CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter examines the pertinent literature on the water sorption behaviour of wood and other relevant areas necessary for understanding the work in this thesis. The literature concerning the water sorption of wood is huge and it is not possible to cover every paper published on the subject. Only the most relevant work is examined. The presence of OH groups associated with the cell wall macromolecules is the main reason why wood strongly interacts with atmospheric moisture. The take-up of one or more water molecular layers onto the internal surface of the wood cell wall from the vapour phase is defined as adsorption and the process of removing water molecules from the cell wall is called desorption. It is necessary to define terms precisely, because there is often confusion in the literature. Adsorption refers to a process occurring on a surface, whereas absorption refers to a process of sorption into the bulk of a material.

Adsorption is used throughout this thesis to describe sorption onto the internal surface of the cell wall. At the molecular level, the distinction between the surface and bulk of the cell wall is blurred and the term internal surface is much preferred. As noted, the microstructures of the wood cell wall are composed of crystalline microfibrils embedded in a matrix composed of amorphous polysaccharides and lignin (Siau 1995). The incomplete filling of the intermicrofibrillar regions of the cell wall results in the existence of what are usually referred to as micropores (or microvoids, microcapillaries) in the cell wall

(Hill 2006). IUPAC (International Union of Pure and Applied Chemistry) classifies pores with diameter of less than 5 Å as ultramicropore, 5-20 Å as micropore, 20-500 Å as mesopore and those having diameters greater than 500 Å as macropore. Therefore, based on the size of voids in the cell wall, it can be concluded that, the wood cell wall is according to IUPAC, mainly microporous (Stamm 1964, IUPAC 1972). The size for the wood cell wall micropores are in the region of 2-4 nm and the evidence for their existence had been obtained by various studies (Figure 2.1 and 2.2) (Hill 2006, Hill *et al.* 2005, Hill and Papadopoulos 2001, Persson *et al.* 2004).
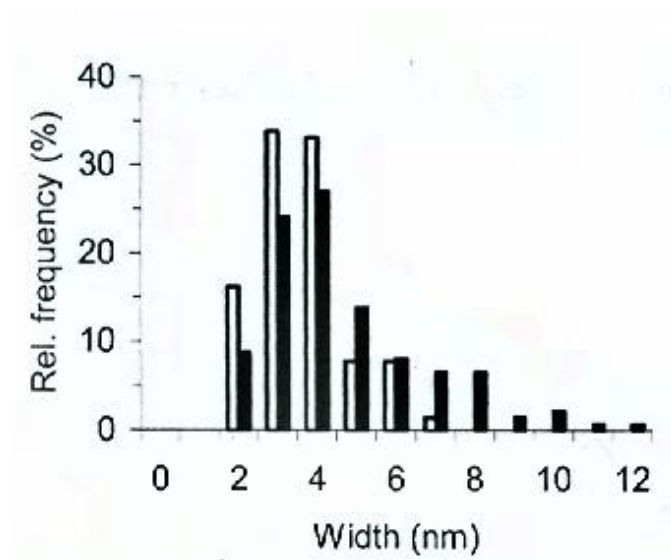
Figure 2.1 Analysis of the pore size distribution in the cell wall as obtained using silica nanocast techniques (Persson *et al.* 2004).
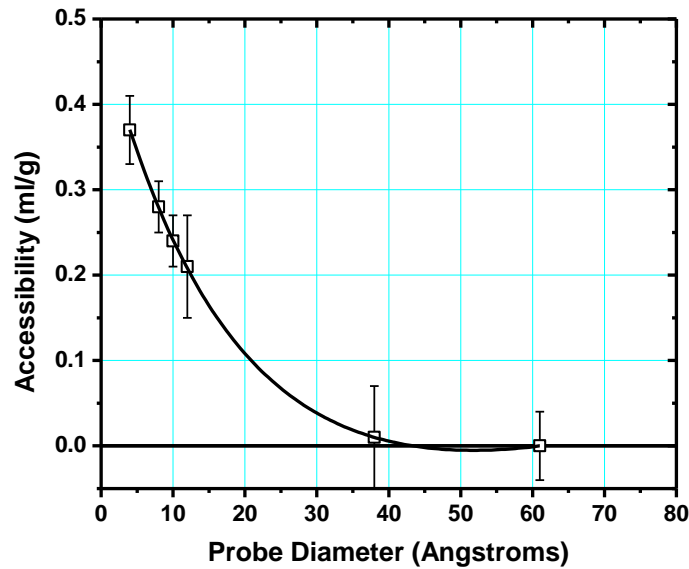
Figure 2.2 Cell wall accessibility of wood determined using the solute exclusion method (Hill *et al.* 2005).

Adsorption of water onto hygroscopic natural polymers, such as wood and cellulose, is thought to depend entirely on the OH groups on the internal surface (Venkateswaran 1970). Stamm (1964) was the first person to refer to the 'internal surface', which is the internal geometry of the wood cell wall comprising the micropores. When the wood cell wall absorbs moisture, the sorbed water molecules occupy space between the microfibrils and due to this the material is expanded. This swelling of the cell wall involves expansion of the lignin-hemicellulose matrix in which the microfibrils are embedded. The space which the water molecules occupy in the matrix is referred to in the literature as the transient microcapillary network (Hill 2010a). Since water adsorption involves expanding the matrix

between the microfibrils this means that work is performed. Expansion of the matrix can be considered analogously to extending a spring, with energy being stored in the matrix as water molecules are absorbed. This concept will be developed later in the thesis.

2.2 Gel theory of wood

The matrix of the wood cell wall also can be considered comparable to a gel, which is similar to a solution in some respects but different in others as noted below. Barkas (1949) was the first person to fully examine this concept and defined a gel as a material which can swell during the adsorption of a sorbate and which at the same time, possesses a certain amount of rigidity. Six characteristics of gels which correspond to the sorption properties of wood have been listed by Barkas (1949). These are:

1. Gels are hygroscopic. They adsorb moisture from the surrounding atmosphere (vapour pressure less than saturation value) and hold it in equilibrium.

2. Gels swell on adsorption. The total volume increase can be greater or less than the volume of liquid adsorbed but in wood the volume increase is usually considered to be of the same magnitude as the adsorbed liquid volume.

3. Gels exert forces if restrained from swelling when exposed to vapour pressures higher than their equilibrium vapour pressures. These forces

may be different in different directions. Gels also adsorb less moisture at a given vapour pressure when so restrained.

4. Gels possess some rigidity which can withstand static shear stresses, unlike solutions.

5. Gels show limited sorption and swelling in a saturated atmosphere. Thus they differ again from solutions, which swell to infinite dilution in a water vapour saturated atmosphere.

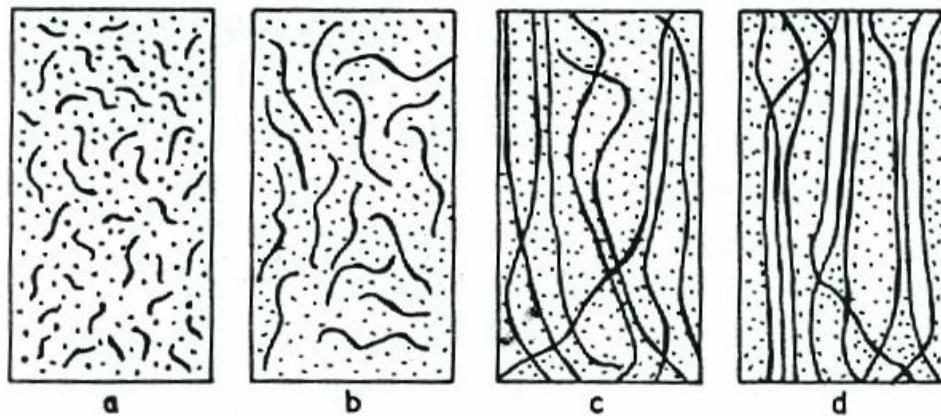6. Gels show sorption hysteresis, in contrast to solutions.

Figure 2.3 Illustration of a hypothetical sequence in the development of the cell wall showing: (a) Sugar molecules in solution. (b) Sugar molecules partially polymerised into randomly oriented cellulose molecules. (c) Cellulose molecules completely polymerised and partially oriented. (d) Cellulose molecules in final oriented configuration (Skaar 1988).

The first three characteristics are similar to solutions but the last three differ, since gels exhibit some rigidity, limited sorption and swelling and sorption hysteresis. A hypothetical sequence of development of the cell wall of wood is shown schematically in Figure 2.3, illustrates the difference between solutions and

the gel which makes up the cell wall of wood. Sugar molecules shown in 'a' are in solution in the cell lumen. In 'b' they have begun to polymerize into cellulose molecules. As the molecules continue to polymerise they may attain the configuration shown in 'c', in which some of the cellulose molecules become aligned. Finally they become further polymerised and aligned into the gel system of cellulose and water which constitutes the cell wall of wood, as shown in 'd'. Lignin and other cell wall components are omitted in this simple schematic diagram for reasons of clarity. Skaar (1988) noted that the three differences between the solutions and gels are apparent in contrasting the solution of sugar molecules in water shown in Figure 2.3(a), and with those of the cell wall shown in (d). The rigidity of the gel in this model is caused by the cellulose network which resists distortion. The limited sorption and swelling is a result of the same network.

2.3 Sorption isotherms

The sorption process results in changes in moisture content (MC) and this is usually expressed as a fraction or percentage of the wood dry weight, i.e. the ratio of the mass of water vapour sorbed to the oven dry mass of the wood. Wood as a hygroscopic material will change its MC in an environment until it attains an equilibrium state (Figure 2.4). This is a dynamic equilibrium with the water vapour in the atmosphere and is called the equilibrium moisture content (EMC). At EMC, the flux of water molecules entering the cell wall is exactly balanced by the flux of water molecules leaving the cell wall.
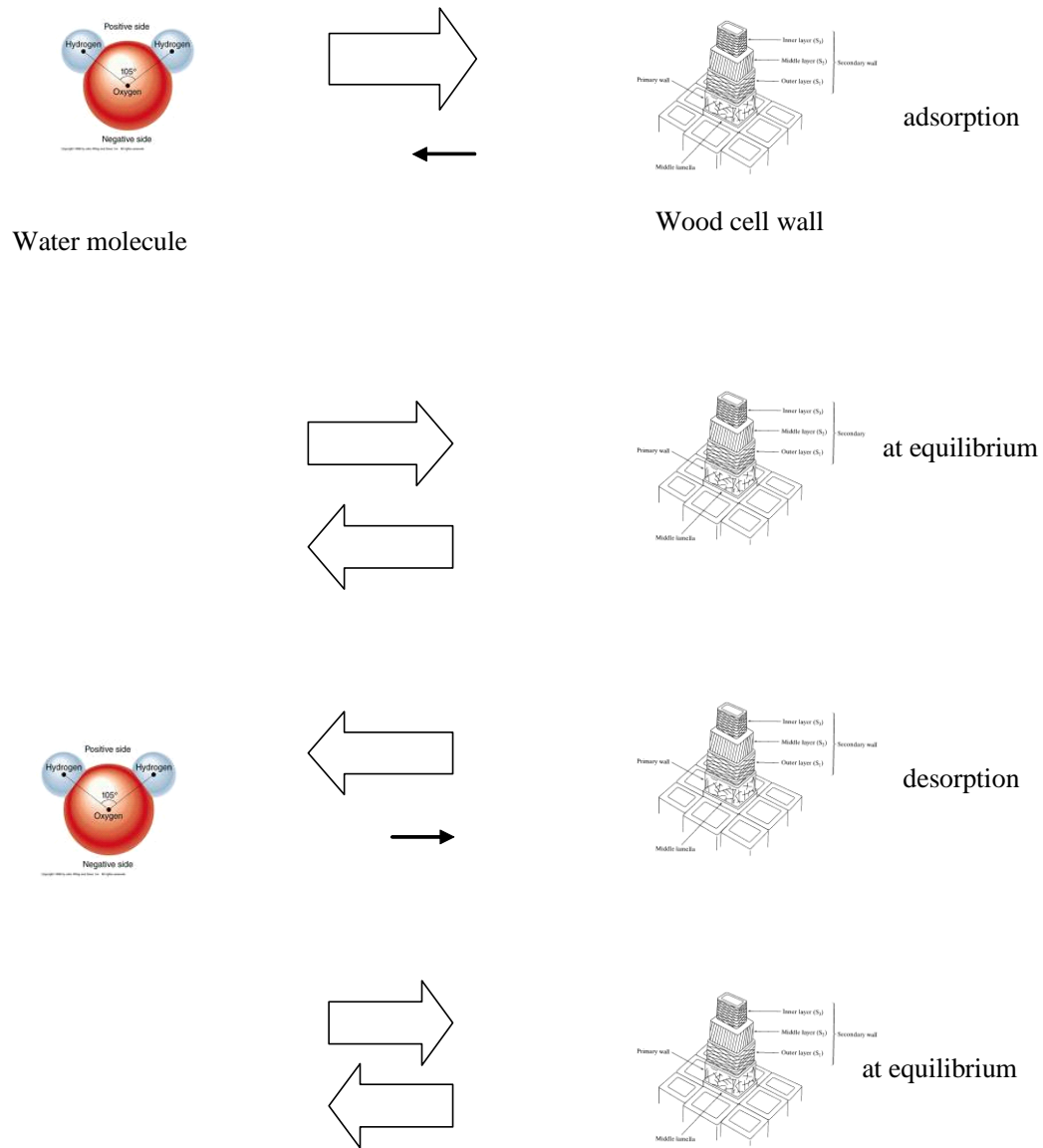
adsorption

Water molecule

Wood cell wall

at equilibrium

desorption

at equilibrium

Figure 2.4 A schematic-diagram showing the dynamic nature of the sorption process even at equilibrium.

