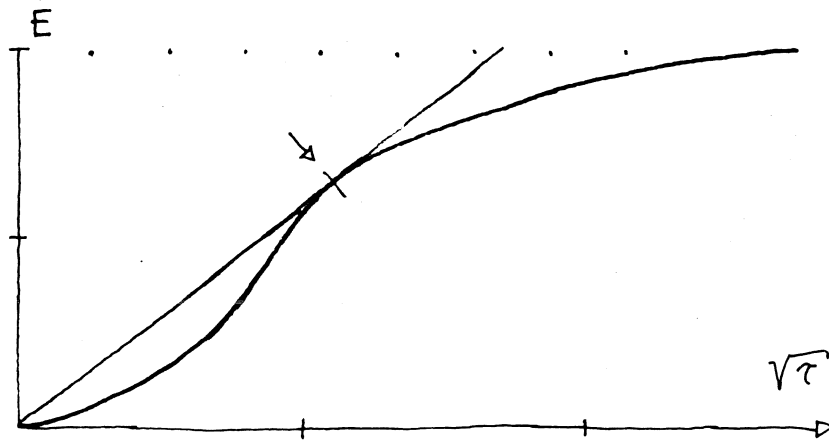


Figure 4.6: My rule to choose a point where to calculate the diffusivity \tilde{D}_w when there is a surface resistance

b/a	surface resistance	legend to figures 4.7-4.9
2,5	high	— — — — —
0,25	normal	- - - - -
0,025	low	- · - · - · - · - · -
0	no	— — — — —

Table 4.5: Simulated levels of surface resistance

I have chosen to use equation 1.7, and I think this gives certain advantages when I have surface resistances, even if these advantages are quite small. When there is a surface resistance the initial sorption will no longer be proportional to the square root of time, and I will therefore have to have a new rule how to choose the diffusivity. In figure 4.6 is shown how I have done: I calculate the diffusivity with equation 1.7 at the point of largest slope from the origin to any point on the curve.

As I wrote in the first two chapters I have been working with dimensionless variables. This means for example that D° is in the range from zero to unity, which is to be compared with a real value of D_w of around $10^{-9} \text{ m}^2/\text{s}$. If I know the value of a real surface resistance, which value should I then use when working with the dimensionless variables to get the same effect on the sorption?

I have let the equivalent thickness of the surface resistance (b) divided by the actual thickness (a) become an invariable, a variable which does not change its value upon transformation.

$$\text{invariable} \quad \frac{b}{a} = \frac{D_w \cdot Z_w}{a} = \frac{D_w}{S \cdot a} = \frac{D_w \cdot Z_\phi \cdot \xi}{a} \quad (4.13)$$

Knowing b/a it is easy to calculate Z_ϕ if we know $\xi = dw/d\phi$ (which is unity during my simulations).

As I showed in section 4.6 a value of $b = 0,0025 \text{ m}$ is probably quite normal for samples with a half thickness of a centimeter. I have worked with a b/a -value of 0,25 as normal in my simulations. I have also simulated one case with high, one with low, and one with no surface resistance.

In figures 4.7-4.9 are shown the $E - E_{th}$ -diagrams for three different $D^\circ(w^\circ)$.

When looking at these curves, remember that \tilde{D} is taken where it has its maximum value (see chapter 3.4). The diagrams shows therefore not only the effect of the surface resistance,

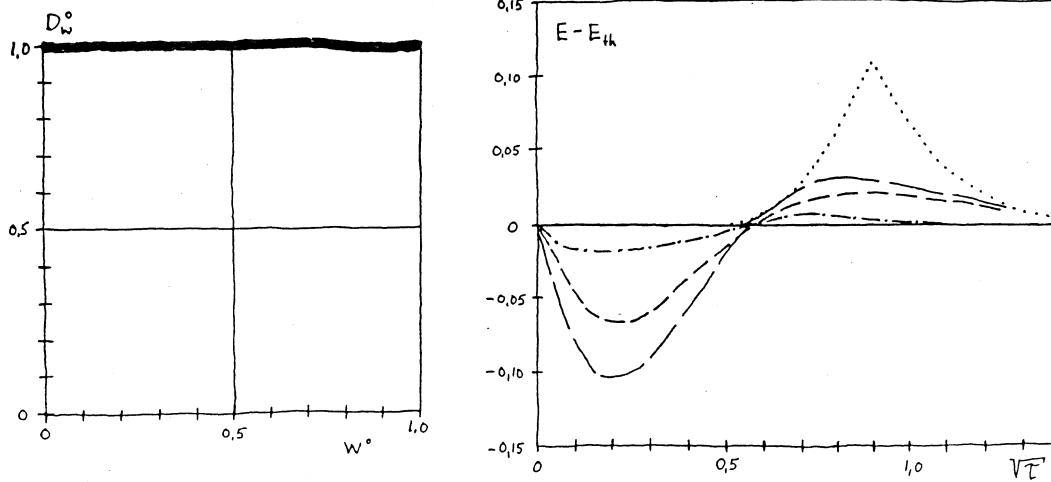


Figure 4.7: The effect of different surface resistances with constant diffusivity

