CHAPTER 7

DETERMINATION OF THE ACTIVATION ENERGY, ENTROPY AND GIBBS FREE ENERGY OF THE SORPTION PROCESS

7.1 Introduction

This chapter reports on the PEK parameters for sorption that were further interpreted in terms of the activation energies, the entropies of activation and the Gibbs free energies of activation. The established Arrhenius relationship was used to determine the activation energy and the activation entropy on two hardwoods (*A. mangium* and *E. malaccense*). The Gibbs free energy of activation for the sorption process was determined using standard relationships. The interpretation of these data invokes a model describing the polymeric relaxation processes taking place within the wood cell wall matrix during water vapour sorption process. The possible link between sorption kinetics, polymeric relaxation processes and sorption hysteresis is further discussed. The data for this study is identical with that used in Chapter 6 (five isotherm temperatures).

7.2 Background in analysing sorption kinetics data with Ea, ΔSa and ΔGa

The sorption kinetics were deconvoluted into two first-order kinetic processes (PEK model) with the reciprocals of the characteristic times (fast and slow processes) giving the rate constants ($k_1 = 1/t_1$, $k_2 = 1/t_2$). The rate constants for the two processes at different temperatures can then be used to determine activation energies for this sorption process by using the Arrhenius relationship:

$$k = \mathrm{A}.\exp(-Ea/\mathrm{RT}) \qquad \textbf{(7.1)}$$

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:

$$\ln (k) = \ln (A) - Ea/RT \quad \textbf{(7.2)}$$

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 R (8.314 J $K^{-1}mol^{-1}$) yields the activation energy.

The intercept ln (A) at infinite temperature ($1/T = 0$) is related to the activation entropy (ΔSa) by the following relationship (Glasstone and Lewis 1960, Hill and Papadopoulos 2002):

$$A = (eRT/nh).\exp(\Delta Sa/R) \quad \textbf{(7.3)}$$

Where n is Avagadro's number (6.02 x 10^{23} mol^{-1}), h is Planck constant (6.623 x 10^{-34} J s) and e is mathematical constant (2.718) (it should be noted that although the time units used to calculate the activation energy are not important, it is essential to use reciprocal seconds for the rate constants in order to determine the activation entropy).

The Gibbs free energy of activation (ΔGa) can be calculated by applying the following formula based on thermodynamic functions (Low *et al*. 1973):

$$\Delta Ga = \Delta H - T.\Delta Sa \quad \textbf{(7.4)}$$

By using the relationship of the enthalpy and the activation energy, $\Delta H = Ea - RT$, the Gibbs free energy of activation can be determined as follow:

$$\Delta Ga = Ea - RT - T.\Delta Sa \quad \textbf{(7.5)}$$

7.3 Results and Discussion

6.3.1 Activation energy

Two example Arrhenius plots for the fast adsorption kinetic process for a RH step change of 35% to 40% for *A. mangium and E. malaccense* are shown in Figure 7.1a and Figure 7.1b respectively. A plot of ln (k) versus the reciprocal absolute temperature yielded a reasonable linear fit indicating that the Arrhenius relationship is obeyed. Based on the equation 7.2, multiplying the gradient of the slope by the universal gas constant (8.314 J K^{-1} mol^{-1}) yields the activation energy.

The activation energies for the adsorption and desorption are shown for the fast (k_1) and slow (k_2) processes in Figure 7.2 (*A. mangium*) and Figure 7.3 (*E. malaccense*). For clarity, the RH values reported in the plots are the programmed values and each step represents the final RH step in the adsorption mode, i.e., for a step change 0-5% RH it is reported as 5% and the initial RH value under desorption conditions, i.e., for a step a change 95-90% RH it is reported as 95%.