The relationship between the amount of water adsorbed or desorbed from the cell wall with relative humidity (RH) at a constant temperature is called the sorption isotherm (Skaar 1988). The widely accepted sorption isotherm classification methods are those of the IUPAC (1972) that were originally proposed by Brunauer *et al.* (1940) (Brunauer, Deming, Deming, and Teller) (BDDT isotherm classification) (Figure 2.5) which groups isotherms into six categories based on porosity and adsorbate-adsorbent system interaction (Figure 2.6). There are other classifications that complement or improve the IUPAC and BDDT. Isotherms indicated as type I in Figure 2.6 are typical of microporous sorption while II, III and VI are indicators of nonporosity or macroporosity. The ones indicated as IV and V shows the presence of mesoporosity. The shape of isotherms further indicates the prevailing type of interaction between adsorbates and adsorbents. Type-II and IV denote strong adsorbate-adsorbent interactions over type-III and type-V. The last sorption isotherm of type-VI shows a step wise multilayer adsorption with metastable phases of equilibrium. The adsorption/desorption properties of cellulosic and lignocellulosic materials are characterized by the sigmoidal shape of the Type II isotherm IUPAC (1972) and hysteresis between the sorption and desorption loop (Skaar 1972, Skaar 1988, Siau 1984, Siau 1995). The sigmoidal nature of the water vapour sorption isotherm of wood is well established phenomena but is still not fully understood, although many models exist which describe the shape of the isotherm to a greater or lesser accuracy (Venkateswaran 1970). What is clear is that the sorption process is not occurring with a static

substrate and that swelling and shrinking of the material is of paramount importance.
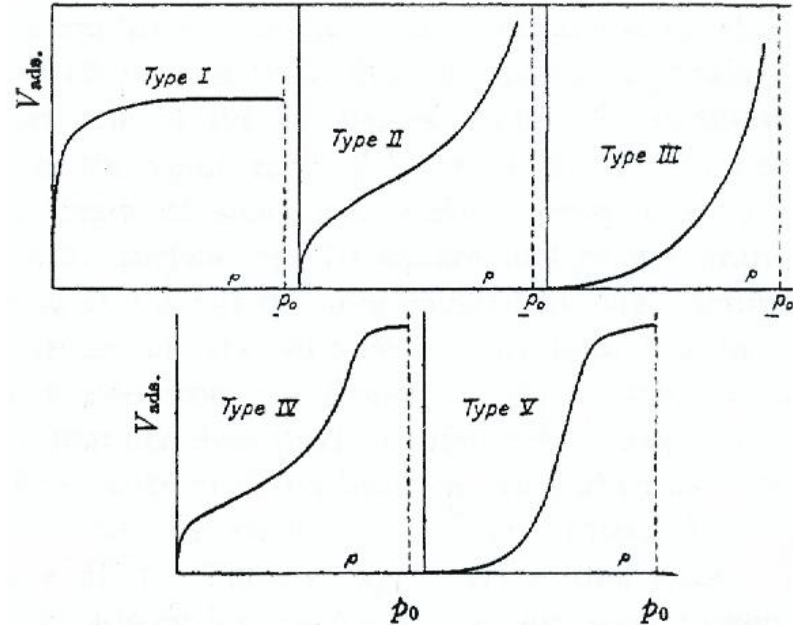

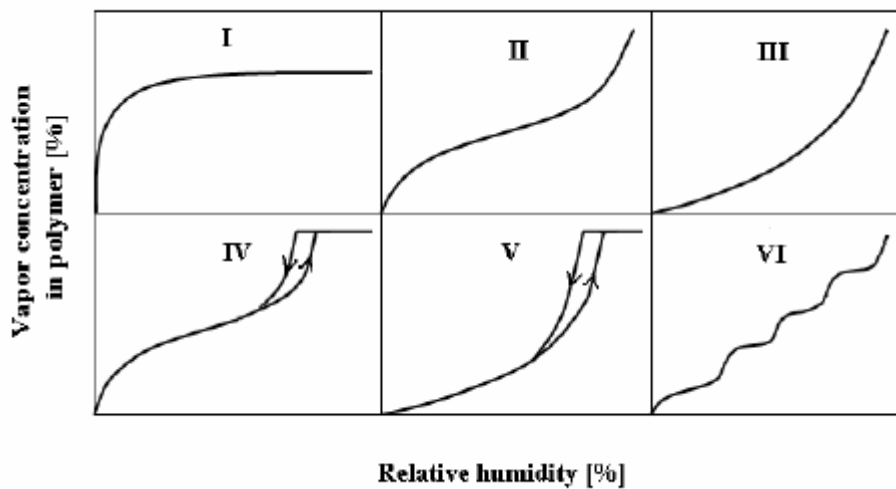**Figure 2.5 The five types of Van Der Waals adsorption isotherms (Brunaeur *et al.* 1940).**

Figure 2.6 The diagrammatic representation of the six types of sorption isotherms drawn to match the IUPAC (1972) classification.
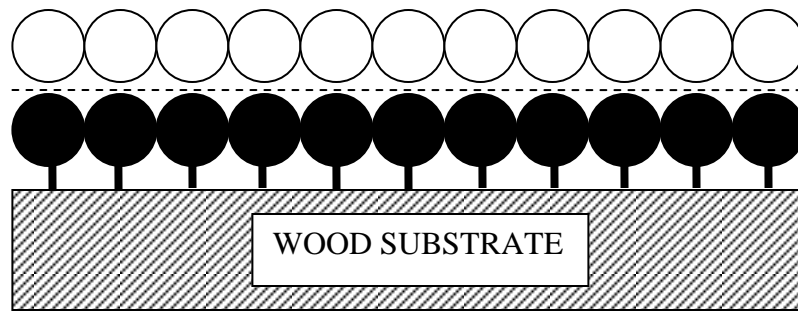
Figure 2.7 Schematic diagram showing multimolecular layering: The vertical lines represent sorption sites, the dark circles (●) represent primary molecules (monolayer), and the open circles (○) represent secondary molecules.

2.4 Multimolecular layering and cluster theory

The basis for a sorption theory is the interaction of the sorbing molecule (sorbate or water molecules) with the internal surface or bulk of the sorbent (wood cell wall). In current sorption theories for wood, Skaar (1988) reported two primary concepts that have been used: one is a multi-molecular layer concept and the other is a polymer-solution concept. The BET and Dent theories are examples of sorption models based on a "layering" concept. Figure 2.7 shows a schematic idealised view of the formation of layers during sorption. Molecular layering based theories describe the monolayer as primarily adsorbed with the highest energy of interaction. The BET model assumes the primary monolayer sorption to take place on a planar surface and additional molecules to be sorbed in subsequent layers with further assumption of equal energy of sorption to that of bulk (i.e. liquid state) molecules. According to this theory, adjacent molecules in a layer are restricted from interacting with each other or the interaction can be neglected. It recognises the

existence of sorption sites that are vacant, with one or multiple layers under equilibrium conditions. The BET model was an extension of the monolayer sorption isotherm of the Langmuir model (Langmuir 1918). Although it has been used in many studies of sorption isotherms with wood, it is not sufficient to describe the majority of sorption isotherms especially at higher vapour pressure. In a further development of the BET model, Dent (1977) proposed a model that is based on the same concept of primary and secondary and subsequent sorbed layers, but with additional consideration of the sorption energy in the secondary and subsequent layers to be different from the bulk molecules. The question that arises is what is the nature or geometry of the surface on which the monolayer adsorbs? This is assumed to be planar in models such as BET or Dent.

The clustering theory of adsorbed molecules in polymers was proposed to explain some of the thermodynamic inconsistencies in multilayer sorption theories first by Zimm (1953), Zimm and Lundberg (1959) and later by Starkweather (1963, 1975). Subsequently, Hartley *et al.* (1992) used aspects of both Goring (1978) and Caulfield (1978) theories to develop their theory of water cluster adsorption in wood. Goring (1978) proposed that cellulose fibres disrupt the structure of water creating a perturbed layer which is hydrogen bonded to the hydroxyl groups on the cellulose surface (Figure 2.8). Caulfield (1978) also proposed a hydrogen bonding interaction between fibre and water, but he suggested that this hydrogen bonding structured the water around the fibre rather than perturbing it (Figure 2.9). Cluster theory has been used successfully, in order to understand the nuclear magnetic resonance (NMR) results obtained with hydrated porous glass, in which it is shown

that a bulk water cluster is reduced to smaller clusters caused by the influence of the pore wall (Figure 2.10) (Belfort and Sinai 1980). NMR studies carried out on wood equilibrated in a moist environment have shown that water in the wood cell wall exists in at least two states (Riggin *et al.* 1979, Nanassy 1976). One state consists of water tightly bound to the wood substance through hydrogen bonding, and the other state consists of weakly bonded water that constitutes a mobile phase within the cell wall. Rawat and Khali (1998) have explained that the clustering of water molecules in wood is a result of interactions of the molecules with each other and with the accessible hydroxyl groups within the cell wall. Based on the Starkweather (1975) equation, Rawat and Khali (1998) derived a relationship for calculating the average size cluster of water in wood at different RH. At low RH, water molecules do not form clusters, whereas the average cluster size increases continuously with an increase in RH. At RH corresponding to fibre saturation, larger clusters are formed.

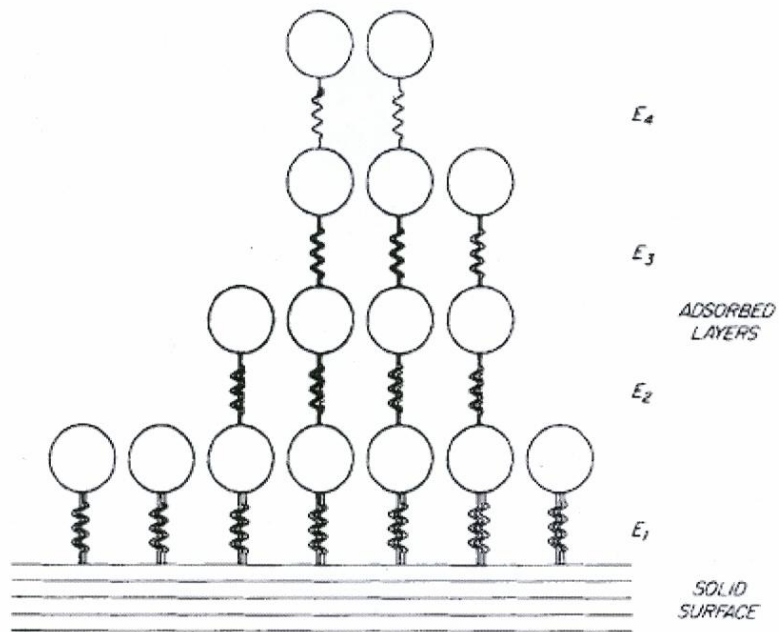**Figure 2.8   Goring's model of fibre water interaction (Goring 1978).**

Figure 2.9 Caulfield's fibre water theory (Caulfied 1978).
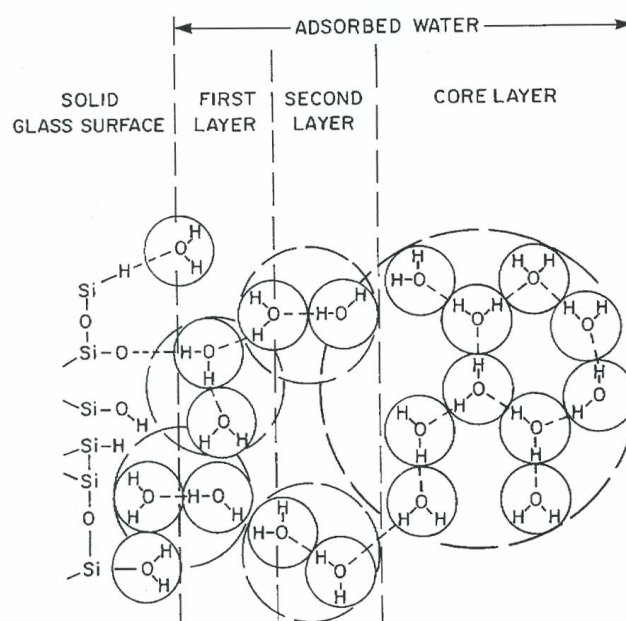

Figure 2.10 Cluster formation at a hydration site on glass surface (Belfort and Sinai 1980).