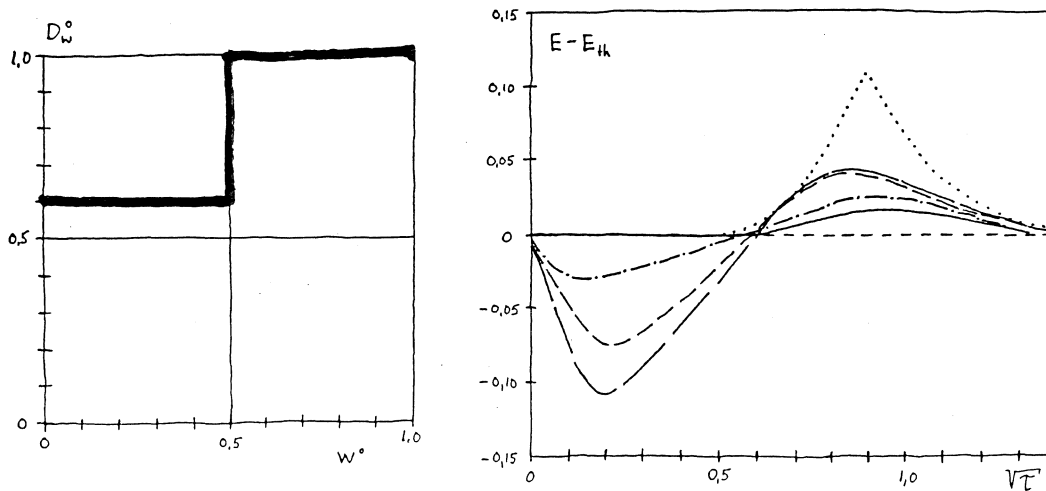


Figure 4.8: The effect of different surface resistances with an increasing diffusivity

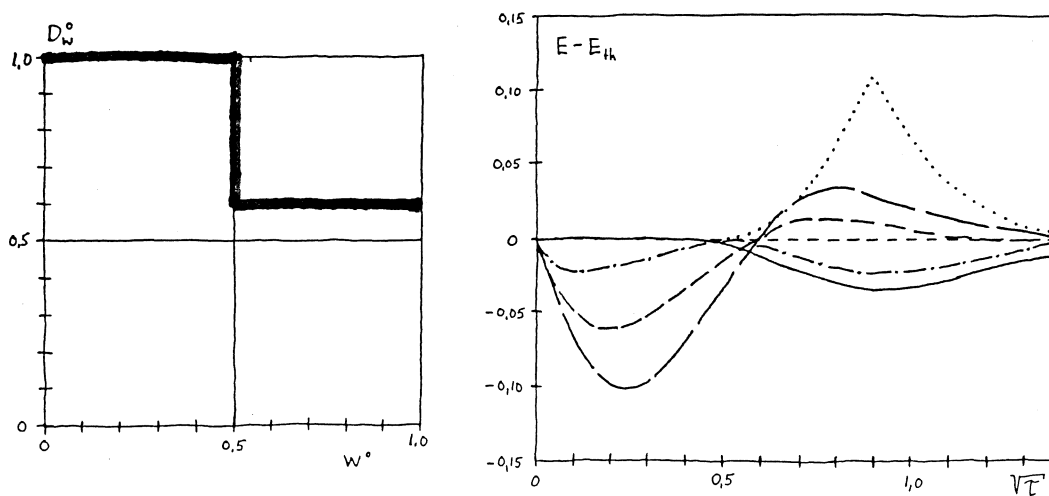


Figure 4.9: The effect of different surface resistances with a decreasing diffusivity

