



Comprehensive Analytical Sorption Thermodynamic (CAST) model for water vapor sorption in cellulosic materials

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Abstract

Water vapor sorption is a fundamental property of cellulosic materials. Numerous theoretical and empirical models have been developed to describe the relationship between water activity, temperature, and equilibrium moisture content (EMC). However, a meaningful connection between model parameters and thermodynamic properties related to the sorption process is often lacking. In cases where models yield thermodynamic properties, such as through use of the Clausius-Clapeyron equation, these are limited to temperatures where the ideal gas equation is applicable. In this paper we advance a thermodynamic framework and formulate a new semi-empirical sorption model based on the differential Gibbs energy of sorption as a function of EMC and temperature, intended for high temperature applications such as steam drying or fire modeling. We refer to this as the Comprehensive Analytical Sorption Thermodynamic (CAST) model. It has six parameters, includes temperature explicitly, and is invertible. The CAST model includes analytical equations for the differential enthalpy of sorption, the differential entropy of sorption, and the integral heat of wetting. The model is evaluated using sorption data and calorimetric data over a range of temperatures from the wood science literature and compared with several existing models. Overall, the CAST model fits the experimental sorption and calorimetric data with higher accuracy than existing models.

Keywords Wood · Water vapor sorption · Heat of wetting · Differential enthalpy of sorption · Isosteric heat · Equilibrium moisture content

Notation

a_w	Thermodynamic water activity (dimensionless)	$k_1 \dots k_3$	Constants in equation for compressibility factor and fugacity coefficient
a_w^i	Conventional (ideal gas) water activity, i.e., relative humidity (dimensionless)	M_w	Molar mass of water (0.018015268 kg mol ⁻¹)
C	Integration constant	n	Water content (mol kg ⁻¹)
f	Fugacity (Pa or bar)	P	Total pressure (Pa or bar)
G	Specific Gibbs energy of the solid (J kg ⁻¹)	p	Partial vapor pressure or vapor pressure of single component (Pa or bar)
g	Molar Gibbs energy (J mol ⁻¹)	p_c	Critical pressure of water (22.064 MPa)
$\bar{g}_a$	Differential molar Gibbs energy of absorbed water (J mol ⁻¹)	q_{wet}	Heat of wetting (J kg ⁻¹)
H	Specific enthalpy of the solid (J kg ⁻¹)	R	Gas constant (8.314462618 J K ⁻¹ mol ⁻¹)
h	Molar enthalpy (J mol ⁻¹)	s	Molar entropy (J K ⁻¹ mol ⁻¹)
$\bar{h}_a$	Differential molar enthalpy of absorbed water (J mol ⁻¹)	$\bar{s}_a$	Differential molar entropy of absorbed water (J K ⁻¹ mol ⁻¹)
$K(T)$	Empirical function of temperature for compressibility factor and fugacity coefficient (dimensionless)	T	Temperature (K)
		T_c	Critical temperature of water (647.096 K)
		u	Moisture content (kg kg ⁻¹)
		V_s	Specific volume of the solid (m ³ kg ⁻¹)
		v	Molar volume (m ³ mol ⁻¹)
		$\bar{v}_a$	Partial molar volume of absorbed water (m ³ mol ⁻¹)
		X	Integration variable for CAST model
		Z	Compressibility factor (dimensionless)

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Uppercase Greek symbols

Δ	Change in property
$\Delta_\alpha^\beta y$	Change in property y from phase α to phase β ($\Delta_\alpha^\beta y = y_\beta - y_\alpha$)

Lowercase Greek symbols

$\alpha_1 \dots \alpha_6$	Generic fitting parameters
$\beta_1 \dots \beta_6$	Constants in CAST model
$\gamma_1 \dots \gamma_3$	Constants in GAB isotherm model
$\delta_1 \dots \delta_6$	Constants in GAB6 model
$\varepsilon_1, \varepsilon_2$	Constants in ODE4 model
$\zeta_1 \dots \zeta_4$	Constants in ODP6 model
κ_1, κ_2	Constants in Nelson isotherm model
$\lambda_1 \dots \lambda_6$	Constants in NA6 model
μ	Chemical potential (J mol ⁻¹)
ρ	Density (kg m ⁻³)
ρ_c	Critical density of water (322 kg m ⁻³)
φ	Fugacity coefficient (dimensionless)
$\omega_1 \dots \omega_3$	Constants in OC3 model

Subscripts

a	Absorbed water
c	Critical value
ds	Dry solid
f	Final value
g	Water vapor (gaseous phase)
gl	Saturated water vapor (gas-liquid equilibrium)
i	Initial value
l	Liquid water
ref	Reference value
s	Solid
w	Water
wet	Wetting

1 Introduction

The properties of cellulosic materials strongly depend on interactions with water. The hygroscopic nature of such materials has important implications for processing and performance across a range of industries, including agricultural products, insulation materials, packaging, pulp and paper, textiles, and wood products. For example, moisture affects the strength and stiffness of wood [1], as well as its physical properties including heat capacity and thermal conductivity [2, 3]. Control of moisture content is necessary to avoid dimensional instability [4, 5], corrosion of embedded metal fasteners [6], surface microbial growth [7–9], and fungal decay [9–11].

Plant–water interactions also strongly influence wildfire behavior [12–14]. Moisture affects the preheating and ignition of forest fuels (live and dead plants) and slows the rates of combustion, fire spread, and heat release. Furthering the

fundamental understanding of plant–water relations is necessary to improve the modeling of wildland fire, particularly the influence of moisture on pyrolysis, flame spread, and fire growth [13–17]. Physical models used in these applications need to account for a wide range of conditions that include temperatures above the boiling point and moisture contents from the green condition in live plants to bone dry.

Water can be present in cellulosic materials in the solid, liquid, and vapor phases. In addition, water molecules can be adsorbed on surfaces or taken up within the biopolymer matrix, where they are energetically bound through hydrogen bonds or other intermolecular attractions. We refer to these interactions collectively as absorption. The water vapor sorption isotherm is a fundamental property of hygroscopic materials that relates the equilibrium moisture content (EMC or u , the ratio of the total mass of water in the material to its dry mass) and the relative humidity (RH) or water activity (a_w) at a given temperature (T). Additional factors such as material moisture history and external constraints on moisture-induced swelling may influence the equilibrium state. Equilibrium refers to the condition where the material is neither gaining nor losing moisture. Sorption isotherms are important for understanding plant–water interactions and modeling the material behavior.