2.5 Introducing the Hailwood-Horrobin (H-H) model

Hailwood and Horrobin (1946) developed a model for sorption by assuming that the process is controlled by the formation of a solid solution of water in the polymer and the formation of hydrates between water and definite units of the polymer molecule. The mixture of polymer, polymer hydrates and dissolved water forms a single solid phase, which is in an equilibrium state with the vapour phase. In this solution theory, the initial sorption is attributed to surface binding, with water combining with units of the polymer to form hydrates. In the following secondary phase, water is assumed to be in solution with the polymer (dissolved water). The H-H model is a solution-based theory that has been used extensively in wood science and continues to be used (Papadopoulos and Hill 2003, Dieste *et al.* 2008, 2009, Hill *et al.* 2008, 2009, 2010a, Xie *et al.* 2011). However, only adsorption isotherms can be evaluated using the H-H model because evaluation of an isotherm which is partly composed of a scanning curve (desorption isotherm) is of doubtful validity. Despite shortcomings, the H-H model has the virtue of simplicity and the model will be used in this thesis to examine the effect of wood species and thermally modified wood on water vapour sorption properties. It is to be appreciated that there is no shortage of models available to explain sorption in different materials such as food (GAB model), textile (BET, Dent, Pierce, Enderby-King and Bradley model) and cotton (H-H model) (Skaar 1972).

Figure 2.11 Physical representation in H-H model (Dieste *et al.* 2009).

A detailed discussion of the Hailwood-Horrobin model follows (Figure 2.11). The H-H model (Hailwood and Horrobin 1946) has been regularly used to explain the sigmoid shape of the sorption isotherm observed with the sorption of water vapour on plant-based materials, including wood. Originally the H-H model was developed to describe the sorption isotherm of cotton, but has subsequently been widely used to investigate the sorption behaviour of wood and also chemically modified wood (Spalt 1958, Skaar 1972, Siau 1984, Popper and Bariska 1972, Yasuda *et al*. 1995, Chauhan *et al*. 2001, Papadopoulos and Hill 2003, Papadopoulos *et al.* 2005, Dieste *et al*. 2008, Dieste *et al*. 2009, Hill *et al.* 2008, Xie *et al.* 2011). It has proved to be useful, although it has been criticised for some of the assumptions used in its derivation (Spalt 1958, Skaar 1972, Skaar 1988, Okoh and Skaar 1980, and Simpson 1980). It nonetheless has the virtues of simplicity and requires no knowledge of the geometry of the cell wall internal surface. The H-H model considers the process of sorption to be one of solvation in which there may be two or more phases in equilibrium (Hailwood and Horrobin 1946).

The BET model has also been used extensively and is found to fit the sorption isotherms for wood reasonably well at low moisture contents, up to a relative humidity of about 40% (Skaar 1972). A modification of the BET theory as proposed by Dent (1977), predicts a sigmoidal isotherm identical with that of the H-H single hydrate theory. In the H-H model, the monolayer (water of hydration) can change over the whole range of RH and is thus a much more appropriate description for an evolving surface associated with a material that changes dimension as sorption proceeds, compared to models such as the BET isotherm.

The H-H model assumes that water sorbed by wood can exist in two forms; water of hydration corresponding to water molecules that are H-bonded to the cell wall polymeric OH groups (monolayer water) and solid solution or dissolved water corresponding to water molecules that are less constrained, but nonetheless are located within the cell wall micropores (polylayer water). The H-H model considers that three chemical species are present: 'dry' polymer, hydrated polymer (chemisorbed water), and dissolved water (polylayer water). These three components are considered to act as an ideal solution. It is convenient to treat this in terms of molar concentrations but nonetheless located in the wood cell wall. If we assign X_o as the number of moles of unhydrated polymer, X_h the number of moles of hydrated polymer (and therefore the number of moles of water of hydration, assuming one mole of water of hydration per mole of hydrated polymer), and X_s as the number of moles of dissolved or unhydrated water.
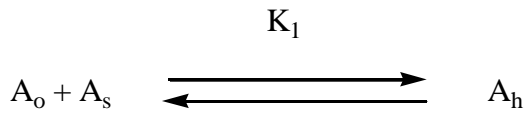
The molecular weight (W) of the wood cell wall polymers is unknown, but it is possible to calculate this in terms of the molecular weight of polymer per mole of water sorption sites (i.e. accessible OH groups). If the number of moles of sorption sites per gram of dry wood is known, then the molecular weight per sorption site can be calculated based upon H-H theory. The total number of moles of the three species is $X_o + X_h + X_s$. It is assumed that this solution behaves as an ideal solution; thus the activities A_o, A_h, A_s, of the three species are equal to their mole fractions in solution, as follows:

$$A_h = X_h / (X_o + X_h + X_s) \quad \text{(hydrated)} \tag{2.1}$$

$$A_o = X_o / (X_o + X_h + X_s) \quad \text{(unhydrated)} \tag{2.2}$$

$$A_s = X_s / (X_o + X_h + X_s) \quad \text{(solution)} \tag{2.3}$$

When an equilibrium condition exists between the three components, the equilibrium constant (K_1), is defined as the ratio of the chemical activity A_h of the reaction product (hydrate) to the product of the activities of the two reactants (water and unhydrated wood), an equation of the form can be written:
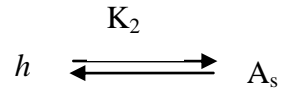
$$A_o + A_s \xrightleftharpoons[\hspace{3cm}]{K_1} A_h$$

Thus:

$$K_1 = A_h / A_o A_s = X_h / X_o A_s \tag{2.4}$$

or

$$X_h = K_1 X_o A_s \tag{2.5}$$

There also exists equilibrium between the water in the atmosphere given by its relative vapour pressure (p/p_o) or h and the dissolved water. The equilibrium constant (K_2) for this system is given as:

$$h \xrightleftharpoons{K_2} A_s$$

$$K_2 = A_s / h \qquad\qquad\qquad (2.6)$$

or

$$A_s = K_2 / h$$

The ratio $X_h / (X_h + X_o)$ gives the number of moles X_h of hydrated polymer (and thus water of hydration) per mole of polymer. This is because the total number of moles of sites is equal to $X_h + X_s$. Thus, combining equations 2.5 and 2.6 gives:

$$\frac{X_h}{X_h + X_o} = \frac{K_1 X_o K_2 h}{K_1 X_o K_2 h + X_o} = \frac{K_1 K_2 h}{K_1 K_2 h + 1} \qquad (2.7)$$

The ratio $X_s / (X_h + X_o)$ gives the number of moles of dissolved water per mole of dry wood. This is obtained by rewriting equation 2.3 in inverted form and rearranging to give:

$$(X_h + X_o) / X_s = (1/A_s) - 1 = (1 - A_s) / A_s \qquad (2.8)$$

Inverting, and using equation 2.6 to eliminate A_s, gives:

$$\frac{X_s}{X_h + X_o} = \frac{K_2 h}{(1 - K_2 h)} \qquad\qquad (2.9)$$

The sum of equations 2.7 and 2.9 gives the total number of moles of water in the wood per mole of dry wood. This can be related to the wood moisture content M, since the moles of water are equal to the number of grams of water divided by the molecular weight of water (18), and also the moles of dry wood are equal to the number of grams of dry wood divided by the molecular weight of wood per mole of sorption sites. Since the latter is unknown, it will be represented by the symbol W. Thus:

$$\frac{X_h}{X_h + X_o} + \frac{X_s}{X_h + X_o} = \text{[(g hydrated water/18)+(g dissolved water/18)]/(g dry wood/}W) \quad (2.10)$$

$$\frac{X_h + X_s}{X_h + X_o} = \frac{W}{18} \quad \text{[(g hydrated water) + (g dissolved water)]/(g dry wood)} \quad (2.11)$$

$$\frac{X_h + X_s}{X_h + X_o} = (W/18)(m_h + m_s) = (W/18)m \quad (2.12)$$

Where m_h and m_s are the fractional moisture contents of the hydrated and dissolved water respectively, and m is the total fractional moisture content, all based on the dry weight of wood. Equation 2.12 can be combined with equations 2.7 and 2.9 to give:

$$m = m_h + m_s = \frac{18}{W}\left(\frac{K_1 K_2 h}{1 + K_1 K_2 h} + \frac{K_2 h}{1 - K_2 h}\right) \quad (2.13)$$

or, in terms of relative humidity, $H = 100h$, and percentage moisture content $M = 100m$:

$$M = M_h + M_s = \frac{1,800}{W}\left(\frac{K_1 K_2 H}{100 + K_1 K_2 H}\right) + \frac{1,800}{W}\left(\frac{K_2 H}{100 - K_2 H}\right) \quad (2.14)$$

The first term on the right is equivalent to M_h, the percentage moisture content consisting of water of hydration. The second term is equivalent to M_s, the percentage moisture content consisting of water of solution, or dissolved water.

The term 18/W, is equal to the ratio of the grams of water per mole of water in the wood, to the grams of dry wood per mole of sorption sites. It is therefore equivalent to the fractional moisture content m_1 of the wood when there is one molecule of water on each sorption site, therefore:

$$m_1 = 18/W \text{ (g/g)}; m_1 = 1,800/W \text{ (\%)} \qquad \qquad \textbf{(2.15)}$$

According to equations 2.13 and 2.14, there are three constants K_1, K_2, and W (or m_1) which determine what the relationship of M and H (the sorption isotherm) will be. These three constants also determine what proportion of the total moisture content M at any given humidity H is water of hydration M_h and water of solution M_s. Evaluation of these parameters from the sorption isotherm is possible but difficult. However, the equation 2.14 can be transformed thus:

$$\frac{H}{M} = \frac{W}{1,800}\left[\frac{(100 + K_1 K_2 H)(100 - K_2 H)}{K_1 K_2(100 - K_2 H) + K_2(100 + K_1 K_2 H)}\right] \qquad \textbf{(2.16)}$$

$$\frac{H}{M} = \frac{W}{18}\left[\frac{1}{K_2(K_1+1)}\right] + \frac{W(K_1-1)H}{1,800(K_1+1)} - \frac{W}{180,000}\left(\frac{K_1K_2H^2}{K_1+1}\right) \qquad \textbf{(2.17)}$$

or

$$\frac{H}{M} = A + BH - CH^2 \qquad \textbf{(2.18)}$$

Where

$$A = \frac{W}{18}\left[\frac{1}{K_2(K_1+1)}\right] \qquad \textbf{(2.19)}$$

$$B = \left(\frac{W}{1,800}\right)\left[\frac{K_1-1}{K_1+1}\right] \qquad \textbf{(2.20)}$$

$$C = \left(\frac{W}{180,000}\right)\left[\frac{K_1K_2}{K_1+1}\right] \qquad \textbf{(2.21)}$$

From equation 2.18, it can be seen that the H-H theory predicts a parabolic relationship between the ratio H/M and H. The constants A, B and C are obtained from the fitting parameters of the second order polynomial. From these parameters it is possible to determine the values of K_1, K_2 and W, and hence M_h and M_s. The values of K_1, K_2 and W are derived from the fitting parameters thus:

$$K_1 = 1 + \frac{B^2 + B\sqrt{B^2 + 4AC}}{2AC} \qquad \textbf{(2.22)}$$

$$K_2 = \frac{50(-B + \sqrt{B^2 + 4AC})}{A} \qquad\qquad \textbf{(2.23)}$$

$$W = 1800\sqrt{B^2 + 4AC} \qquad\qquad \textbf{(2.24)}$$

The H-H model has been discussed in detail because it has been used extensively in wood water vapour sorption isotherm studies in this thesis.

2.6 Fibre Saturation Point

The fibre saturation point (FSP) was originally defined as the equilibrium moisture content (EMC) of the sample when the cell wall is at saturation, but there is no water in the macrovoids (such as cell wall lumina) of the material (Tiemann 1906). Hill (2008) noted that the definition is useful theoretically but it does not take into account the possibility that the situation occurring during adsorption may be far more complex and there may be condensation occurring in the lumen before the cell wall is saturated. Stamm (1971) examined nine methods to determine the FSP of wood. One of them was extrapolating moisture adsorption isotherms at constant temperature to 100% RH. Although a method much used in the literature, even now, Stamm pointed out that this was not an appropriate method for the determination of FSP. There is no doubt that FSP does have meaning, since it is very well established that the physical properties of wood (dimensional change, modulus of elasticity, modulus of rupture, etc.) do vary over a specific MC range (often stated to be 0-30% MC) but remain constant above this value (Figure 2.12)

(Dinwoodie 2000). Methods such as the use of solute exclusion, pressure plates/membranes, or NMR yield much higher values for the FSP compared to extrapolation of sorption isotherms. Saturation methods and sorption methods yield different FSP values (Siau 1995). In addition, the use of extrapolated sorption isotherms to determine FSP can be questioned, since in the region 98-100% RH the sorption isotherm is rising very rapidly and slight errors in measurement can lead to large errors in extrapolation, as was pointed out by Stamm (1971), yet this incorrect practice continues to be used, as noted by Hill (2008).
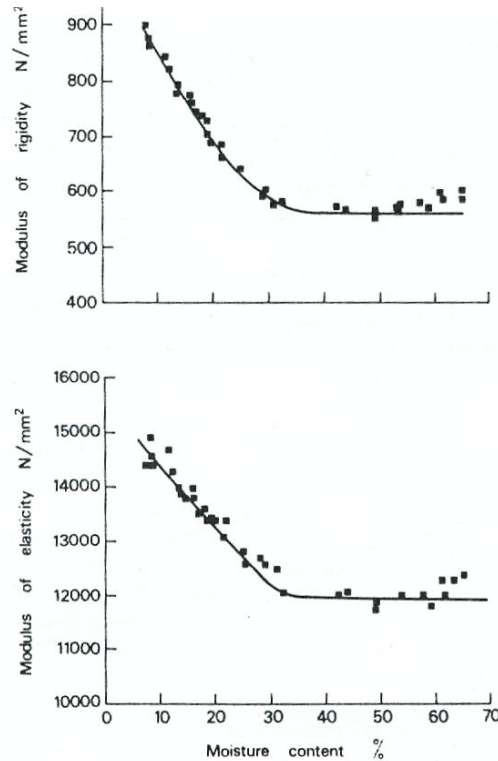

Figure 2.12 Effect of MC on the longitudinal modulus of elasticity and the modulus of rigidity in Sitka spruce. Both moduli were determined dynamically (Dinwoodie 2000).