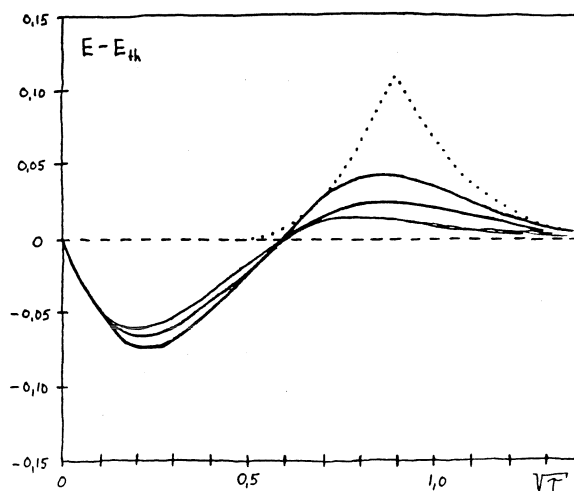


Figure 4.10: The effect of different diffusivities on the $E - E_{th}$ -diagram when the surface resistance is normal ($b/a = 0,25$). The curve with the largest "amplitude" is curve c (with increasing diffusivity). The one with the smallest is g. The middle curve is from the constant diffusivity (curve a).

but also the effect of this rule for taking the value of \tilde{D} . There is however no uncertainty where to take this value once I have chosen a rule to do it.

Some interesting observations can be made:

- The influence of the surface resistance is most easily seen when $\tau < 0,5$, as the curves then have minimas. This is a good test for the existance of a surface resistance.
- For increasing D the $E - E_{th}$ -values does not differ very much if $\tau > 0,6$.
- For decreasing D the $E - E_{th}$ -value is very different for different b/a . All curves with surface resistance have both maximum and minimum (though they are hard to see for small b/a). A high surface resistance makes the curve look very much like a curve for increasing D . Maybe there is more information in a measurement with decreasing diffusivity, as these take much longer time.

These observations makes the curves look confusing. It seems to be impossible to sort out the different effects, but if we accept that $b/a = 0,25$ it is possible to draw another diagram which contains only different diffusivities and this normal surface resistance.

In figure 4.10 we see that the curves for different $D(w)$ are only slightly different. I do not know how much this depends on the examples I have choosen, but it does not seem to be easy to differ different diffusivities from each other. Still I draw the following conclusion:

- $E - E_{th}$ -curves for decreasing D have larger minima then the curves for increasing D

As these curves are hard to use for determining the shape of $D(w)$ from an experiment, it is probably best to use a program (for example SORP) to try to calculate the $E - E_{th}$ -curve from the $D(w)$ which you think is the right one. If the experimental and the simulated curves agree this can mean that your $D(w)$ is a good approximation (though this is no proof that it really is). If the curves do not agree you have made a bad guess of $D(w)$.

Chapter 5

A FEW TEST EXAMPLES

I have taken three sorption curves from articles by Rosen, Crank & Park and Liu. I have measured these curves as exactly as possible with a ruler. This is of course not a method to be encouraged and I will try to remake the calculations with real measured data.

In Rosen (1978) a curve for longitudinal adsorption in a 1,6 cm thick sample of silver maple is shown. The adsorption is from $\phi = 0,26$ to $\phi = 0,97$ and the air velocity was 3,8 m/s. In figure 5.1 we can see that there seems to be an initial delay (because of a surface resistance) and a later slowing up of the sorption process (possibly due to a decreasing diffusion coefficient).

In figure 5.2 I have drawn the $E - E_{th}$ -diagram which shows these two effects more clearly.

Crank & Park (1949) made measurements of adsorption of chloroform by polystyrene at 25°C . I have taken one of their diagrams, showing a sorption up to a percentage regain of 9,5 % (figure 5.3). This looks different from the one from Rosen in figure 5.2. Here it is clear that the diffusivity is increasing.

I have also a third example from Liu (1987) in which two half hard fibreboard samples were equilibrated at $\phi = 0,65$. One of them was then put in a drier climate of $\phi = 0,30$ and the other was put in a climate which was $\phi = 0,80$.

On page 35 a $E - E_{th}$ -diagram is shown, with two sets of data. Even if the number of data points are quite few, especially for the desorption, we can draw some conclusions from them. The data from the absorption experiment indicates that there is a surface resistance and that the diffusivity probably is increasing. The data from desorption shows no surface resistance as there are no data-points in this region, but seems to indicate that the desorption is increasing in this ϕ -interval too (remember that desorption plots are interpreted the other way as I showed