An important thermodynamic quantity is the energy involved in absorption of water molecules by a material, or desorption of water molecules from a material. The enthalpy of vaporization of pure water is well known and provides a convenient reference curve as a function of temperature. The enthalpy of water vapor sorption in a material depends not only on temperature but also on the composition of the system, which is usually expressed as material moisture content. Two general approaches exist for quantifying this enthalpy change: calorimetric methods and the analysis of sorption isotherm data across multiple temperatures. The latter is commonly referred to as the isosteric method (“isosteric” meaning constant coverage, originating from the study of adsorption on surfaces, but broadly adapted to mean constant EMC). Because sorption involves equilibrium between two phases, the Clapeyron equation describes the relationship between pressure, temperature, and changes in volume and enthalpy (or entropy) between the phases [18], Ch. 15). The Clapeyron equation, however, is rarely used; typically, the simpler Clausius-Clapeyron equation is used in the literature, which relies on two assumptions. First, the molar volume of absorbed water is assumed to be negligible compared to the molar volume of water vapor. Second, the ideal gas equation is assumed to adequately describe water vapor. Although these assumptions are reasonable at low temperatures and pressures, the Clausius-Clapeyron equation becomes more and more inaccurate as temperature and pressure increase, as demonstrated later in this article.

Numerous equilibrium sorption models have been applied to water vapor sorption in cellulosic materials in the literature [19–27]. These models range from simple empirical equations to theoretical models based on an idealized physical system. Regardless of the type of model, a meaningful connection between model parameters and thermodynamic properties is often lacking. Common theoretical models widely used in the literature, for which the parameters are assumed to represent physical quantities such as changes in enthalpy or Gibbs energy, fail to predict values in agreement with independently measured data for wood [22, 24, 28]. In practice, models often serve merely as EMC/RH fitting equations for the purpose of interpolation prior to applying the Clausius–Clapeyron equation [29–32]. However, use of non-optimal fitting equations for interpolation may bias the subsequent thermodynamic analysis [23, 33–36].

In contrast, a few sorption models have been formulated specifically using empirical relationships between thermodynamic properties and EMC. For example, Anderson and McCarthy [37] developed an isotherm model relating the differential enthalpy of sorption to EMC, and Chung and Pfost [38] and Nelson [39] formulated isotherm models relating the differential Gibbs energy of sorption to EMC. Anderson [12] expanded the model of Nelson [39] with additional parameters such that temperature was included as a variable. This model will be described in detail and evaluated later in this article.

We take a similar approach in this article and develop a sorption model using an empirical relationship between macroscopic thermodynamic properties and EMC. Although our approach does not aim to build a theoretical model from the molecular level or describe all the complex physicochemical phenomena involved in the sorption of water vapor by cellulosic materials [24, 25], this type of model may be useful for accurately simulating heat and moisture transfer in high temperature applications such as steam drying or wildland fire. Prior literature on the thermodynamics of water vapor sorption in cellulosic materials is limited by reliance on the Clausius–Clapeyron equation [23, 33, 35, 39, 40]. Here we advance a thermodynamic framework that overcomes this limitation, adapting the work of Myers and Monson [41] on absolute adsorption of gases in microporous solids. Building on this framework, we develop a semi-empirical sorption model that is valid over a wide range of temperature and pressure conditions. We wanted the model to have the following attributes:

- The model should include temperature explicitly, and the equation giving $u(a_w, T)$ should be readily invertible to give $a_w(u, T)$.
- The model should analytically describe real gas behavior of water vapor in accordance with reference data (i.e., the steam table) between the triple point and the critical point.

- The model should be inherently consistent with the thermodynamics of phase equilibria and specifically include the condition that the chemical potential of water vapor is equal to the chemical potential of absorbed water in the solid material.
- The number of model parameters should be limited, preferably to six or fewer.
- The model should be adaptable to a range of different cellulosic materials.
- The model should fit experimental sorption data accurately over a wide range of temperatures, including the high and low RH regions.
- The model should provide the ability to calculate thermodynamic quantities analytically, including the differential Gibbs energy of sorption, the differential enthalpy of sorption, the differential entropy of sorption, and the integral heat of wetting, with reasonable accuracy in comparison to independent measurements.

Section 2 of this article provides the thermodynamic framework for formulating the model. In Section 3, we describe the Comprehensive Analytical Sorption Thermodynamic (CAST) model, which is based on the differential Gibbs energy of sorption. Section 4 details the methods used for evaluating the model's ability to fit sorption data and calorimetric data from the wood science literature in comparison to several existing models. Section 5 presents results showing the CAST model fits experimental data with higher accuracy than existing models.

2 Thermodynamic framework

Before considering water vapor sorption in hygroscopic materials, we discuss vapor–liquid equilibrium for pure water to provide context on real gas behavior and the effects of temperature.

2.1 Vapor–liquid equilibrium of pure water

The thermodynamics of phase equilibria classically begins with the Clapeyron equation [18, 42, 43], which relates the slope of the saturation pressure vs. temperature curve to differences in entropy and volume between the phases, or alternatively, differences in enthalpy and volume:

$$\frac{dp_{gl}}{dT} = \frac{s_{gl} - s_l}{v_{gl} - v_l} = \frac{h_{gl} - h_l}{T(v_{gl} - v_l)} \quad (1)$$

where p_{gl} is the pressure of the gas phase in equilibrium with the liquid phase, i.e., the saturation vapor pressure (Pa), T is absolute temperature (K), s_{gl} and s_l are the molar entropies of vapor and liquid ($\text{J K}^{-1} \text{mol}^{-1}$), v_{gl} and v_l are the molar

volumes of vapor and liquid ($\text{m}^3 \text{mol}^{-1}$), and h_{gl} and h_l are the molar enthalpies of vapor and liquid (J mol^{-1}).

The molar enthalpy of vaporization can be expressed as $\Delta_l^g h = h_{gl} - h_l$, where the subscript following the delta symbol indicates the initial phase and the superscript indicates the final phase (this notation is recognized by the International Union of Pure and Applied Chemistry; Cohen et al. [44] p. 60). Standard reference values [45–47], which we subsequently refer to as the steam table, are plotted as the thick light blue curve in Fig. 1 between the triple point (273.16 K) and the critical point (647.096 K). Calculations using Eq. (1) with numerical differentiation of the saturation vapor pressure with respect to temperature based on the empirical equation of Wagner and Pruss [48], and with molar volumes of vapor and liquid calculated using empirical equations for density from Wagner and Pruss [48], give the enthalpy of vaporization to high accuracy (within 0.05% up to 360 °C), yielding the black dotted curve in Fig. 1. These calculations account for real gas behavior that is inherent in the pressure-volume-temperature data of the steam table. Further details are provided in Supplementary Information (SI) Part I.