Based on the water potential concept, by using pressure plate methods the isotherm in the higher region of RH (96-99%) can be accurately determined (Hernandez and Pontin 2006). The difference of FSP by using extrapolation and saturation methods (solute exclusion and pressure plate methods) clearly indicates that the term FSP cannot be used universally, and the term "projected fibre saturation point" (p-FSP) is more appropriate for the extrapolation method (Hill 2008). In addition, the term cell wall total water capacity can be used for the solute exclusion method where true saturation of the cell wall is involved in the measurement process (Ibbett *et al*. 2007).

2.7 Hydroxyl (OH) accessibility

Many of the properties of wood are related to the availability of OH groups associated with the cell wall polymers. On a molecular level, the cell wall OH groups represent the dominant chemical functionality influencing the performance of wood. OH groups are associated with cellulose, hemicelluloses and lignin in the cell wall. Cellulose, which is the primary reinforcing element of the cell wall, is made of linear chains of glucose residues aggregated into microfibrillar units. These units possess a high crystalline content (inaccessible to water molecules) but also a paracrystalline component, to which water molecules can gain access. Hemicelluloses are predominantly amorphous polysaccharides and highly accessible to water molecules. Both cellulose and hemicelluloses have a high OH-carbon ratio, however, in cellulose not all the OH content is accessible. Lignin is an

amorphous cross-linked polymer composed of phenolic units with a relatively low OH-carbon ratio by comparison with carbohydrates.

The number of OH groups per unit mass of dry wood can be calculated on the basis of an estimate of the number of the OH groups associated with each of the cell wall polymeric constituents (Rowell 1980). Taking Scots pine as an example, the cell wall chemical composition is as given in Table 2.1.

The theoretical OH group calculation for the cell wall is stated below:

Lignin + Cellulose + Hexosan + Pentosan

(0.26 x 1)/180 + (0.52 x 3)/162 + (0.14 x 3)/162 + (0.08 x 2)/132

Table 2.1 The distribution of OH groups composition of Scots pine (Hill 2006)

Component	Composition (%)	OH groups per unit	Molecular weight of unit
Lignin	26	1/C9	180
Cellulose	52	3/C6	162
Hexosan	14	3/C6	162
Pentosan	8	2/C5	132

Based on this calculation, the total value of OH groups in Scots pine is approximately 14.8×10^{-3} mol g^{-1} of dry wood mass (Hill and Jones 1996, Hill 2006). If a crystalline cellulose content of 60% by mass is assumed, then the corresponding value for the accessible OH content becomes 9.2 mmol g^{-1}.

The actual number of available OH groups in wood is not known precisely. However, studies of wood exposed to deuterated or triatiated water can be used in order to estimate the accessible OH content and which give results that are comparable with the calculated values. Deuterium or tritium, can exchange with the labile hydrogen of the OH groups in wood, resulting in the ability to characterise OH accessibility. The exchange in mass is determined by measuring the increase in the dry weight of a sample after each cycle of adsorption and desorption is complete. Sumi *et al.* (1964) reported that tritium exchange with microtomed sections of white birch (*Betula papyrifera*) and black spruce (*Picea mariana*) yielded OH accessibility values of 6.9 and 8.0 mmol g^{-1}, respectively. Chow (1972) found that for deuterium exchange using never-dried microtomed sections of Douglas fir sapwood, roughly 45% of the total OH content of the wood was accessible in the latewood, but only about 24% in the earlywood at an EMC of 40%, with the accessibility declining in direct proportion with the cell wall MC. Taniguchi (1978) studied the sapwood of Japanese cypress wood and Japanese red pine wood and showed that the accessibility values of the OH groups to deuterium oxide were about 47% and 42% respectively. Phuong *et al*. (2007) has reported that the amount of accessible OH groups in *Styrax tonkinensis* wood was 6.8 mmol g^{-1} using hydrogen-deuterium exchange.

Using the H-H model, Hill *et al.* (2009) found that if it was assumed that each water molecule of the 'monolayer' (i.e. hydrated polymer water) was associated with a primary sorption site (OH group) then this yielded a value of 3 mmol g^{-1} for accessible OH content, which shows a large difference between the

OH groups calculated from the cell wall composition (9.2 mmol g^{-1}). This indicates that the assumption of one water molecule per primary sorption site is not correct and the value is closer to three cell wall OH groups per water molecule in the monolayer water (Papadopoulos and Hill 2003). Nakamura *et al.* (1981) in studies on bound water of cellulose by differential scanning calorimetry (DSC) found that the amount of water bound to each glucose unit was 3.4 moles. White and Eyring (1947) suggested the monolayer water is held to two primary sorption sites.

2.8 Hydrogen bonding and water sorption

It is understood that wood is hygroscopic primarily because of the hydroxyl or OH groups which exist throughout its structure, particularly in the cellulosic and hemicellulosic portions of the wood and which attract and hold water molecules by hydrogen bonding. Water molecules as polar molecules, have a weak, partial negative charge at one region of the molecule (the oxygen atom in water) and a partial positive charge associated with the hydrogen atoms in the water (Figure 2.13). The OH group in wood can be viewed as half a water molecule forming hydrogen bonds with water (Figure 2.14).

The bonding energy of a hydrogen bond is approximately one quarter of that of a primary chemical bond, but it is nevertheless very important in materials which contain water. In liquid water it is believed that groups of molecules are connected together into polymer-like aggregates which are loosely held together by hydrogen bonds. In ice, the arrangement is tetrahedral and three dimensional, with each molecule bonded to four others by hydrogen bonds. The bond energy of a hydrogen

bond is of the order 20 to 40 kJ mol^{-1} (Siau 1995, Mantanis *et al.* 1994, Palin and Petty 1983, Morrison and Dzieciuch 1959, McQueen-Mason and Cosgrove 1994, Markovitch and Agmon 2007).
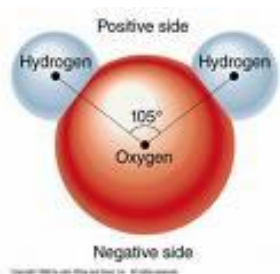

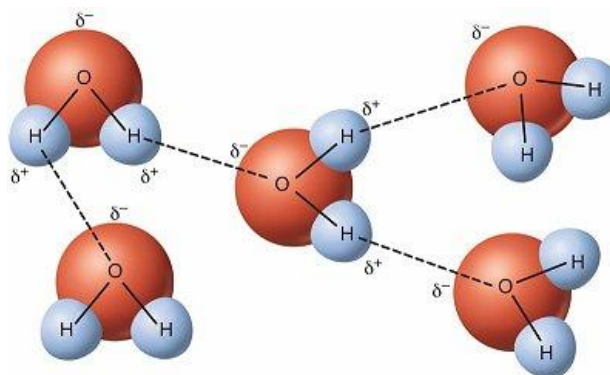**Figure 2.13 A water molecule.**

Figure 2.14 Hydrogen bonds (dotted lines) between water molecules.

Hydrogen bonding of water molecules to the OH groups in wood and of the OH groups to each other may occur in a manner similar to these bonds in ice or in liquid water. Cellulose is a major constituent in wood, in which each monomeric unit contains three OH groups and the chemical formula of the cellulose molecule is regularly given as $(C_6H_{10}O_5)_n$. A straightforward calculation can be made of the moisture content of cellulose when each of the OH groups is hydrogen-bonded to one molecule of water; that is, when the cellulose is fully hydrated. In this condition

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there are three water molecules per unit of ($C_6H_{10}O_5$), giving the hydrated formula of ($C_6H_{10}O_5$).$3H_2O$ (Skaar 1972). The moisture content of the hydrated cellulose based on its dry weight is one mole of dry cellulose weighs 162 grams, and three moles of water weighs (3 x 18 = 54) grams, giving a moisture content for fully hydrated cellulose of (100%)(54/162) = 33%. This is a calculation for monomeric water. This calculation obviously assumes that all of the cellulose is accessible. Because cellulose is only partially accessible to water and other chemical constituents in wood such as hemicelluloses and lignin, which may have different sorption properties, this 33% can be considered as the absolute maximum amount of monolayer water that can be held by the cell wall. OH groups if the crystalline regions of cellulose are mutually bonded to adjacent OH groups to form parallel chains and therefore are not available for bonding water. For the cellulose component only 40 to 50% of the OH groups are considered in the calculation as 50 to 60% of the groups are assumed to be in the crystalline region and thereby inaccessible (Skaar 1972, Siau 1984, Papadopoulos and Hill 2003, Fengel and Wegener 1984, Hill *et al.* 2010a).

2.9 Sorption hysteresis

Generally, two types of hysteresis can be observed with wood. When 'green' wood undergoes initial desorption, the isotherm does not coincide with the adsorption loop nor with subsequent desorption cycles. This phenomenon is called as an open hysteresis loop (Figure 2.15). Curve A indicates fully saturated wood that is desorbed to zero percent moisture content. However, it should be noted that

in practice, it is not possible to know for certain that all of the water is located in the cell wall. If the wood is initially dry and then exposed to successive increases in RH, curve B is obtained. In curve C, the wood starts to desorb at a point less than 100% RH and joins the boundary desorption curve after scanning across the region between the adsorption and desorption curves (scanning curve) and is called a closed hysteresis loop. Curves A and B, are called boundary curves.
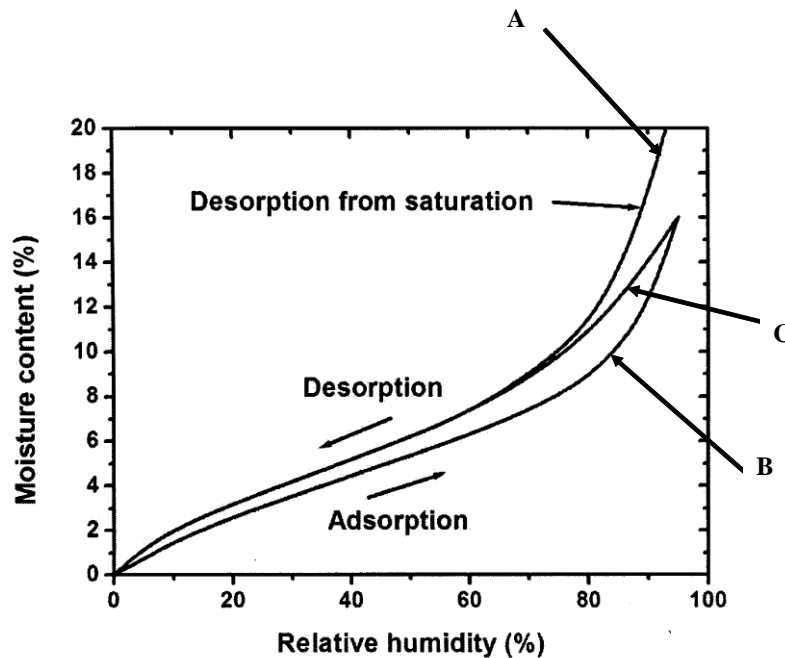

Figure 2.15 Illustration of typical behaviour exhibited by a lignocellulosic material when desorbing moisture from a fully water saturated state and when desorbing moisture from a non water-saturated cell wall moisture content.