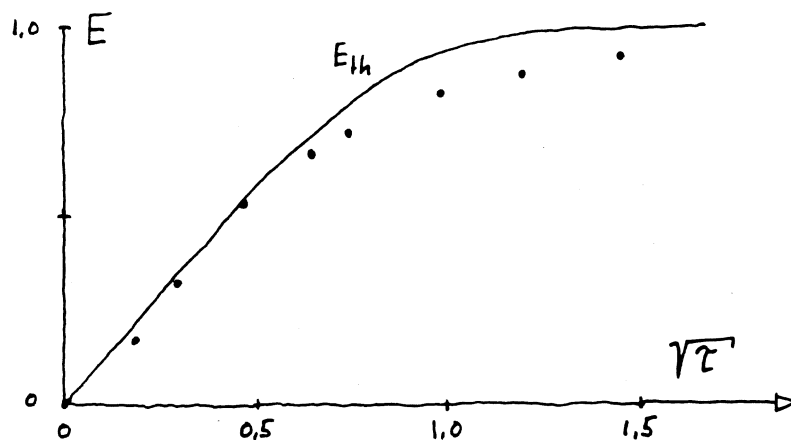


Figure 5.1: Sorption-data taken from Rosen (1978)

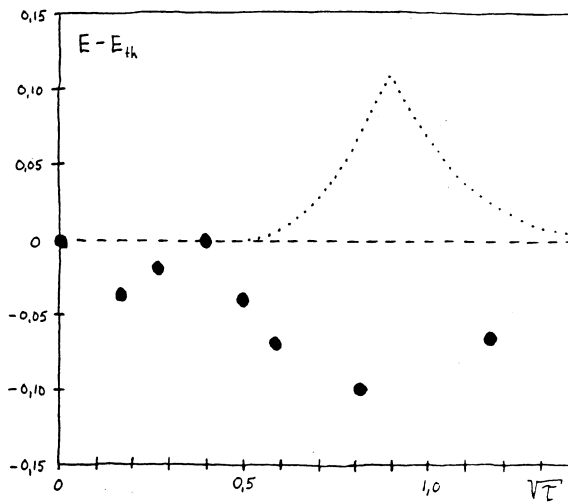


Figure 5.2: $E - E_{th}$ -diagram for data taken from Rosen (1978)

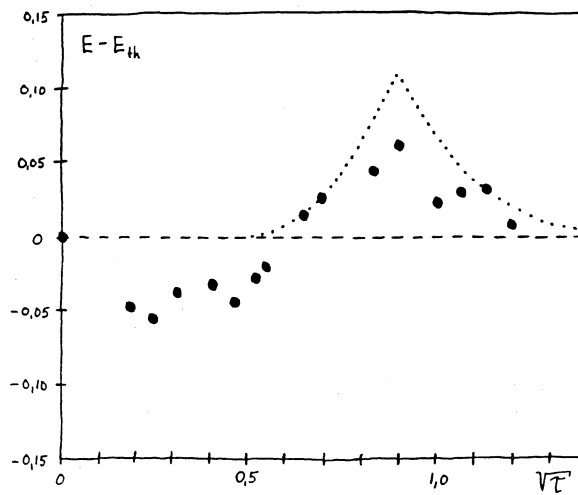


Figure 5.3: $E - E_{th}$ -curves from measurements by Crank & Park (1949)

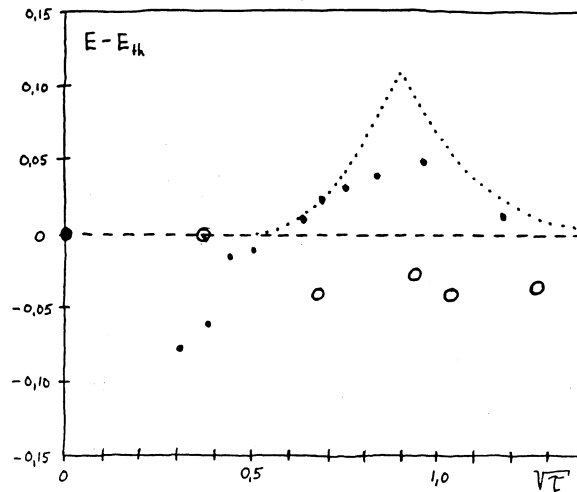


Figure 5.4: $E - E_{th}$ -curves taken from Liu 1987. Filled circles are for absorption and open circles are for desorption

in section 3.4). The diagram seems to indicate that the diffusivity is increasing in the whole ϕ -interval.

I do not know if this theoretical method is reliable or not when it comes to real measurements. Some reasons why it might not be good enough are listed below.

- Unavoidable errors in the measurement:
 - non-constant ϕ
 - leaks in the sealed surfaces
 - fluctuating air velocity
 - etc.
- The material does not fulfill the requirements of the method:
 - cracks
 - late- and earlywood having different properties
- Other effects which are not accounted for:
 - mechanical effects from swelling and shrinking
 - decomposition of the wood
 - non Fickian behavior

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