Real gas behavior can be quantified using the compressibility factor $Z = p_g v_g / RT$, where R is the gas constant ($8.31446 \text{ J K}^{-1} \text{ mol}^{-1}$). The ideal gas equation is equivalent to $Z=1$. The compressibility factor for saturated water vapor, calculated from the steam table, is plotted in Fig. 2a as a function of temperature. Various functional forms for Z have been proposed based on real gas equations of state [18, 43] or empirical approximations [49]. Here we approximate Z as

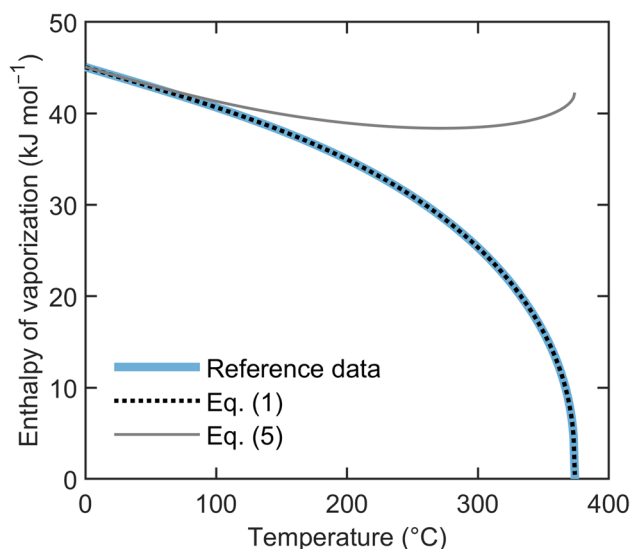


Fig. 1 Enthalpy of vaporization of water as a function of temperature from reference data, Clapeyron equation, and Clausius-Clapeyron equation

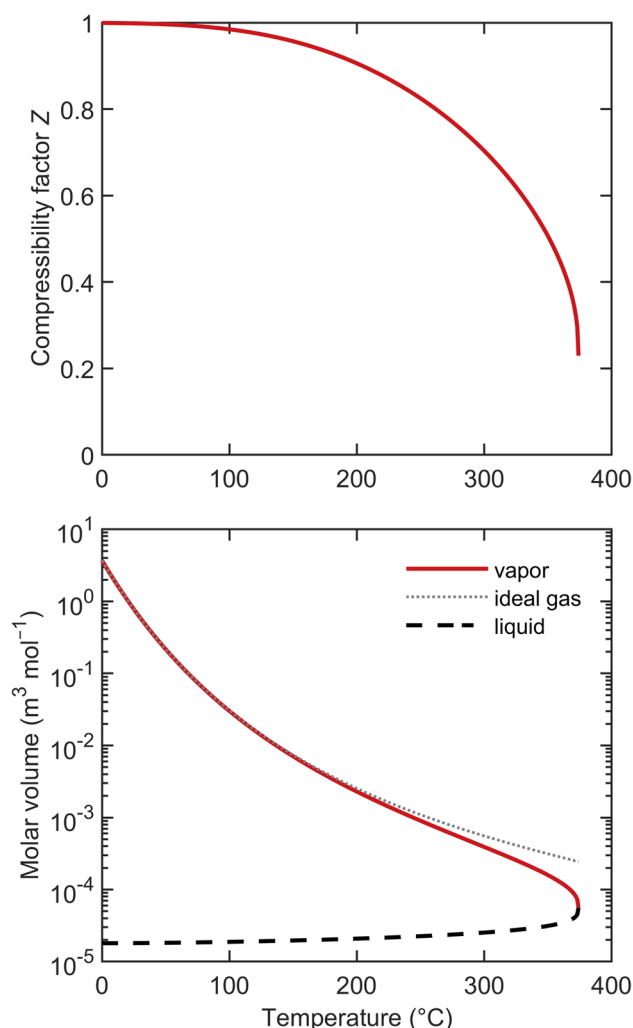


Fig. 2 **a** Compressibility factor of saturated water vapor vs. temperature; **b** molar volume of saturated water vapor and liquid water vs. temperature

$$Z = 1 - \frac{K(T)p_g/p_c}{1 - K(T)p_g/p_c} \quad (2)$$

where $K(T)$ is an empirical function of temperature given below and p_c is the critical pressure of water (22.064 MPa). Equation (2) was proposed previously [50], but we developed a new empirical function for $K(T)$ based on fitting data from the steam table (SI Part I):

$$K(T) = k_1(T/T_c - k_2)^{-k_3} \quad (3)$$

where T_c is the critical temperature of water (647.096 K) and k_1 , k_2 , and k_3 are constants (0.186, 0.233, and 2.70, respectively), which were identified by minimizing the sum of squared residuals between the enthalpy of vaporization of water from the steam table and the enthalpy calculated with the Clapeyron equation expressed as

$$\Delta_l^s h = \left(1 - \frac{p_{gl} v_l}{ZRT}\right) \frac{ZRT^2}{p_{gl}} \frac{dp_{gl}}{dT} \quad (4)$$

where Z was approximated using Eqs. (2) and (3). The calculated enthalpy of vaporization is accurate to within 0.05% for temperatures up to 318 °C. Across the full range of pressures below saturation, the calculated value of Z is accurate to within 0.2% below 200 °C and to within 1.4% up to 300 °C (SI Part I).

At low temperatures, two simplifications can be made to Eq. (1). First, water vapor can be described using the ideal gas equation ($Z \cong 1$). Second, the molar volume of liquid water can be neglected relative to that of water vapor (Fig. 2b). With these approximations, the Clapeyron equation is reduced to the Clausius-Clapeyron equation:

$$\Delta_l^s h \cong RT^2 \frac{d \ln p_{gl}}{dT} \quad (5)$$

This is shown as the gray curve in Fig. 1. At 100 °C, the relative error in the enthalpy of vaporization is only 1.6%, but it increases considerably with temperature.

Another approximation convenient for low temperatures is a linear equation for the enthalpy of vaporization, which gives the saturation vapor pressure through a relatively simple integration of the Clausius-Clapeyron equation [42]. This is described further in SI Part I.

2.2 Water vapor sorption in hygroscopic materials

The literature on thermodynamics of gas sorption in porous solids provides two different approaches, both of which we adapt to describe water vapor sorption in hygroscopic materials. These are based on (i) the Clapeyron equation, which gives the difference in enthalpy between the vapor phase and the absorbed phase, and (ii) the Gibbs energy, which generates a full set of thermodynamic properties. Here we introduce these approaches and show that they are consistent in order to provide the relevant thermodynamic framework for the CAST model in Section 3.

The enthalpy of water vapor varies with pressure and temperature according to the steam table. Figure 3 is a plot of relative enthalpy (h_g/h_{gl}) vs. relative humidity (p_g/p_{gl}) for a series of temperatures. At low temperatures, where water vapor can be described as an ideal gas, $h_g \cong h_{gl}$ across the full range of vapor pressures. Differences between h_g and h_{gl} at low RH become more pronounced with increasing temperature.