Sorption hysteresis has been defined as the difference between the adsorption and desorption isotherms for the same sample under the same conditions (Skaar 1972, Skaar 1988, Siau 1994, Hill *et al.* 2009, 2010a, c). Hysteresis can be reported in two ways, either by subtraction of the adsorption from the desorption

EMC values, or by taking the hysteresis ratio of these two values. The hysteresis ratio (HR) is calculated as follows:

$$HR = \frac{MC_{desorption} - MC_{adsorption}}{MC_{adsorption}} \times 100 \qquad \textbf{(2.25)}$$

where $MC_{desorption}$ is the EMC during desorption process and $MC_{adsorption}$ is the EMC during the adsorption process at the same target RH. The sorption hysteresis using a subtraction method will give absolute values of MC and the hysteresis ratio will give normalised values that are expressed as a percentage of the $MC_{adsorption}$ measurement which provides a stable reference point (adsorption/boundary curve). This ratio is commonly used and is supposed to allow for comparison between samples with different sorption characteristics. The magnitude of hysteresis is affected by the difference between the adsorption and desorption isotherms, but is also dependent upon the sorption capacity. For example, with thermally modified wood there is a reduction in overall sorption. This also leads to a reduction in the absolute hysteresis. But the normalised value may be higher. This is because the hysteresis ratio is higher even though sorption is lower. Thus, different methods of calculation can yield different conclusions. The safest way of reporting hysteresis is to use both methods.
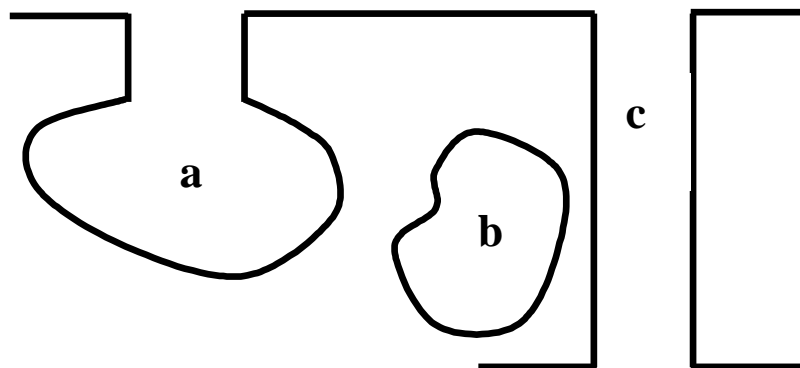
Figure 2.16 Pore types; a) open (ink-bottle) b) closed c) open (cylindrical).

It has been known that plant fibre and wood materials exhibit sorption hysteresis between adsorption and desorption loops of the isotherm for nearly a century (Zsigmondy 1911, Barkas 1941, 1949, Cassie 1945, White and Eyring 1947, Stamm 1952, 1964, Chen and Wangaard 1968). That the sorption behaviour of lignocellulosic materials could possibly be linked to the microporosity of the cell wall as has been proposed by several workers in the field (Barkas 1949, Stamm 1964). The sorption hysteresis properties of microporous materials have been reported in the literature with various explanations of the phenomenon. It is well known that microporous materials exhibit sorption hysteresis (Gregg and Singh 1982, Rouquerol *et al.* 1999) and various physical phenomena can be applied to explain this property. Several types of pores can exist in such a material, as shown in Figure 2.16. With 'ink-bottle' pores, the diameter of the interior of the pore is much larger than the throat and the filling of the pore is not dependent upon the pore diameter. However, during desorption the escape of sorbate molecules is

dependent upon the radius of the meniscus of the liquid at the throat of the pore. Desorption from pores of different diameter occurs at various partial pressures, as given by the Kelvin equation (Skaar 1972):

$$\ln p/p_o = -2\gamma MW/r\rho RT \tag{2.26}$$

where p is the actual vapour pressure, p_o is the saturated vapour pressure, γ is the surface tension of water at 25 ^oC (0.072 N m^{-1}), MW is the molecular weight of water (18 g mol^{-1}), r is the radius of the meniscus (m), ρ is density of water (g cm^{-3}), R is the universal gas constant (8.314 J K^{-1} mol^{-1}) and T is absolute temperature (K). Thus pores of larger diameter will empty at higher partial pressures and those of smaller diameter at lower partial pressures.

The model of Barrett Joyner and Halenda (BJH) (Barrett *et al.* 1951) also gives a description of hysteresis based upon the emptying of pores containing liquid as the partial pressure of sorbate in the surrounding atmosphere is reduced. Models of this type assume that the sorbate molecules form successive layers on the internal surface and eventually form a liquid within the pore (Figure 2.17). However, when pore diameters reach dimensions as small as 4 nm (commonly encountered within the wood cell wall) the concept of a bulk liquid becomes meaningless (Jakob *et al.* 1996, Hill and Papadopoulos 2004, Hill 2006). This property is well illustrated by the observation that with nitrogen sorption onto micro-porous solids there is a collapse of hysteresis occurring at a nitrogen partial pressure corresponding to a pore diameter of 4 nm (Figure 2.18) (Rigby and Fletcher 2004). Under the BJH

model, the sudden change in the desorption isotherm can be mistakenly interpreted as being due to a large population in pores of 4 nm in diameter (Barrett *et al.* 1951, Joyner *et al.* 1951.) whereas it is actually an artefact (Gregg and Singh 1982, Rouquerol *et al.* 1999).
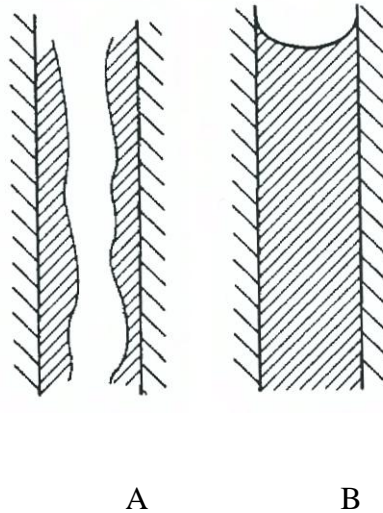

A   B

Figure 2.17 Schematic representation of adsorption in micropores. A monolayer is first formed on each cell wall (A) and then merges at higher relative humidity (B) to fill the micropores (Pierce and Smith 1950).
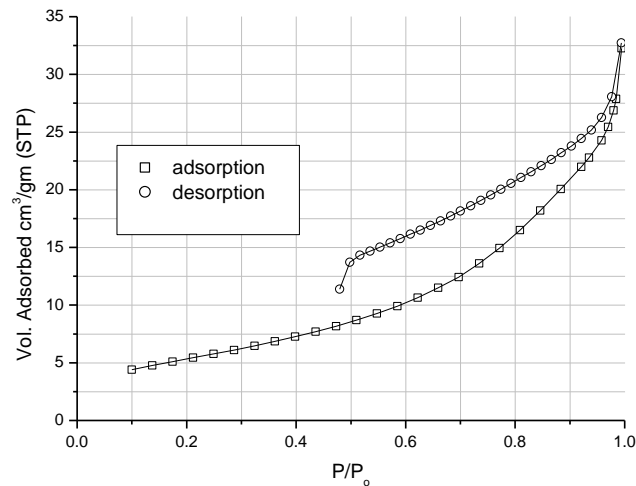

Figure 2.18 The observation of the hysteresis loop with the nitrogen sorption isotherm of critical point CO$_2$ dried cellulose. This shows the form of hysteresis typical of a rigid microporous structure.

Collapse in hysteresis occurring at this point is clearly not observed with hysteresis occurring with plant materials. However, whilst microporosity of this type undoubtedly can be observed with inert porous materials, it is not a good model for the plant cell wall, where an evolving microporosity occurs as the substrate swells and shrinks in response to changes in relative humidity. There is also a strong interaction between the polar molecules of water (cohesive forces) and between the water molecules and the substrate (adhesive forces). Nitrogen is non-polar and such strong interactions do not exist.

In early work with plant based materials, it was thought that hysteresis occurred because of a failure to establish 'true equilibrium' and that if the sample was exposed for a sufficiently long time period the hysteresis would disappear (Stamm 1964). However, it has been conclusively demonstrated that hysteresis is a real phenomenon and is observed even when samples are allowed to equilibrate over a considerable time period (months to years).

The phenomenon has also been postulated as being due to the irreversible formation of hydrogen bonding occurring during the initial drying process (curve A of Figure 2.15) and that subsequent re-wetting of the sample fails to reopen a proportion of this hydrogen bonding network. This is known as hornification and is well established in pulp samples, particularly where there is a hemicellulosic component present (Stamm 1971). However, hornification does not appear to be particularly significant with lignified materials. For example, the open hysteresis behaviour has been observed again when dry wood is re-saturated and run through a subsequent desorption cycle (Chen and Wangaard 1968).

In a paper by Stamm and Loughborough (1935) it was assumed that the hysteresis phenomenon was due to irreversible hydrogen bond formation and that if this process was prevented no hysteresis would occur and the isotherm would exhibit true reversibility. The argument then followed that with a reversible isotherm it would be possible to apply thermodynamic analyses. In order to obtain the 'true' isotherm, large wood samples were employed that in fact never achieved equilibrium with the environment. The data from this study has been used in the Wood Handbook no. 72 "Wood as an engineering material" (USDA 1974) published by the United States Department of Agriculture (USDA) and the data continues to be used to this day, but in reality it is not a real isotherm (Hill *et al.* 2009). Stamm and Loughborough (1935) clearly showed the 'oscillating vapour pressure desorption' curve falling between the adsorption and desorption curves as is reproduced in Figure 2.19.
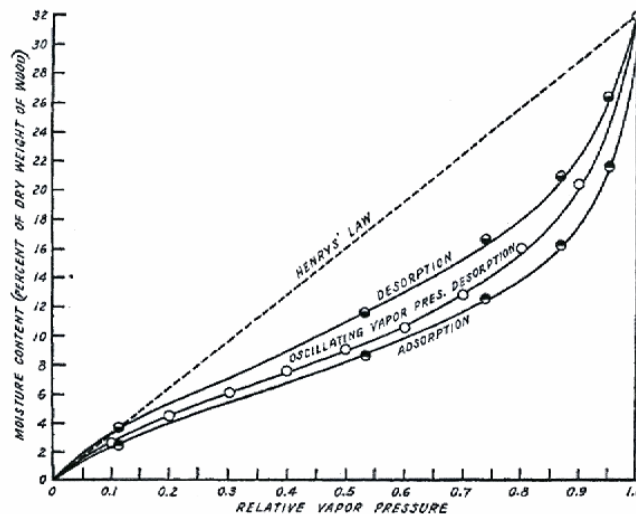

Figure 2.19 Original graph reproduced from Stamm and Loughborough (1935) showing the 'oscillating vapour pressure desorption isotherm'.

Chen and Wangaard (1968) suggested that the differences between advancing and receding contact angles of water against the microcapillary wall produced conditions of higher wettability under desorption compared with adsorption conditions. They considered that in the desorption process, the water contact to the internal micropore surface of the cell wall is with an already fully wet surface but in adsorption, the water contact is with a non-wetted surface. However, wetting is a colligative phenomenon occurring in a liquid state. Sorption does not involve liquids in the classical sense and yet hysteresis still occurs. The concept of contact angle when explaining the sorption processes inside the internal surface is thus essentially meaningless and furthermore in this study only approximate actual contact angles can be assumed in the capillary condensation region of the cell wall, whilst hysteresis occurs throughout the sorption range. Much confusion exists in the literature regarding hydrophobicity (a wetting effect at the surface) and sorption phenomena which are related to the OH accessibility and cell wall elasticity.

It has been argued that the hysteresis phenomenon was an artefact caused by the presence of permanent gases in the substrate. Hamm and Patrick (1936) reported that with scrupulous degassing of the material (purified cotton cellulose) there is no hysteresis. However, Spalt (1957) (among many others) studied vapour sorption isotherms in a vacuum which still clearly showed the existence of hysteresis. Therefore the contention that hysteresis is an artefact is not correct. Stamm (1964) also argued that hysteresis caused by the presence of permanent gases was only applicable in non-swelling samples and not for a gel-like system such as wood or other lignocellulosic materials. Permanent gases are supposed to mask sorption

sites, but this is not likely to have any significance in a substrate where the micropores expand and collapse, thereby creating new sorption sites.

A number of workers have considered that hysteresis was related to the effect of mechanical restraint acting as the cell wall swelled in the presence of water. Cassie (1945) made an analysis of this property with respect to wool fibre. It was stated that the isotherm could only be properly analyzed when the above effect had been taken account of. When an analysis was completed for adsorption with wool, it was found that the classic sigmoidal shape of the isotherm was no longer observed (Cassie 1945).