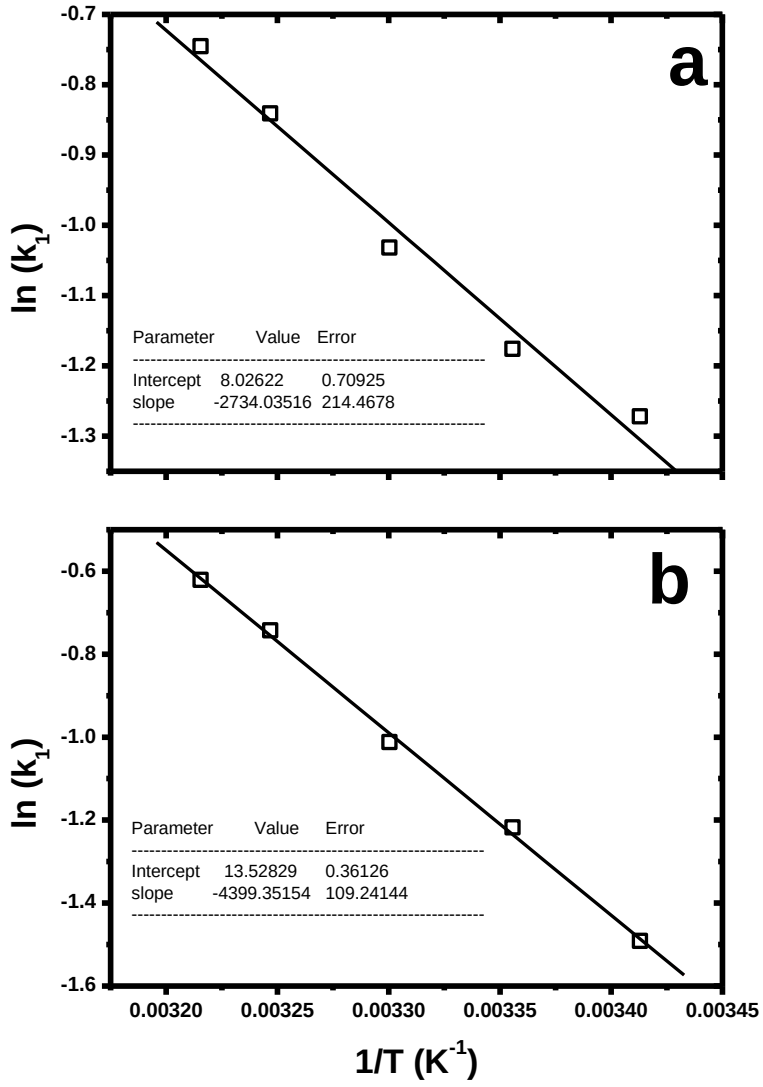

Figure 7.1 Two examples of Arrhenius plots for the fast adsorption kinetic process for a RH step change of 35% to 40% for *A. mangium*) (a) and 10% to 15% for *E. malaccense* (b).

Several findings can be made regarding the variation of activation energy of sorption throughout the hygroscopic range:

a) The *Ea* values related to the fast or slow processes of *A. mangium* or *E. malaccense* are on average lower than 40 kJ mol^{-1} and more typically

between 10-30 kJ mol^{-1}. These values are consistent with hydrogen bond breaking/formation being associated with the rate determining step (Morrison and Dzieciuch 1959, McQueen-Mason and Cosgrove 1994, Markovitch and Agmon 2007). In a study of the swelling kinetics of wood in water Mantanis *et al.* (1994) reported values for the *Ea* of Sitka spruce and Scots pine as 32 kJ mol^{-1} and 48 kJ mol^{-1}, respectively indicating that H-bond breaking is the rate determining step in the swelling process.

b) There is no clear pattern in the *Ea* values, for *A. mangium* and *E. malaccense* throughout the hygroscopic range (and hence the MC of the sample increases) except in Figure 7.2d, which has shown a decreases in *Ea* from low RH to high RH values. Hill *et al.* (2010b) and Hill *et al.* (2010c) in studies using flax and Sitka spruce, respectively, interpreted the variation in activation energy over the hygroscopic range as being due to H-bond breaking being related to the rate determining step at lower RH values, but that the amorphous matrix network became more open at higher RH.