The equilibrium between water vapor and absorbed water in a hygroscopic material can be characterized by water vapor pressure, temperature, and composition, which is expressed here either as water content n (mol_w

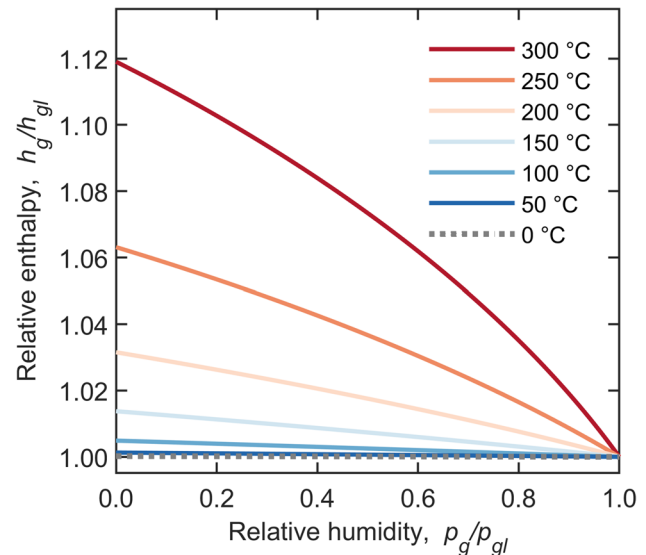


Fig. 3 Enthalpy of water vapor relative to enthalpy at saturation as a function of relative humidity for various temperature series based on the steam table

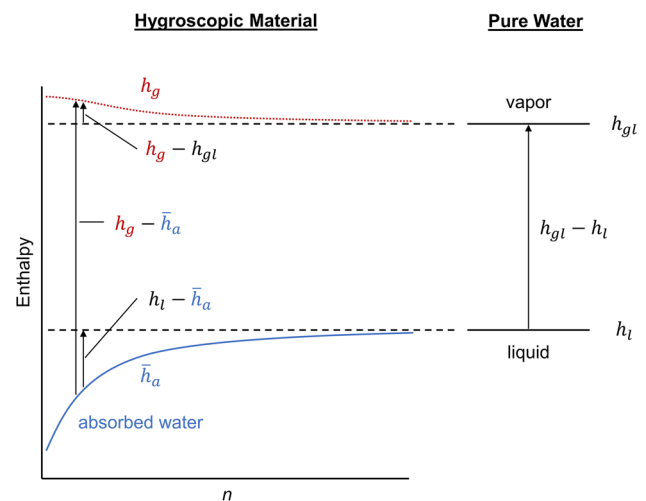


Fig. 4 Conceptual enthalpy diagram showing states of water: (left) water vapor in equilibrium with a hygroscopic material as a function of water content n ; (right) pure water system

kg_{ds}^{−1}) or moisture content u (kg_w kg_{ds}^{−1}, where the subscript “w” refers to water and the subscript “ds” refers to dry solid; $u = n \cdot M_w$, where M_w is the molar mass of water, kg mol^{−1}). The enthalpy of absorbed water varies with n as depicted conceptually in Fig. 4 for constant temperature, in comparison to the states in the pure water system (adapted from Skaar [23] and Nopens et al. [35]). Figure 4 includes the enthalpy of water vapor from Fig. 3 but as a function of n instead of RH. At low temperatures, where water vapor can be described as an ideal gas, h_g would

follow the dashed line rather than the dotted red curve. The enthalpy of absorbed water is properly expressed as a differential quantity [41, 51]: $\bar{h}_a = \left(\frac{\partial H}{\partial n}\right)_T$, where $\bar{h}_a$ is the differential molar enthalpy of absorbed water (J mol_w^{-1}) and H is the total enthalpy of the solid phase ($\text{J kg}_{\text{ds}}^{-1}$), which reflects both solid–water interactions and water–water interactions. The bar over the symbol indicates a differential quantity; this distinction is necessary for absorbed water because the differential and integral values are not the same, whereas differential and integral enthalpies are identical for phases with one component (i.e., water vapor and pure liquid water). In general, as the water content approaches the maximum, $h_g \rightarrow h_{gl}$ and $\bar{h}_a \rightarrow h_l$.

2.2.1 Clapeyron equation

The Clapeyron equation can be applied to multi-component systems such as gas sorption in solids [18, 43, 49]. The change in phase from water vapor to absorbed water is exothermic and therefore has a negative enthalpy change (heat is released from the system). For the sake of continuity with the literature, we use positive quantities (reversing the process and temporarily neglecting sorption hysteresis). Adapting Eq. (1) for absorbed water and introducing Z as was done in Eq. (4), the enthalpy difference can be expressed as

$$\Delta_a^s \bar{h} = h_g - \bar{h}_a = (v_g - \bar{v}_a)T \left(\frac{\partial p_g}{\partial T} \right)_n = \left(1 - \frac{\bar{v}_a p_g}{ZRT} \right) \frac{ZRT^2}{p_g} \left(\frac{\partial p_g}{\partial T} \right)_n \quad (6)$$

where v_g is the molar volume of water vapor ($\text{m}^3 \text{mol}^{-1}$), $\bar{v}_a = \left(\frac{\partial \bar{V}_s}{\partial n}\right)_{T,P}$ is the partial molar volume of absorbed water ($\text{m}^3 \text{mol}^{-1}$), V_s is the total specific volume of the solid phase ($\text{m}^3 \text{kg}^{-1}$), and p_g is the water vapor pressure (Pa). This enthalpy difference is also referred to as the *isosteric heat of sorption* in the literature. Equation (6) becomes identical to Eq. (4) in the limiting condition where the water content of the material approaches its maximum, $p_g \rightarrow p_{gl}$, and $\bar{v}_a \rightarrow v_l$. On the other hand, Eq. (6) reduces to a form of the Clausius-Clapeyron equation when $Z \cong 1$ and $\bar{v}_a \ll v_g$:

$$\Delta_a^s \bar{h} \cong RT^2 \left(\frac{\partial \ln p_g}{\partial T} \right)_n \quad (7)$$

Note that Eq. (7) becomes identical to Eq. (5) in the limiting condition where the water content of the material approaches its maximum.

2.2.2 Gibbs energy approach

The Gibbs energy can serve as a generating function for other thermodynamic properties. Here we adapt the solution thermodynamics description of gas adsorption in microporous solids [41, 51] for the case of water vapor sorption in hygroscopic materials. We formulate the differential Gibbs energy of sorption based on chemical potential and use it to derive the differential enthalpy of sorption, the differential entropy of sorption, and the integral enthalpy of wetting.

For a constant mass of solid hygroscopic material at constant temperature, the criterion for equilibrium is the equality of the chemical potentials of absorbed water and water vapor: $\mu_a = \mu_g$. We focus first on the gas phase. The equations for thermodynamic properties of a real gas are formulated to resemble those of an ideal gas, but with fugacity instead of pressure. The fugacity f_g (which has units of pressure) is given by $f_g = \phi p_g$ where ϕ is the fugacity coefficient, which varies with temperature and pressure. A convenient reference state is pure water at saturation. The chemical potential of water vapor relative to saturation is given by

$$\mu_g - \mu_{gl} = RT \ln \left(\frac{f_g}{f_{gl}} \right) = RT \ln a_w \quad (8)$$

where $a_w \equiv f_g/f_{gl}$ is the thermodynamic water activity ([43], p. 279; [44] p. 57). At low temperatures, where $\phi \rightarrow 1$ and $f_g \rightarrow p_g$, the thermodynamic water activity is equivalent to the conventional water activity, a_w^i , which is identical to RH expressed as a decimal: $a_w \cong a_w^i \equiv p_g/p_{gl}$. The influence of temperature on the ratio $a_w/a_w^i = \phi_g/\phi_{gl}$ is illustrated in Fig. S6 with calculated values based on the steam table (SI Part I).