Everett and Whitton (1952), Everett and Smith (1954), Everett (1954), Everett (1955) and Enderby (1955) constructed a model to explain sorption hysteresis based on the 'independent domain theory' with scanning curves running through the space delineated by the boundary adsorption and desorption curves. This theory has been applied to wood by Peralta (1995a, b, 1996) and Peralta and Bangi (1998), which revealed that the shape and area bounded by the hysteresis loop is determined by the path of the adsorption and desorption boundary curves and also depends upon the minimum and maximum RH obtained in the isotherm, which determines the onset of the scanning curves (Figure 2.20). However, such a model fails to explain the fundamental reason for hysteresis. It requires a material that has bistable states, but does not go any further in explaining how such behaviour may arise. Independent domain theory is a universal description covering all hysteresis phenomena not just sorption. It has been stated that in swelling gels the amount of hysteresis can be correlated with the elastic properties of material

(Cassie 1945, Barkas 1949). Tarkow (1979) noted that restraining wood from swelling reduces moisture adsorption, at least up until the point where plastic flow of the wood occurs. It is clear that this type of behaviour has to be included in any explanation of hysteresis.
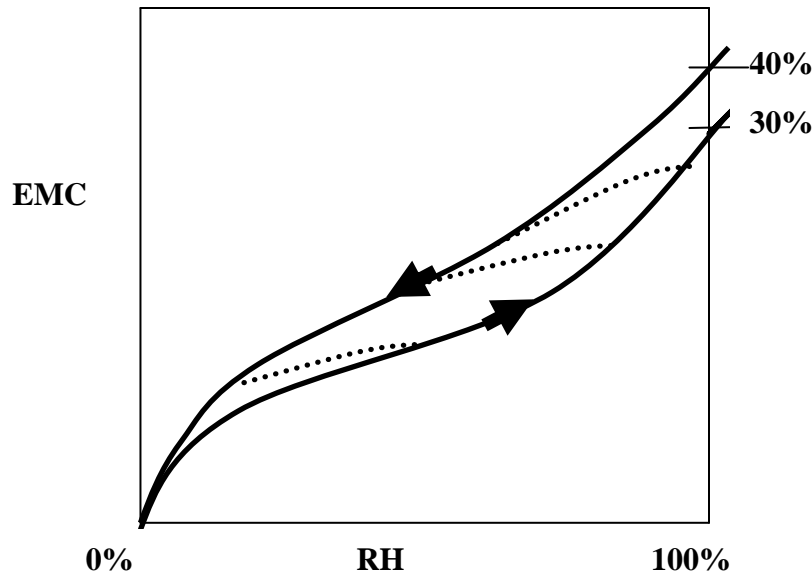

Figure 2.20 The difference between the boundary curves of adsorption and desorption explain why FSP is different with the saturation compared with the projection methods (dotted lines are the scanning curves).

In recent studies of isotherms of various pollutants in humic soil by Lu and Pignatello (2002, 2004) considered the importance of matrix stiffness in glassy solids and applied the 'dual mode' model of Vrentas and Vrentas (1996) to explain sorption hysteresis. This 'dual mode' model has also been applied to cellulosic and lignocellulosic materials (Hill *et al.* 2009, 2010a, b, c). Based on this model the response of a glassy solid to the ingress or egress of sorbate molecules under

adsorption and desorption below the glass transition temperature (Tg) is considered. The Tg is the temperature below which the physical properties of amorphous materials are similar to those of a solid (glassy state), and above which amorphous materials have characteristics of a rubbery state. The glassy solid state is specified as a material possessing molecular-scale micropores embedded in a matrix which is unable to fully relax to a thermodynamic equilibrium state due to the stiffness of the matrix macromolecules. The glassy solid state is favoured by matrix crosslinking that reduces the flexibility of the macromolecules; this being a characteristic of humic substances in soils and lignin in the wood cell wall. The structure of all plant fibres is one of crystalline microfibrils embedded within the amorphous matrix. Adsorption of water vapour into the fibre cell wall results in the creation of micropores between the microfibrils and within the matrix substances.

Lu and Pignatello (2002, 2004) noted that the process of adsorption in glassy solids results in a time lag in the creation new internal surface or micropores in response to the incoming sorbate molecules. Below the Tg the response of the micropores to the dynamic sorbate molecules is not instantaneous on the time scale of molecular diffusion. During the desorption process, there is a response lag in collapse of the micropores in the intermicrofibrillar matrix as water molecules exit. As a result, adsorption and desorption therefore take place in different physical environments, giving rise to the property of hysteresis (Figure 2.21). This lack of elasticity in the response of the substrate leads to irreversibility.
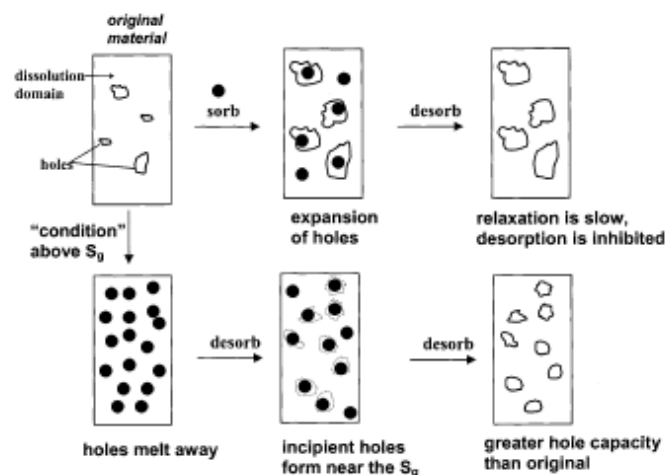
Figure 2.21 Conceptual diagram of the proposed mechanisms of isotherm nonsingularity and conditioning effect in natural organic matter based on glassy polymer theory. The glassy material initially contains holes interspersed in a solid-phase dissolution domain (Lu and Pignatello 2002).

All the explanation above relates to a glassy material that is below the glass transition temperature (Tg). In humic soils, the magnitude of hysteresis is greater where the cross-linking density of the matrix has been increased due to the addition of aluminium ions (Lu and Pignatello 2004). Hill *et al.* (2009) has argued that the presence of an amorphous cross-linked glassy polymer such as lignin in the cell wall matrix would also be expected to result in an increase in the area bounded by the hysteresis loop and this has been shown experimentally. Adsorption of water is known to decrease the glass transition temperature of cellulose (Paes *et al.* 2010, Salmén and Back 1977), starch (Chang *et al.* 2000) and lignin (Salmén 1984). Chang *et al.* (2000) report that the Tg of starch derived from tapioca shows a reducing Tg as the moisture content increases, ranging from 175 ^{o}C at 5% MC, to 70 ^{o}C at 15% and dropping to 30 ^{o}C at 27% MC. Studies on starch (pistachio)

sorption isotherms showed that hysteresis is larger at the lower end of the hygroscopic range (Figure 2.22) (Tavakolipour and Kalbasi-Ashtari 2008). This is a universal feature of starch sorption isotherms. This behaviour is consistent with the dual mode model.
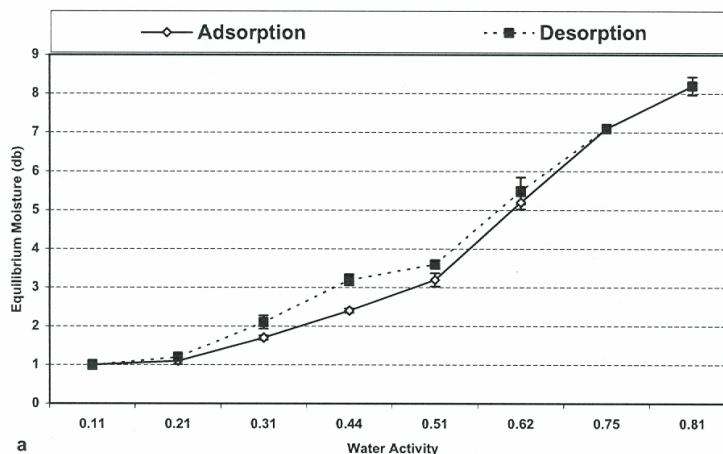

Figure 2.22 Effects of water activity on equilibrium moisture content and hysteresis of pistachio powder at 15 ^{o}C (Tavakolipour and Kalbasi-Ashtari 2008).

As the isotherm temperature increases and the *Tg* is approached, the size of the hysteresis loop decreases and becomes zero at the *Tg*. If the material is above the *Tg*, it will turn to a rubbery state and having greater molecular flexibility it has an ability to respond to the incoming/outgoing water essentially instantaneously. The glass transition temperature of lignin in the presence of moisture is in the region of 60 to 90 ^{o}C and linear projections of the decrease in hysteresis loops reached zero in this temperature range for Sitka spruce (Figure 2.23) (Hill *et al*. 2010a).
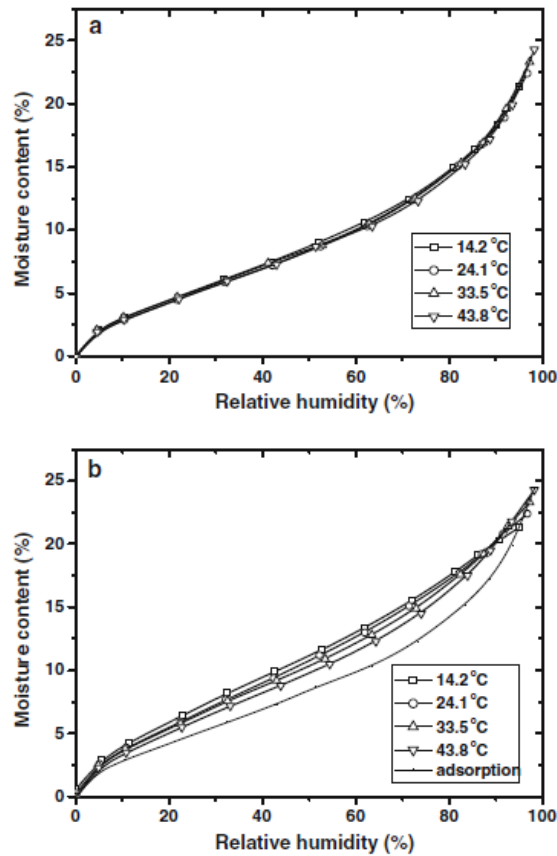
Figure 2.23 Experimental isotherms for adsorption (a) and desorption (b); the desorption curves are compared with a generic adsorption curve (Hill *et al.* 2010a).

Weichert (1963) reported a reduction in sorption hysteresis with increasing wood temperature for European Spruce. According to Kelsey (1957), sorption hysteresis decreases between 25 °C and 55 °C for *Araucaria klinkii* of Australia which agrees with the Weichert (1963) study (Figure 2.24). White and Eyring (1947) also noted that the hysteresis in cotton decreases with an increase in temperature. In food science, Yan *et al.* (2008) in a study on banana showed that the sorption hysteresis is affected by the temperature which the magnitude of hysteresis

was smaller in 40 ^{o}C than at 10 ^{o}C, which was attributed to the increased in elasticity of micro-capillary walls.
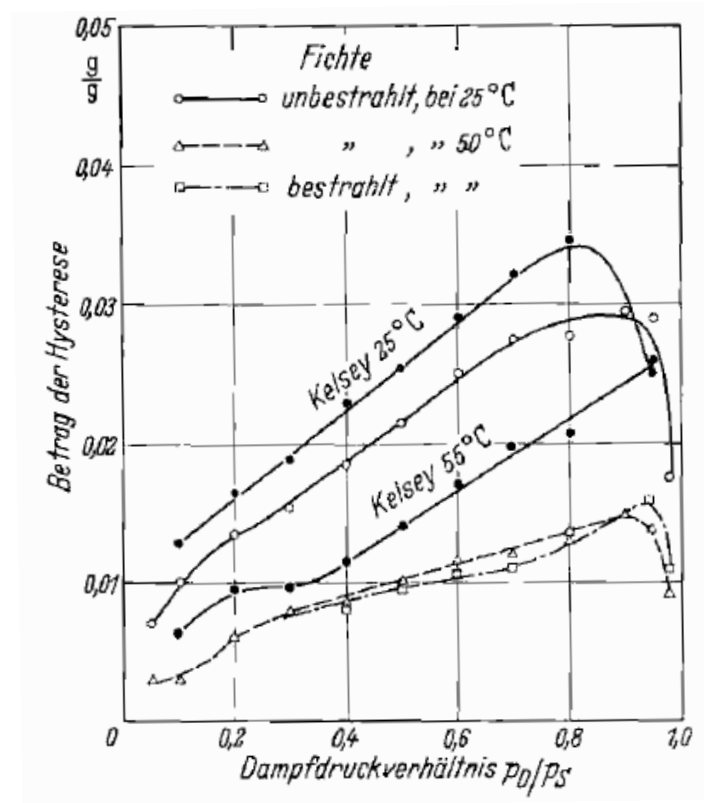

Figure 2.24 Sorption hysteresis ratio for European Spruce at different temperatures (Weichert 1963).

2.10 The parallel exponential kinetics (PEK) model

Most studies on the sorption isotherms of wood were usually performed until recently using saturated salt solutions. Generally with this kind of method it takes a very long time to reach equilibrium and manually weighing is susceptible to incorrect/inaccurate reading. Furthermore with this method only a few RH values can be tested based on the available types of the inorganic salt. Nowadays, an

increasing number of studies are applying DVS methods, which can provide a wealth of data relating the rate of change of the sample mass over time as the sample adsorbs or desorbs moisture as it approaches equilibrium. The DVS technique can provide very accurate isotherms over a wide RH range and at different temperatures. When the RH is changed, the wood cell wall responds to this by establishing a new equilibrium MC value, but this takes a finite time to achieve. The ability to gather 'real time' data using DVS allows for the accurate analysis of the sorption kinetics behaviour of wood.