c) The limitation of the DVS apparatus resulted in data points being obtained, within a narrow temperature (the range between 20-40 ^{o}C), there is a consideration on variation in the quality of the data obtained. A minimum of five temperatures was used in an attempt to improve data quality, with the variable results seen here. However, although it is hard to differentiate any trends in the data, the *Ea* is nonetheless invariably lower than 40 kJ mol^{-1}, giving confidence in the validity of the data set if not necessarily each individual data point. The values of the *Ea* obtained are consistent with H-bond breaking being a rate determining step.

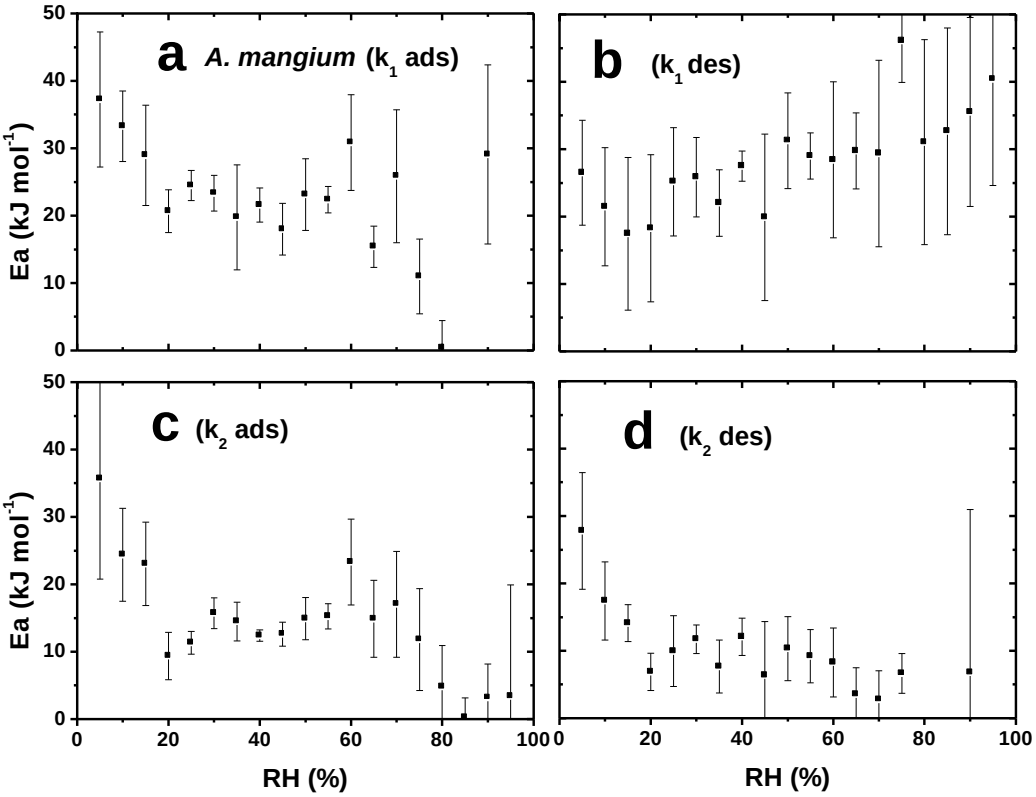

Figure 7.2 Variation in activation energy (*Ea*) in 5% RH steps over the hygroscopic range for the fast adsorption (a) and desorption (b) and slow process of *A. mangium* and the fast and slow adsorption (c) and desorption (d) processes, as derived from PEK fits to the sorption data.