Below the critical point, the fugacity coefficient varies approximately linearly with pressure ([18], Fig. 10.2; see SI Part I). We select the following empirical equation for the fugacity coefficient:

$$\phi = 1 - K(T) \frac{p_g}{p_c} \quad (9)$$

where $K(T)$ is given by Eq. (3). Equation (9) for ϕ is consistent with Eq. (2) for Z , as shown in SI Part I.

An independent method of obtaining the chemical potential of water vapor μ_g , for the purpose of evaluating the adequacy of Eq. (9), is by way of the steam table, noting its equivalence to the molar Gibbs energy of water vapor g_g (J mol^{-1}):

$$\mu_g = g_g = h_g - Ts_g \quad (10)$$

where h_g is the molar enthalpy (J mol^{-1}) and s_g is the molar entropy of water vapor ($\text{J K}^{-1} \text{mol}^{-1}$). Calculated values of $\mu_g - \mu_{gl}$ from Eq. (8), with ϕ from Eq. (9) and $K(T)$ from Eq. (3), agree with $g_g - g_{gl}$ from the steam table to within

0.18% at 200 °C, 0.44% at 250 °C, and 1.2% at 300 °C (SI Part I). This demonstrates the validity of the approximation for the fugacity coefficient up to 300 °C and confirms the equivalence of the chemical potential (calculated using fugacity) and the molar Gibbs energy of water vapor (calculated from molar enthalpy and entropy from the steam table) for the subcritical region.

For a constant mass of solid hygroscopic material, the chemical potential (J mol^{−1}) of absorbed water is

$$\mu_a = \left(\frac{\partial G}{\partial n} \right)_{T,P} \quad (11)$$

where G is the total Gibbs energy of the solid phase (J kg_{ds}^{−1}) and the partial derivative is at constant temperature and total pressure. The differential Gibbs energy of sorption is expressed as a positive quantity (with a sign change) as $\Delta_a^l \bar{g} = \mu_l - \mu_a$ where μ_l is the chemical potential of pure

liquid water. Recalling that $\mu_a = \mu_g$ for equilibrium between water vapor and absorbed water in the hygroscopic material, and $\mu_l = \mu_{gl}$ for vapor–liquid equilibrium of pure water, the differential Gibbs energy of sorption can be related to thermodynamic water activity from Eq. (8):

$$\Delta_a^l \bar{g} = -RT \ln a_w \quad (12)$$

The differential enthalpy of sorption, $\Delta_a^l \bar{h}$, can be generated from $\Delta_a^l \bar{g}$ as follows. For a process at constant total pressure, the Gibbs-Helmholtz relation links the change in enthalpy to the change in Gibbs energy [18, 43]:

$$\Delta h = -T^2 \left[\frac{\partial(\Delta g/T)}{\partial T} \right]_P \quad (13)$$

Because $\Delta_a^l \bar{g}$ is a function of n , the partial derivative is taken at constant P and n :

$$\Delta_a^l \bar{h} = h_l - \bar{h}_a = -T^2 \left[\frac{\partial(\Delta_a^l \bar{g}/T)}{\partial T} \right]_{P,n} = -T^2 \left(\frac{\partial[(-RT \ln a_w)/T]}{\partial T} \right)_{P,n} = RT^2 \left(\frac{\partial \ln a_w}{\partial T} \right)_{P,n} \quad (14)$$

A full derivation of this equation is given in SI Part II. At low temperatures, a_w in Eq. (14) can be considered equivalent to a_w^i (RH expressed as a decimal). This enthalpy difference is also referred to as the *net isosteric heat of sorption* or the *differential heat of wetting* in the literature.

Given the equations for $\Delta_a^l \bar{g}$ and $\Delta_a^l \bar{h}$ above, the differential entropy of sorption, $\Delta_a^l \bar{s}$, can be calculated using $\Delta_a^l \bar{g} = \Delta_a^l \bar{h} - T \Delta_a^l \bar{s}$.

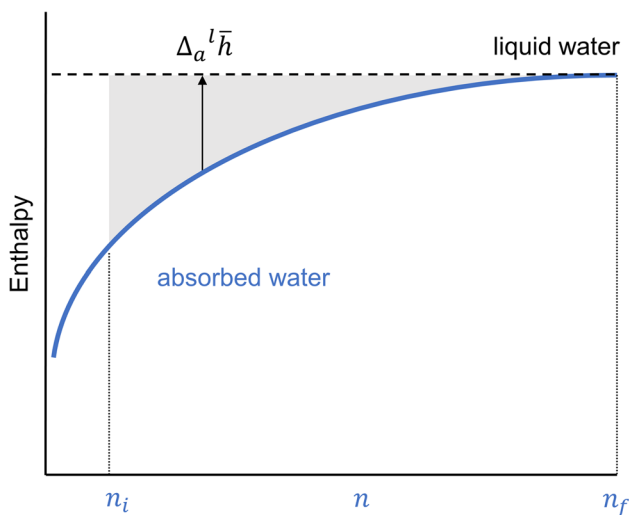


Fig. 5 Conceptual enthalpy diagram showing absorbed water in a hygroscopic material as a function of water content n ; the shaded area corresponds to the heat of wetting

In addition to these differential quantities, the integral enthalpy of wetting can be generated as follows. Consider the process of water absorption in a hygroscopic material from an initial equilibrium state with water content n_i (mol_w kg_{ds}^{−1}). Liquid water is added such that the material becomes fully water-saturated, with final water content n_f . The heat released by the (exothermic) absorption process can be measured with a calorimeter [23, 35]. For convenience, we express this heat of wetting (and the corresponding integral enthalpy) as a positive quantity with the symbol q_{wet} (J kg_{ds}^{−1}), which is related to the differential enthalpy of sorption by

$$q_{\text{wet}} = \int_{n_i}^{n_f} \Delta_a^l \bar{h} dn \quad (\text{constant } T) \quad (15)$$

The magnitude of the heat of wetting depends on the initial water content. This relationship is depicted graphically in Fig. 5, where the heat of wetting corresponds to the area of the shaded region. For the case where the material is initially completely dry, the total heat of wetting (J kg_{ds}^{−1}) is found by integrating Eq. (15) from $n_i = 0$. The rigorous definitions of differential and integral thermodynamic quantities from this framework are used in the development of the CAST model in Section 3.