The wood science literature abounds with studies on sorption isotherms (e.g. Venkateswaran 1970, Simpson 1980, Skaar 1972, Siau 1984, Skaar 1984, Siau 1995) and there have also been many reports on the sorption kinetic behaviour of wood, although the practical determination of accurate kinetics has required skilled experimental work. These have invariably been confined to macroscopic wood specimens, where Fickian diffusion models are invoked as a sorption kinetics analysis (e.g. Droin *et al.* 1988, Wadsö 1994a, b, Houška and Koc 2000, Time 2002, Krabbenhoft and Damkilde 2004, Shi 2007, Neimsuwan *et al*. 2008, Salin 2010).

In steady-state diffusion, concentration is assumed to be constant with time and as a result, the flux is constant. The actual mathematical relation is known as Ficks's first law of diffusion and its one dimensional representation reads:

$$J = -D\ \partial c/\partial x \quad (\text{mol m}^{-2}\text{s}^{-1}) \tag{2.27}$$

where J [mol m^{-2}s^{-1}] is the flux, D [m^{-2}s^{-1}] is the coefficient of diffusion, c [mol L^{-1} or mol m^{-3}] is the concentration of molecules and x [mm or m] is the thickness in the direction of diffusion or mass flow. In unsteady-state diffusion where the boundary conditions in terms of concentration and flux are continuously changing, the process of diffusion is more complicated. It is expressed in terms of rate of change of concentration and takes up the form of Fick's second law of diffusion that reads

$$\partial c/\partial t = D.\partial^2 c/\partial x^2 \text{ (mol m}^{-3}\text{s}^{-1}) \qquad\qquad (\textbf{2.28})$$

where t [s] is time. Equation (2.28) can be solved by setting corresponding boundary conditions for the transport problem. The diffusion coefficient D varies with changes of concentration and temperature (Robertsen and Lönnberg 1991, Siau 1995).

Fick's law, given by equations 2.27 and 2.28, falls short in describing the process of diffusion in viscoelastic, semi-crystalline and amorphous polymers and hence is not always obeyed (Kalospiros *et al.* 1991, Wadsö 1992, Roy *et al.* 2000). In Fickian diffusion, the sorption rate has a comparatively very small relaxation effect on the polymer matrix, hence equilibrium is achieved rapidly and boundary conditions are independent of time. However, when viscoelastic phenomena are significant, the rate of sorption is affected by swelling kinetics (relaxation of the polymer matrix). In this case, the overall diffusion process deviates very much from Fick's law resulting in a phenomenon commonly known as non-Fickian. Non-

Fickian diffusion (curve 2 of Figure 1.40 with sigmoid curve and curve 3 of Figure 2.25 with non linear relationship) can be distinguished from the Fickian (curve 1 of Figure 2.25 with linear relationship for 50% or more of the total change) by the shape of the sorption half time curves and relative rates of adsorption and desorption (Kelly and Hart 1972).
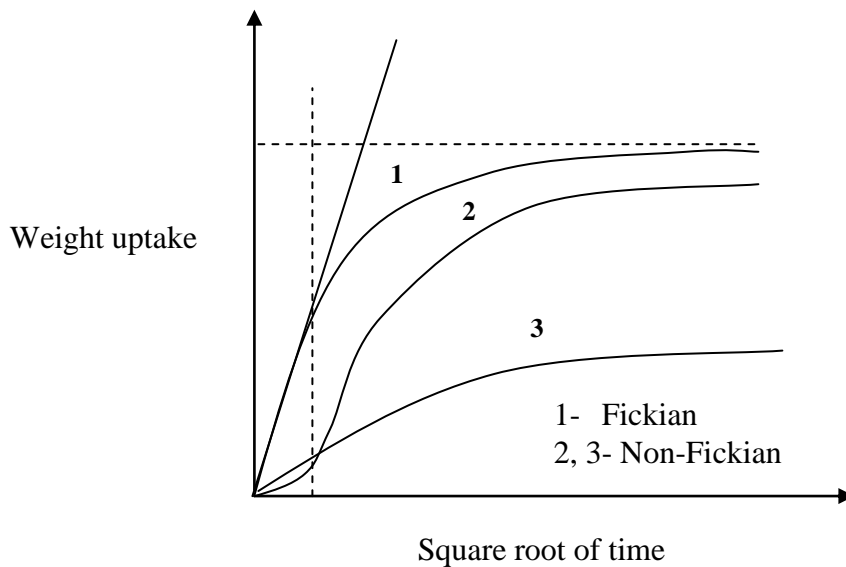

Figure 2.25 Dependence of water vapour weight uptake on the square root of time for Fickian and non-Fickian diffusion.

Whilst Fickian-derived models may be valid when considering large wood specimens, these are not applicable when considering small sample sizes (Wadsö 1994a, 1994b). It has been demonstrated that non-Fickian diffusion is observed when the water vapour sorption kinetics of thin wood and cellulosic samples is examined and that the sorption kinetics is related to the swelling of the substrate (Christensen and Kelsey 1959, Christensen 1965). Christensen and Kelsey (1959)

also noted that the occurrence of stress relaxation of the structure of wood resulted in non-Fickian behaviour. Using thin samples of wood of variable length (one-dimensional samples with half lengths of 6.7 mm to 11.4 mm), Krabbenhoft and Damkilde (2004) were able to show the non-Fickian nature of the sorption process (Figure 2.26). If Fickian behaviour occurs the two graphs should be superimposed. Krabbenhoft and Damkilde (2004) also considered that the swelling effect was affecting the sorption kinetics and developed a model based upon the premise that the sorption process was limited by the rate of swelling of the substrate. Recently, the non-Fickian behaviour of water vapour sorption kinetics has also been reported in thermally modified wood (Pfriem *et al.* 2010).
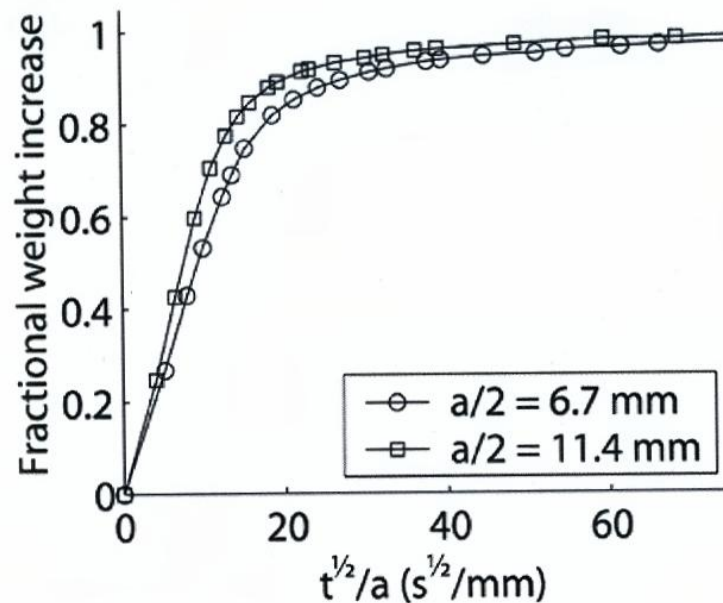

Figure 2.26 Failure of the Fickian model demonstrated by length dependence of data (Krabbenhoft and Damkilde 2004).

It is well established that the diffusion behaviour of swelling polymers cannot be described by Fickian models, particularly in the case of glassy polymers below

the T_g (Crank 1998). Three models or types of behaviour can potentially be observed to describe transport phenomena in glassy polymers (Alfrey *et al.* 1966):

Case I − Classical Fickian diffusion, where the rate of diffusion is lower than the rate of relaxation of the polymer. The mechanism is controlled by diffusion. According to Masaro and Zhu (1999), Case I is often observed in the polymer networks when the temperature is well above the glass transition temperature (*Tg*) when the polymer is in a rubbery state.

Case II − Relaxation-limited diffusion, where the rate of diffusion is very fast compared to the relaxation rate. The mechanism is controlled by relaxation.

Case III − Anomalous or non-Fickian diffusion, which is observed when the rates of relaxation and diffusion are comparable.

Among the models, Case II is considered to be applicable to wood where the experimental sorption data fits the parallel exponential kinetics (PEK) model; in this situation the sorption kinetics is also determined by the swelling rate of the wood matrix (Krabbenhoft and Damkilde 2004). It is known that the swelling behaviour of cereal grains obeys a PEK model (Tang *et al.* 2008) suggesting that the sorption kinetics is rate limited by the ability of the cell wall matrix to deform in response to the ingress or egress of water molecules. The PEK model has been found to give exceptionally good fits under adsorption and desorption conditions in natural fibres, regenerated cellulose fibres, microcrystalline cellulose, and some foodstuffs (Okubayashi *et al*. 2005a, b, Okubayashi *et al*. 2004, Kachrimanis *et al*. 2006, Kohler *et al*. 2003, Tang *et al*. 2008). In the first such study, Kohler *et al*. (2003) found that the parallel exponential kinetics (PEK) model produced an excellent fit

to the experimental sorption data for flax fibres. Such an analysis reveals the existence of two distinct mechanisms for the exchange of water vapour that were thought to relate to different sorption sites. The applicability of the PEK model has been recently confirmed for flax fibres by Hill *et al*. (2010b). The PEK equation is a double exponential of the form:

$$MC = MC_o + MC_1[1 - \exp(-t/t_1)] + MC_2[1\text{-}\exp(-t/t_2)] \tag{2.29}$$

where *MC* (%) is the moisture content at time *t* (min) of exposure of the sample at a constant RH, and MC_o (%) is the moisture content of the sample at time zero. The sorption kinetics curve is composed of two exponential terms, which represent a fast and slow process having characteristic times of t_1 and t_2, respectively, with associated moisture contents at infinite time of exposure MC_1 (%) and MC_2 (%). However, even though it has been established that the PEK model is applicable, there is as yet no consensus as to what the two processes represent.

There are very few studies of the sorption kinetics of water vapour with wood at a cell wall level (i.e. in specimens approximating to a single cell). In this latter case, it has been clearly demonstrated that the water vapour sorption kinetics of wood flour is accurately determined using the PEK model (Hill *et al.* 2010a, c). It is known (Harding *et al.* 1998) that water sorption onto charcoal is accurately modelled by a single exponential process only. Thus one hypothesis that can be advanced is that the double exponential process is related to the swelling/shrinking

of the substrate under conditions of adsorption and desorption, respectively. This hypothesis will be examined in some detail in this thesis.

2.11 The rheological model of the wood cell wall

Wood, like polymeric materials, shows viscoelastic behaviour. Wood under a static load exhibits three types of deformation behaviour; elasticity, delayed elasticity (reversible creep) and plasticity (irreversible creep) (Figure 2.27) (Dinwoodie 2000). This type of behaviour can be modelled by considering a mixture of Maxwellian and Kelvin-Voigt viscoelastic elements (Figure 2.28). This involves interpretation using a combination of springs (stiffness, E) and dashpots (viscosity, η); the springs act as a mechanical analoque of the elastic component of deformation, while the dashpots simulate the viscous or flow component. Energy involved in extending the spring is recoverable that lost in the dashpot is dissipated as heat.
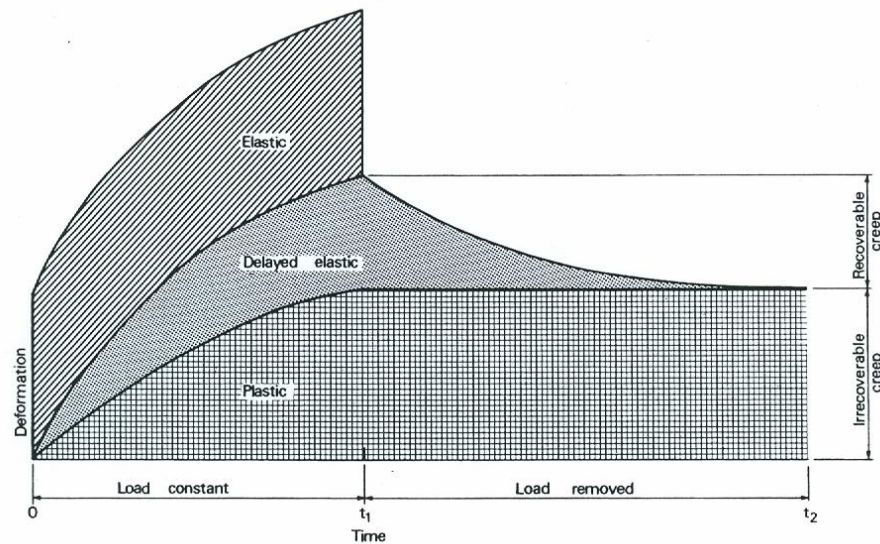

Figure 2.27 The various elastic, delayed elastic and plastic components of the deformation of wood under constant load (Dinwoodie 2000).