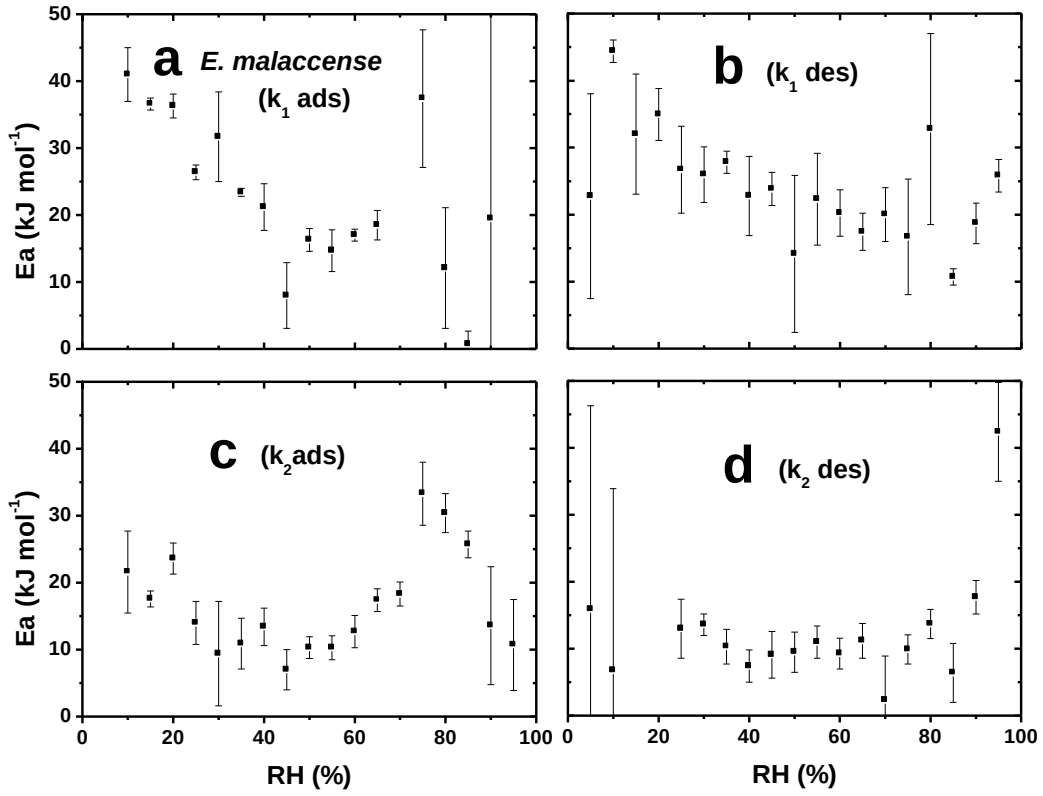

Figure 7.3 Variation in activation energy (*Ea*) in 5% RH steps over the hygroscopic range for the fast adsorption (a) and desorption (b) and slow process of *E. malaccense* and the fast and slow adsorption (c) and desorption (d) processes, as derived from PEK fits to the sorption data.

7.3.3 Entropy of activation

The intercept ln (*A*) at infinite temperature ($1/T = 0$) is related to the activation entropy (ΔSa) by the equation 7.3 and can be further developed through natural logarithms of both sides and it becomes:

$$\ln (A) = \ln (eRT/nh) + \Delta Sa/R \quad \textbf{(7.6)}$$

The value of ln (A) is similar to ln (k) once 1/T = 0 (Figure 7.1). The rate constant must be in reciprocal seconds to calculate the activation of entropy as explained before. The activation of entropy for the adsorption and desorption is shown for the fast and slow processes in Figure 7.4a, b (*A. mangium*) and Figure 7.4c, d (*E. malaccense*). The activation entropy is negative under conditions of both adsorption and desorption with fast and slow processes.

Entropy change is related to the differences in the number of ways of distributing energy between an initial state and a final state. Under adsorption conditions, water vapour molecules lose a considerable amount of translational freedom when they change from a free gaseous state to the highly confined environment of the cell wall micropores. This would lead to a reduction of entropy for the water molecules. But the opposite occurs when the water molecules are desorbed out of the wood cell wall, yet the activation entropy remains negative.