2.2.3 Equivalence of the Clapeyron equation and the Gibbs energy approach

Two different thermodynamic approaches for water vapor sorption in hygroscopic materials were described above:

(i) the Clapeyron equation (Section 2.2.1), which gives the difference in enthalpy between the vapor phase and the absorbed phase, and (ii) the Gibbs energy approach (Section 2.2.2). The equivalence of these approaches was explored for two cases. First, for the limiting condition of absorbed water in a hygroscopic material approaching its maximum water content, the isosteric heat of sorption approaches the enthalpy of vaporization of water. In SI Part III the calculated enthalpy using the Clapeyron equation is shown to be equivalent to that based on the Gibbs energy, or solution thermodynamics approach, both accurate to within 0.05% of the steam table up to 318 °C.

Second, in SI Part IV the sorption data of Engelhardt [52] for beech between 110 °C and 170 °C, over a wide range of RH values, is analyzed using both approaches. The results confirm that the enthalpy values calculated with the two approaches agree to within 0.2%.

3 CAST model formulation

In this section we introduce a new equilibrium sorption model formulated with the differential Gibbs energy of sorption ($\Delta_a^l \bar{g}$) as a function of moisture content and temperature. Additional thermodynamic quantities are generated from $\Delta_a^l \bar{g}$, including $\Delta_a^l \bar{h}$, $\Delta_a^l \bar{s}$, and q_{wet} . Subsequently we simplify the notation by dropping the “a” and “l.”

An approximately linear relationship between the logarithm of $\Delta \bar{g}$ and EMC at constant temperature was reported in previous work for wood, cellulose, and agricultural products [38, 39]. EMC is given the symbol u ($\text{kg}_w \text{kg}_{\text{ds}}^{-1}$). This can be expressed as

$$\Delta \bar{g}(u) = \alpha_1 \exp(-\alpha_2 u) \quad (16)$$

where α_1 and α_2 are positive fitting parameters.

The CAST model builds on this concept of $\Delta \bar{g}(u, T)$ but differs from earlier models in two key aspects. First, it accounts for real gas behavior using the thermodynamic framework of Section 2. Second, it uses a different functional form for $\Delta \bar{g}(u, T)$. Figure 6 is a semi-log plot of $\Delta \bar{g}$ vs. u based on sorption isotherm data for different cellulosic materials; the points were calculated with Eq. (12) using measured vapor pressures and temperatures. The gray dashed line, which represents earlier models [38, 39], clearly does not fit the data adequately across the full range of EMC values. At a given temperature, the following equation provides an improved fit, plotted as the blue curve in Fig. 6:

$$\Delta \bar{g}(u) = (\alpha_3 u + \alpha_4)^{-\alpha_5} - \alpha_6 \quad (17)$$

where $\alpha_3, \dots, \alpha_6$ are positive fitting parameters (Table 1). The form of this equation is an empirical modification of the isotherm model of Halsey [53] with two additional parameters

that allow the curve to fit the data more closely. By fitting data at multiple temperatures, we find that α_3 varies with temperature, but α_4 , α_5 , and α_6 can be considered constants. The temperature dependence of α_3 can be described by $\alpha_3(T) = \beta_1 e^{-\beta_2/T} + \beta_3$, where β_1 , β_2 , and β_3 are positive constants. The term $\beta_1 e^{-\beta_2/T}$ resembles the Arrhenius equation used for describing rates of chemical reactions; this form has been used previously in a modification of the Guggenheim-Anderson-de Boer isotherm model [54].

Combining these equations, the CAST model is formulated as

$$\Delta \bar{g}(u, T) = [u(\beta_1 e^{-\beta_2/T} + \beta_3) + \beta_4]^{-\beta_5} - \beta_6 \quad (18)$$

where $\beta_1, \dots, \beta_6$ are positive constants. This formulation focuses on the properties of absorbed water in the hygroscopic material. Following the pattern of Section 2.2.2, we use $\Delta \bar{g}(u, T)$ as a generating function for additional thermodynamic properties below.

The differential enthalpy of sorption is derived by applying the Gibbs-Helmholtz relation (Eq. 13) to (18):

$$\Delta \bar{h}(u, T) = \Delta \bar{g} + \left(\frac{\Delta \bar{g} + \beta_6}{T} \right) \left[\frac{u\beta_1\beta_2\beta_5 e^{-\beta_2/T}}{u(\beta_1 e^{-\beta_2/T} + \beta_3) + \beta_4} \right] \quad (19)$$

We note the relative simplicity of this equation, which comes from using only two empirical constants (β_1 and β_2) for the temperature dependence of the differential Gibbs energy.

The differential entropy of sorption is given by

$$\Delta \bar{s}(u, T) = \frac{\Delta \bar{h} - \Delta \bar{g}}{T} = \left(\frac{\Delta \bar{g} + \beta_6}{T^2} \right) \left[\frac{u\beta_1\beta_2\beta_5 e^{-\beta_2/T}}{u(\beta_1 e^{-\beta_2/T} + \beta_3) + \beta_4} \right] \quad (20)$$

The heat of wetting is related to the differential enthalpy of sorption through Eq. (15). Adapting this for u in place of n ($u = n \cdot M_w$, where M_w is the molar mass of water), we have:

$$q_{\text{wet}} = \frac{1}{M_w} \int_{u_i}^{u_f} \Delta \bar{h} du \quad (\text{constant } T) \quad (21)$$