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The viscosity behaviour of wood results from the intricate combination of each of three main polymers, i.e. cellulose (partly crystalline), hemicellulose (amorphous) and lignin (amorphous) components response. Placet (2008) reported that the viscoelastic properties are strongly affected by moisture content and temperature. According to Placet (2008) heat allows inter-molecular linking to be broken, allows for molecular mobility and therefore provides more flexibility to the macromolecular network. Barkas (1945) reported that when timber was stressed in tension it gained in moisture content, and conversely when stressed in compression its moisture content was lowered. It is argued, though certainly not proved, that the movement of moisture by diffusion occurs in a series of steps from one adsorption site to the next, necessitating the rupture and subsequent reformation of hydrogen bonds (Hill *et al.* 2010b, c). The process is viewed as resulting in loss of stiffness and/or strength, possibly through slippage at the molecular level. This process becomes less important as the cell wall MC increases.
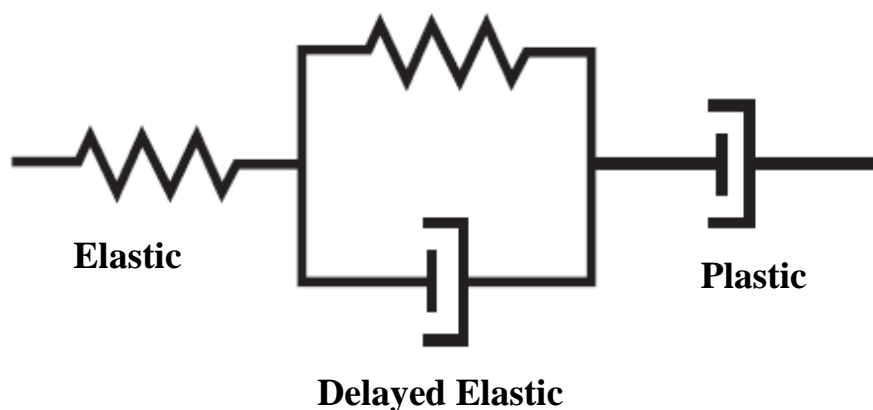

Figure 2.28 The various elastic, delayed elastic and plastic components of the deformation of wood under constant load described using springs and dashpots.

2.12 Activation energy

The sorption of water vapour can be considered to be an activated process. In Figure 2.29 a 'Zipper' model can be used to explain the transport of water molecules into the wood cell wall (Hill *et al.* 2004). In this model, the cell wall micropores are 'sealed shut' by the hydrogen-bonding networks between the walls of the micropores. In order that the water molecules may penetrate the cell wall it requires the breaking of hydrogen bonds in an activated process.
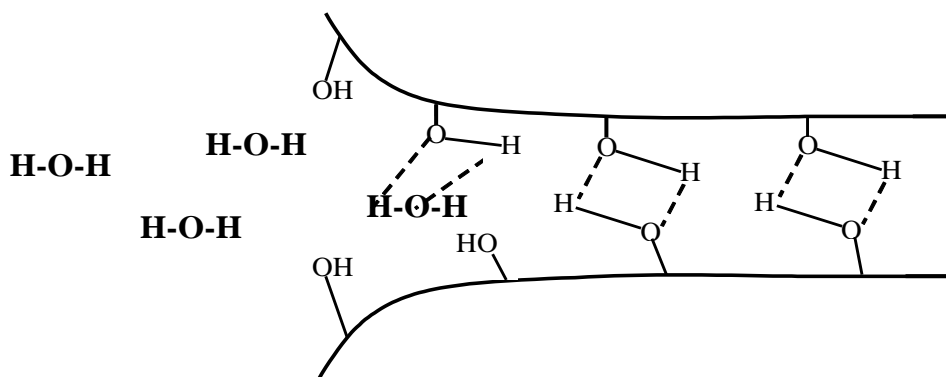

Figure 2.29 Schematic illustrating Hydrogen bonds breaking from the wood cell wall micropores.

Generally the activation energy or the energy of reaction activation (*Ea*) has been defined as the energy that needs to be supplied to molecules to interact (Bala 1997). In order for the molecules of water to chemically react they need to collide with each other, but only those molecules that have a higher energy level than the activation energy can interact. In chemical kinetics the activation energy is the size of the potential barrier that separates the product from the reactants. Molecules can react if their kinetic energy exceeds the activation energy. Therefore if the kinetic energy of water molecules in wood is not high enough, it can at the point collision

turn into potential energy but it will not create an activated complex. If the system of water molecules in wood is supplied with energy, i.e. through heating (by a temperature increase), with the same number of water molecules, but with greater translational energy and with a greater proportion of collisions between reactants result in reaction.

Over the years, many studies on the Ea of wood sorption were interpreted using a diffusion model (Hunter 1992, Siau 1995, Choong 1963, Stamm 1964), which found a linear relationship between the logarithm of the diffusion coefficient and the reciprocal of the absolute temperature in accordance with Arrhenius equation.

$$D_T = D_o \exp (-Ea/RT) \tag{2.30}$$

Where D_T is the transverse diffusion coefficient of bound water in wood, m_w^2/s, where the subscript w indicates a concentration basis of moisture in wood; D_o is a constant; Ea is activation energy (kJ/mol).

However, it was demonstrated that the water vapour sorption kinetics with small samples is not diffusion limited (Wadsö 1994a, b, Krabbenhoft and Damkilde 2004). Mantanis et $al.$ (1994) reported in the swelling kinetics of wood in water values for Ea of Sitka spruce and Scots pine as 32 kJ mol^{-1} and 48 kJ mol^{-1} respectively. In water vapour sorption isotherms, recently, Hill et $al.$ (2010b, c) used the PEK model examined at different temperatures enabling the determination of Ea for the sorption kinetics processes on Sitka spruce (*Picea sitchensis*)

throughout the hygroscopic range (from 5% to 95% RH). Hill *et al*. (2010b, c) found that the *Ea* for the adsorption and desorption processes was of the range of 20-40 kJ mol^{-1} at lower RH values and that the *Ea* decreased at higher RH values. This was interpreted as indicating that H-bond breaking or formation is the rate determining step at low MC.

In water vapour sorption isotherms and by using the PEK model, the sorption kinetics can be deconvoluted into two first order kinetic processes (Equation 2.29), with the reciprocals of the characteristic times of the fast and slow processes giving the corresponding rate constants for those processes ($k_1 = 1/t_1$, $k_2 = 1/t_2$). It is then possible to determine the activation energies associated with the rate determining step of these sorption processes by using the Arrhenius relationship:

$$k = A.\exp(-Ea/RT) \qquad\qquad \textbf{(2.31)}$$

where k is the rate constant, A the collision factor, *Ea* the activation energy, R the universal gas constant and T the absolute temperature. By taking natural logarithms of both sides, the equation becomes:

$$\ln(k) = \ln(A) - Ea/RT \qquad\qquad \textbf{(2.32)}$$

Thus, a plot of ln (k) versus the reciprocal absolute temperature will yield a straight line of gradient $-Ea/R$, if the Arrhenius relationship obeyed. Multiplying the gradient of the slope by the gas constant (R) (8.314 J K^{-1}mol^{-1}) yields the activation energy. At this time (besides the study of Hill *et al.* 2010c in Figure 2.30) there has

been no attempt to determine the activation energies corresponding to sorption kinetics with fast and slow kinetic processes in adsorption and desorption isotherms of wood and only one other such study on flax (Hill *et al.* 2010b). Through this study it may provide further insights of the physical phenomenon of the fast and slow kinetics processes and perhaps hysteresis.
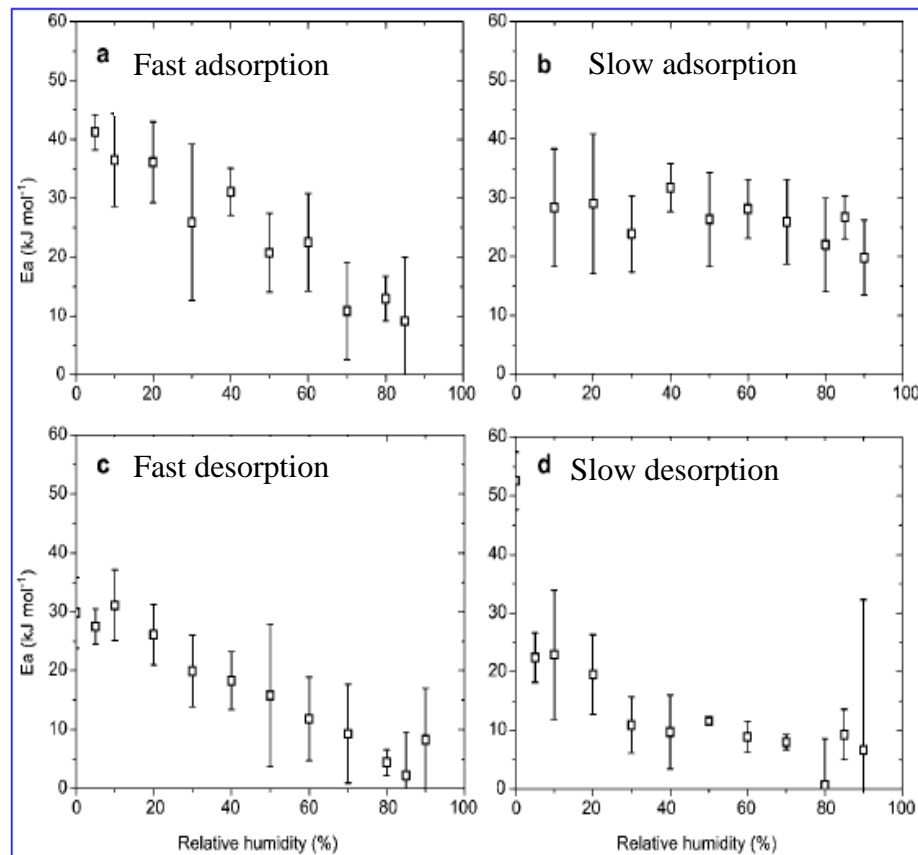

Figure 2.30 Activation energies for the fast adsorption (a), slow adsorption (b), fast desorption (c) and slow desorption (d) kinetics processes for Sitka spruce at different relative humidities (Hill *et al.* 2010c).

2.13 Water vapour sorption of thermally modified wood

Wood modification has been widely used to improve the dimensional stability and fungal resistance of the material. Chemical modification is one of the approaches used to change the moisture sorption properties of wood primarily through the covalent bonding of chemicals to the hydroxyl groups of the cell wall polymers, or by depositing sterically fixed compounds, mainly of high molecular weight, in the cell wall micropores (Hill 2006).

Chemical modification of wood with acetic anhydride (and other linear chain anhydrides) results in changes to the physical and biological properties of the material. These include, dimensional stability (Stamm and Tarkow 1947, Hill and Jones 1996, Li *et al*. 2000), decay resistance (Papadopoulos and Hill 2002, Hill *et al*. 2005), and hygroscopicity reduction (Papadopoulos and Hill 2003, Papadopoulos *et al.* 2005, Hill 2006, Xie *et al*. 2011). Popper and Bariska (1972) reported H-H polylayer and monolayer isotherm data for acetylated fir. Yasuda *et al*. (1995) studied a range of modified woods and Chauhan *et al*. (2001) investigated esterified rubberwood sorption behaviour using the H-H model. Papadopoulos and Hill (2003) investigated the sorption properties of Corsican pine (*Pinus nigra*) modified with a range of anhydride reagents by the same approach. They have shown that in wood modified with anhydrides, the reduction of equilibrium moisture content is due to bulking of the cell wall and that OH substitution plays no role. The modification of wood with 1,3-dimetylol-4,5-dihydroxyethyleneurea (DMDHEU) affects both the pore size and the hygroscopicity (ability to absorb water) or the MC of wood (Dieste *et al.* 2008,

2009). DMDHEU probably does not reduce the number of OH groups but fills the micropores of the cell wall, producing a permanent enlargement of the cell wall (bulking), which reduces the accessibility of water molecules to adsorption sites.

Other than chemical modification, thermal modification can be used to improve dimensional stability, increase biological durability, reduce hygroscopicity and control colour changes (Kamdem *et al.* 2002, Hill 2006, Akyildiz and Ates 2008, Gonzales-Peña and Hale 2009). A few different types of thermal modification have been commercialised in Europe; Thermowood using heat/steam in Finland (Syrjanen & Kangas, 2000), the Retification process using nitrogen in France (Dirol and Guyonet 1993), oil-heat treatment in Germany (Sailer *et al.* 2000), and the Plato process in the Netherlands (Boonstra *et al.* 2007). It is very well known that heating of wood at elevated temperatures causes a reduction in its hygroscopicity. Thermal modification of the wood is invariably performed between the temperatures of 180 ^{o}C and 260 ^{o}C, with temperatures lower than 140 ^{o}C resulting in only slight changes in material properties and higher temperatures resulting in unacceptable degradation to the substrate (Hill 2006). Generally, when wood is exposed to elevated temperatures at 180 ^{o}C or higher, chemical changes in hemicelluloses and lignin occur, resulting in reduced hygroscopicity (Hill 2006). Theoretically, the available OH groups in hemicelluloses have the most significant effect on the mechano-sorptive properties of wood and this component is also the most thermally labile. Hygroscopicity reduction has been related to chemical changes, either the reduction of the OH groups in the three polymers via the decomposition of hygroscopic constituents (mostly hemicelluloses) and the

probable cross-linking of the lignin (maybe with some contribution from degraded hemicelluloses). There has been no report on the water vapour sorption kinetics behaviour of thermally modified wood.