In order to understand why the activation entropy of both adsorption and desorption is negative, it is necessary to consider the nature of the rate determining step of the sorption processes. It has been previously argued in this study that the ability of the material to deform controls the rate of sorption. This deformation is linked to the micro-Brownian motion of the macromolecular components of the cell wall. The

activation entropy changes are therefore associated with these dynamic cell wall molecular processes.

A reduction in entropy indicates that there is a loss of translational, rotational or vibrational degrees of freedom, or a combination of these, associated with the macromolecules in the rate determining step. The ingress or egress of water molecules into or out of the cell wall requires molecular rearrangements to take place to allow for expansion or collapse of the cell wall micropores.

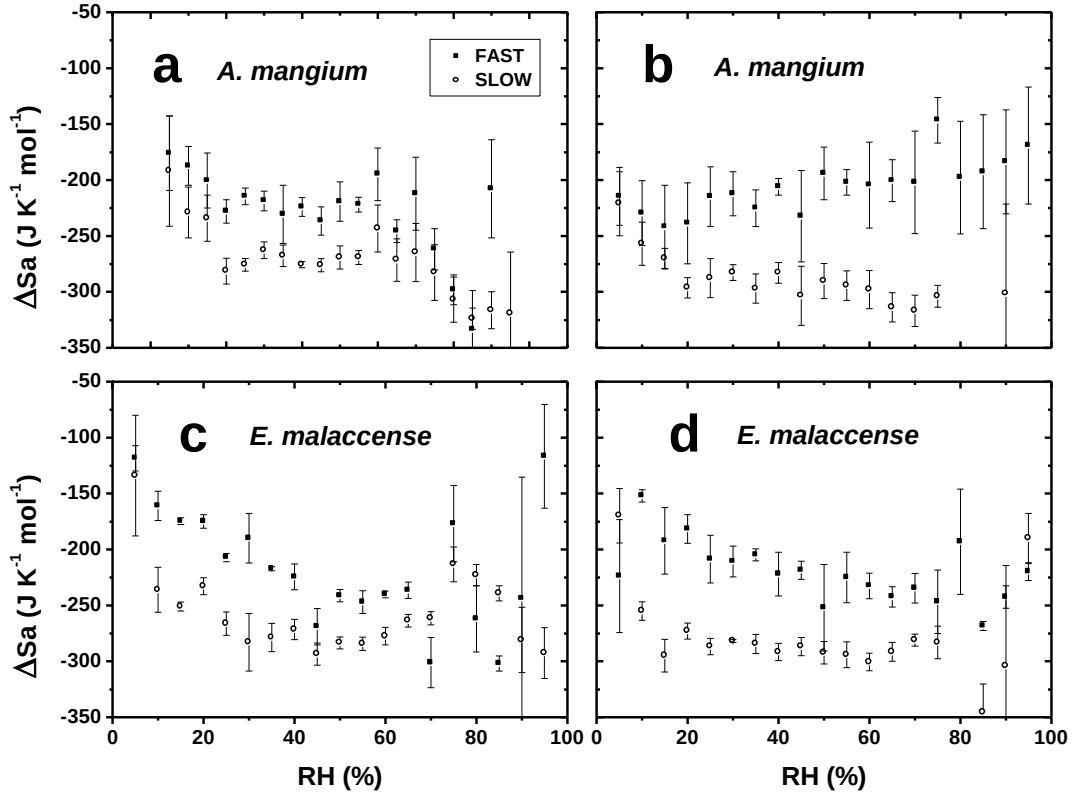

Figure 7.4 Variation in entropy of activation (Δ*Sa*) in 5% RH steps over the hygroscopic range for the fast and slow adsorption (a) and desorption (b) process of *A. mangium* and the fast and slow adsorption (c) and desorption (d) processes of *E. malaccense*.