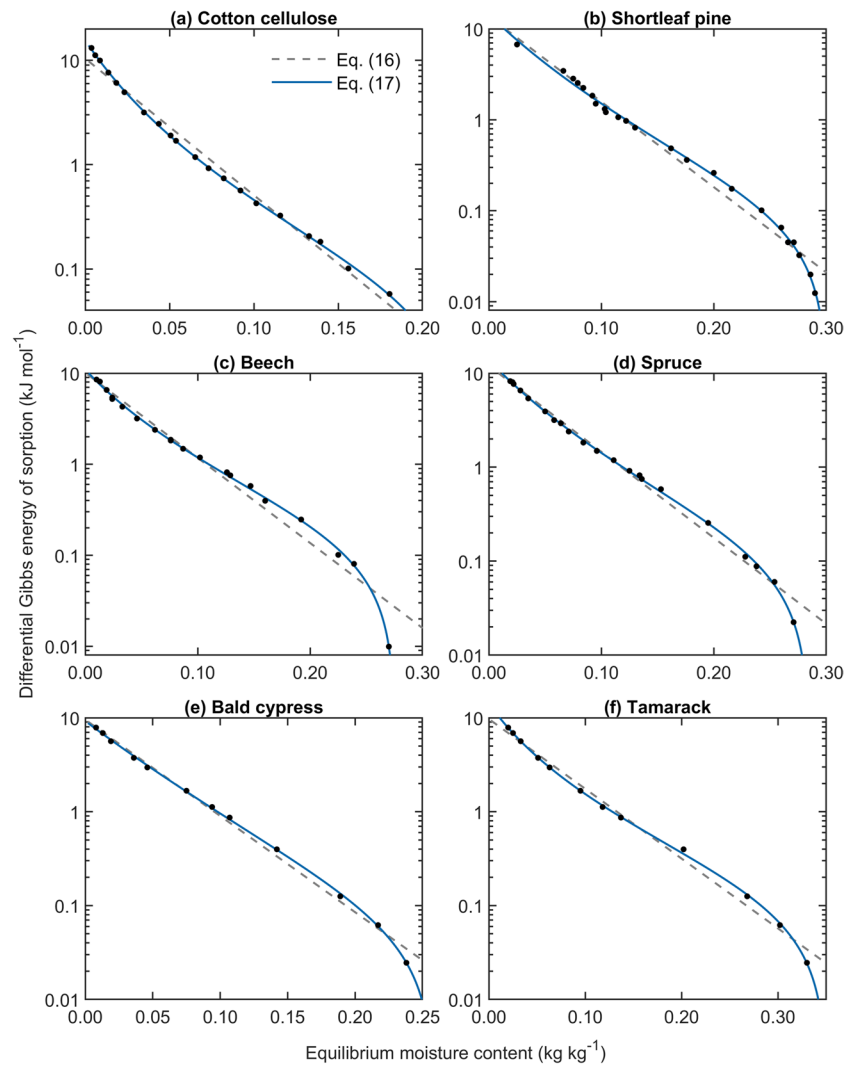
This quantity can be calculated by analytically integrating Eq. (19), which is more convenient by defining a new variable X as

$$X = u(\beta_1 e^{-\beta_2/T} + \beta_3) + \beta_4 \quad (22)$$

Substitution of Eq. (22) into Eq. (18) gives the differential Gibbs energy of sorption as

$$\Delta \bar{g} = X^{-\beta_5} - \beta_6 \quad (23)$$

Fig. 6 Differential Gibbs energy of sorption vs. equilibrium moisture content of **a** cotton cellulose at 25 °C [55]; **b** shortleaf pine sapwood at 25 °C [56]; **c** beech and **d** spruce at 25 °C [57]; **e** bald cypress and **f** tamarack at 21 °C [58]



Combining these equations, the heat of wetting is given by the following formula:

$$q_{\text{wet}} = \frac{1}{M_w(\beta_1 e^{-\beta_2/T} + \beta_3)} \left[\frac{X^{1-\beta_5}}{1-\beta_5} - \beta_6 X + \left(\frac{\beta_1 \beta_2 \beta_5 e^{-\beta_2/T}}{T(\beta_1 e^{-\beta_2/T} + \beta_3)} \right) \left(\frac{X^{1-\beta_5}}{1-\beta_5} - \frac{\beta_4 X^{-\beta_5}}{\beta_5} \right) \right]_{X_i}^{X_f} \quad (24)$$

Table 1 Parameter values for Eq. (17) fitted to experimental data in Fig. 6 (with u in kg kg^{-1} and Δg in kJ mol^{-1})

Material	α_3	α_4	α_5	α_6
Cotton cellulose	7.112	0.478	3.721	0.066
Shortleaf pine	3.230	0.585	4.995	0.110
Beech	4.565	0.432	2.879	0.221
Spruce	3.708	0.524	4.083	0.154
Bald cypress	1.904	0.808	10.429	0.065
Tamarack	4.510	0.364	2.631	0.173

Here X_i is calculated from u_i with Eq. (22). As EMC approaches its maximum, $a_w \rightarrow 1$ and $\Delta \bar{g} \rightarrow 0$. For calculating the heat of wetting by integration, it is necessary to extrapolate the model to a final value u_f and corresponding value X_f where $\Delta \bar{g} = 0$. From Eq. (23) this value is $X_f = \beta_6^{-1/\beta_5}$, which combined with Eq. (22) gives the extrapolated EMC:

$$u_f(T) = \frac{\beta_6^{-1/\beta_5} - \beta_4}{\beta_1 e^{-\beta_2/T} + \beta_3} \quad (25)$$

This extrapolated value corresponds to the point where $\Delta\bar{g} = 0$, $a_w = 1$, and $q_{\text{wet}} = 0$.

In addition to the thermodynamic properties of absorbed water in a hygroscopic material given above, the CAST

model describes water vapor by connecting $\Delta\bar{g}(u, T)$ in Eq. (18) with $\Delta\bar{g} = -RT \ln a_w$ (see Eq. 12). Solving for u leads to an equilibrium sorption model:

$$u = \frac{(-RT \ln a_w + \beta_6)^{-1/\beta_5} - \beta_4}{\beta_1 e^{-\beta_2/T} + \beta_3} \quad (26)$$

This equation can be inverted to give the thermodynamic water activity:

$$a_w = \frac{\varphi_g P_g}{\varphi_{gl} P_{gl}} = \exp \left[\frac{-\Delta\bar{g}(u, T)}{RT} \right] = \exp \left\{ \frac{-[u(\beta_1 e^{-\beta_2/T} + \beta_3) + \beta_4]^{-\beta_5} + \beta_6}{RT} \right\} \quad (27)$$

This results in a parabolic equation for the water vapor pressure p_g after substitution of the empirical expression for the fugacity coefficient from Eq. (9). Solving the parabolic equation completes the analytical inversion process.

Equations (18), (19), (24), (26), and (27) thus allow calculation of quantities that can be compared with experimentally determined values. The model is intended for general application to cellulosic materials for RH levels of 0.995 and below. It is not intended for modeling EMC in the over-hygroscopic region because materials differ considerably in pore volume distribution. In materials such as wood the EMC increases dramatically at higher RH levels with capillary water [25, 59]. The extrapolated values u_f and X_f given above should not be interpreted as being physically significant; they are not intended for comparison with any experimentally determined values. Nevertheless, the form of the equation for u_f provides a convenient way of normalizing the EMC. Combining Eqs. (25) and (26) yields

$$\frac{u}{u_f} = \frac{(-RT \ln a_w + \beta_6)^{-1/\beta_5} - \beta_4}{\beta_6^{-1/\beta_5} - \beta_4} \quad (28)$$

This normalized EMC from the CAST model is a function of $-RT \ln a_w$ alone; this dependence was shown previously by Willems [60] across several datasets for water vapor sorption in wood.

4 Model evaluation methods

This section documents the selection of experimental data from the literature, the additional sorption models used for comparison, and the optimization methods used for fitting the data.