Such rearrangements are controlled by the existence of free volume in the immediate environment where local deformation takes place. However in polymeric networks in the glassy state or below the glass transition temperature (*Tg*), where there is insufficient free-volume or where such motion is otherwise not permitted by, e.g. crosslinking, then the local deformation requires cooperative motion over a more extensive region of the polymeric network (Matsuoka 1992, Matsuoka and Hale 1997, Bartolotta *et al.* 2010) as noted at the end of Chapter 6. This non-random cooperative motion results in a reduction of activation entropy.

7.3.4 Gibbs free energy of activation

Changes in the Gibbs free energy of activation at different RH values are given in Figure 7.5a for *A. mangium* (Fig. 7.5a) and Figure 7.5b for *E. malaccense*. The variation in the ΔGa values shows some clear trends with both of the wood species in this study. There are obvious differences between the adsorption and desorption ΔGa values for both the fast and slow processes. The following observations can be made with reference to the data of Figure 7.5:

(a) Apart from at the highest and lowest ends of the hygroscopic range, the ΔGa values of adsorption are usually lower than those of desorption

(b) ΔGa values are always positive

(c) ΔGa values for the desorption process are always greater than those associated with the adsorption process

(d) The trend in ΔGa is upwards with increasing RH for the slow processes reaching a maximum value at about 60-70% RH for the fast process under desorption. With the fast process, the trend in ΔGa is downwards from 5-30% RH and then begins to increase.

It has been stated that, at least where kinetic studies involving enzymes are concerned, that the use of *Ea* in the determination of reaction mechanisms is inappropriate unless it is known that the entropic term is constant (Low *et al.* 1973). It has been clearly demonstrated herein that the entropy of activation varies at different RH values, indicating that a complete interpretation of the sorption kinetics through the use of activation energies alone is not possible.

The suggestion made in this study is that the sorption kinetics behaviour is controlled by the ability of the cell wall polymer network to deform in the dynamic environment where water molecules are travelling through the inter-microfibrillar matrix. It is considered that hydrogen bond breaking or formation plays a part in this process and that evidence for this may be found in the values obtained for the activation energies. However, there are also matrix polymer deformation processes that contribute towards the entropic component in the rate determining step. The overall process is therefore only fully represented by examination of the Gibbs free energy of activation, which has contributions from both enthalpic (activation energy) and entropic terms. There is no clear reason why ΔGa for the slow process increases and then declines as RH increases.

The initial reduction in ΔGa with cell wall moisture content can be rationalized as being related to the plasticization of the cell wall matrix polymers by water as cell wall MC increases, but since this behaviour is not universally observed, the interpretation can be disputed. There is no simple explanation for the subsequent increase in ΔGa at higher RH contents. The differences in behaviour of ΔGa between the fast and slow processes are also at the present time not understood. This is the first ever study of the entropy and Gibbs free energy of activation associated with water sorption. The results are sufficient interest to warrant a much more comprehensive investigation.

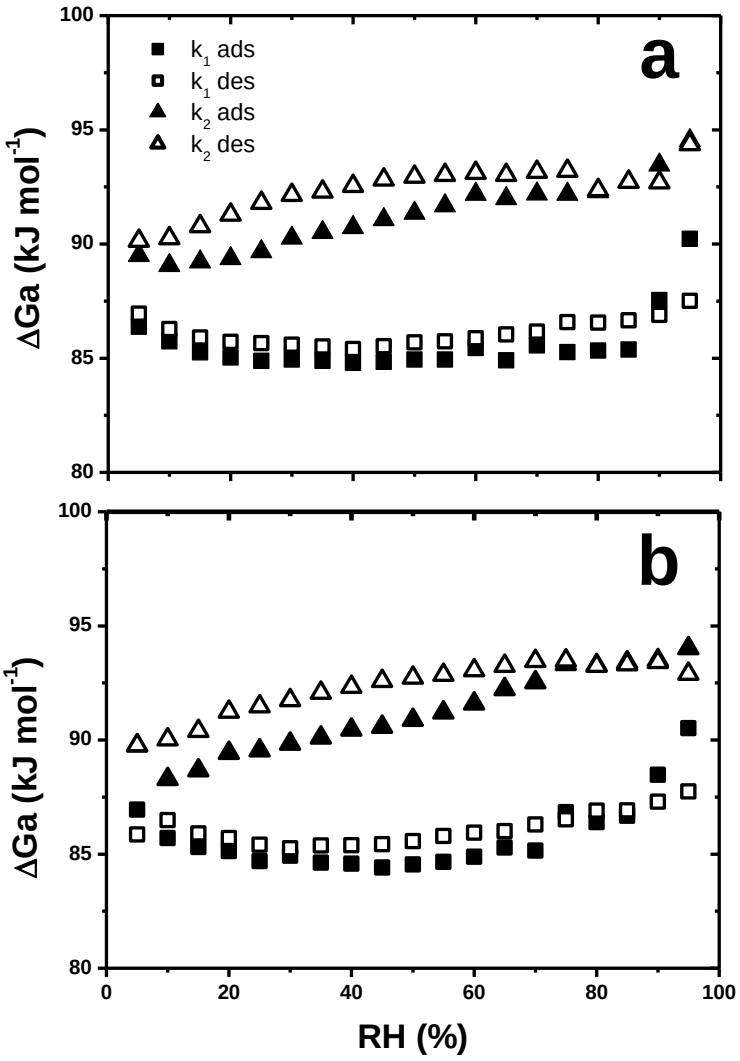

Figure 7.5 Variation in the Gibbs free energy of activation (Δ*Ga*) in 5% RH steps over the hygroscopic range for the fast and slow adsorption and desorption (a) process of *A. mangium* and the fast and slow adsorption and desorption (b) processes of *E. malaccense*.

7.4 Conclusions

It has been possible to obtain values for the activation energy, entropy and Gibbs free energy of sorption throughout the hygroscopic range with the time constants associated with sorption kinetics data according to the parallel exponential kinetics (PEK) model. The trend in behaviour of the activation energy (*Ea*) with relative humidity (RH) has given mixed results. In some cases, the *Ea* decreases from a value approximately of 40 kJ mol^{-1} towards effectively zero at the highest RH levels. This type of behaviour is thought to represent hydrogen bond breaking being the rate-limiting step at low cell wall moisture contents, but with this barrier being removed at high cell wall moisture contents. However this trend in activation energy is not universally observed. Nonetheless, activation energies above 40 kJ mol^{-1} are seldom observed and they are more typically 30 kJ mol^{-1} or lower, magnitudes entirely consistent with the rate limiting step being associated with H-bond breaking or formation.

The values for activation entropy are always negative for both adsorption and desorption conditions for both wood species. This kind of phenomenon can be explained as being due to the rate determining step for dynamic sorption processes being associated with molecular rearrangements within the cell wall matrix. Macromolecular relaxation in the cell wall matrix to allow for the transport of water molecules requires cooperative behaviour between adjacent molecules when the isotherm is performed below the glass transition temperature of the substrate. Due to this cooperative domains matrix behaviour, the entropy of activation is negative for both the adsorption and desorption processes.

Evaluation of the Gibbs free energy of activation (ΔGa) reveals some very clear trends in behaviour as RH is increased. The ΔGa values for the slow process are higher

than those associated with the fast sorption process. Similarly ΔGa values for desorption are invariably higher than those for adsorption except at the higher end of the hygroscopic range. Whilst ΔGa for the fast process initially decreases and then increases as RH rises, the ΔGa values for the slow process increase throughout the hygroscopic range. The reasons for this behaviour with respect to ΔGa are not understood at the present time.

It is however, clear that a full understanding requires the determination of entropy and Gibbs free energy of activation as well as activation energy. This is a very interesting approach for further studies.