4.1 Literature data selection

Zelinka et al. [61] evaluated literature on water vapor sorption measurements in wood at multiple temperatures up to 100 °C to identify datasets that could be used for thermodynamic analysis and testing equilibrium sorption models. They evaluated data quality based on several criteria: the stringency involved in determining when specimens reached equilibrium, often stated as a threshold for change in mass with time; measurement uncertainty for moisture content, temperature, and relative humidity; and stability of temperature and relative humidity conditions. From the datasets considered most reliable by Zelinka et al. [61], the data of Weichert [57] for spruce and beech covered the widest range of temperatures. This dataset was used as digitized by Zelinka et al. [61]. The literature on sorption data at temperatures above 100 °C has not been evaluated with the same level of detail, though Pearson et al. [62] highlighted the experimental challenges involved and the discrepancies between different publications with increasing temperature. To supplement the data of Weichert at temperatures above 100 °C, we included data for beech from Engelhardt [52], which we digitized from the published plot of EMC vs. RH data points at 110–170 °C. In addition, Engelhardt [52] provided a measured sorption curve for beech at 20 °C (though discrete points were not provided); this curve closely matches the beech data of Weichert [57] at 25 °C (SI Part IV).

Calorimetric data for the same wood species is sparse and limited to the low temperature range. We selected the heat of wetting data of Volbehr [63] for spruce and Harmon and Burcham [64] for beech. The former was taken from tabulated values of q_{wet} and initial moisture content, u_i . For the latter, the measured data points were not reported; instead, the published plot of q_{wet} vs. u_i had curves drawn by hand to best represent the data. We thus estimated discrete values from the original curves at u_i intervals of 0.01 kg kg⁻¹. In addition, we selected calorimetric data for beech

Table 2 Synopsis of experimental data from the literature used in model evaluation

Type of measurement	Reference	Wood	Temperature (°C)	RH range or initial EMC (u_i) range
Sorption isotherm	Weichert [57]	Unspecified spruce, unspecified beech	25, 50, 75, 100	RH: 0.02–0.99 (absorption)
	Engelhardt [52]	Beech (<i>Fagus sylvatica</i> L.)	110, 130, 150, 170	RH: 0.10–0.96 (absorption)
Heat of wetting	Volbehr [63]	Unspecified spruce	0	u_i : 0.003–0.277 kg kg ⁻¹
Heat of wetting	Hearmon and Burcham [64]	Unspecified beech	17, 28, 39, 47, 61, 71	u_i : 0–0.25 kg kg ⁻¹
Heat of wetting	Nopens et al. [35]	Beech (<i>Fagus sylvatica</i> L.)	25 ^a	u_i : 0–0.20 kg kg ⁻¹
Sorption calorimetry (differential enthalpy)	Nopens et al. [35]	Beech (<i>Fagus sylvatica</i> L.)	25	RH: 0–0.80 (absorption)

^aTemperature not specified; 25 °C assumed based on related measurements

from Nopens et al. [35] for both heat of wetting measured by solution calorimetry and differential enthalpy measured by sorption calorimetry. Heat of wetting was digitized from the published plot of q_{wet} vs. u_i . Differential enthalpy of sorption (referred to in the original as “mixing enthalpy”) was obtained from the authors, and mean values of three replicates at intervals of 0.01 kg kg⁻¹ were calculated. Relevant details of the various datasets are summarized in Table 2.

For consistency, all sorption data included here were measured in absorption (starting from a dry initial condition), and heat of wetting data were either initially dry or conditioned to an initial EMC by absorption. Desorption is not considered in this evaluation, but the model is expected to have the versatility to fit both absorption and desorption data, which will be examined in future work.

In addition to these primary datasets, we consider the calculated differential enthalpy of sorption from Weichert [65], who applied the Clausius-Clapeyron equation to his sorption data for spruce and beech (25–100 °C). We also draw comparisons with the influence of temperature on the total heat of wetting measured by Kelsey and Clarke [66] for Klinki pine and by Kajita [67] for Hinoki.

The effects of swelling pressures within the wood cell wall on the thermodynamics of sorption are implicitly included in the experimental data summarized above. It is important to note that the thermodynamic framework underlying the CAST model assumes a system at constant total pressure. Measurements of the heat of wetting described above were conducted at atmospheric pressure, so this condition is met. However, water vapor sorption measurements were not strictly at constant total pressure but included a

range of pressures from partial vacuum at 25–100 °C [57] to well above atmospheric pressure at higher temperatures [52]. The influence of external pressure is further discussed in SI Part V, which shows that the effect of this range of pressures on the sorption data and differential enthalpy of sorption is negligible.

4.2 Other sorption models

Several additional equilibrium sorption models were fitted to the same datasets described above. The models are described briefly below with full details in SI Part VI.

4.2.1 Modified Guggenheim-Anderson-de Boer model (GAB6)

The original GAB model, named after Guggenheim [68], Anderson [69], and de Boer [70] is a three-parameter isotherm equation. This model has been widely used for cellulosic materials including agricultural products, paper, textiles, and wood [19, 20, 24, 54, 71, 72]. The GAB model was derived from an idealized view of multilayer adsorption of molecules on the surface of an adsorbent. It was modified to include temperature explicitly, for example, by Weisser [54], where each model parameter was expanded with a form resembling Arrhenius reaction kinetics. The parameters of the original model have been identified with physical quantities in previous literature (e.g., number of sorption sites and enthalpy values). However, Thybring et al. [24] demonstrated that the model-predicted values are not valid for water vapor sorption in wood. We therefore treat the parameters as empirical coefficients and express the model as follows:

$$u = \frac{\gamma_1 \gamma_2 \gamma_3 a_w}{(1 - \gamma_3 a_w) [1 + (\gamma_2 - 1) \gamma_3 a_w]}, \text{ with } \gamma_1 = \delta_1 e^{\delta_2/T}; \gamma_2 = \delta_3 e^{\delta_4/T}; \gamma_3 = \delta_5 e^{\delta_6/T} \quad (29)$$

where $\delta_1 \dots \delta_6$ are fitting parameters. We refer this as the GAB6 model.

4.2.2 Modified Nelson model (NA6)

The original model of Nelson [39] is a two-parameter isotherm equation formulated with the natural logarithm of $\Delta \bar{g}$ as a linear function of EMC, with $\Delta \bar{g}$ related to RH using the ideal gas equivalent of Eq. (12). Anderson [12] modified this model to include temperature explicitly, expanding each parameter as a second order polynomial function of temperature:

$$\ln \Delta \bar{g} = \kappa_1 + \kappa_2 u, \text{ with } \kappa_1 = \lambda_1 + \lambda_2 T + \lambda_3 T^2; \kappa_2 = \lambda_4 + \lambda_5 T + \lambda_6 T^2 \quad (30)$$

where $\lambda_1 \dots \lambda_6$ are fitting parameters. The abbreviation “NA6” is used for this model based on the names Nelson & Anderson and the number of parameters. The original and modified forms have been applied to wood, cellulose, and foliar materials in fire modeling [12–14, 23, 39]. Although the original models assumed ideal gas behavior, which was suitable for the temperature ranges considered, here we use thermodynamic water activity and express the model as

$$a_w = \exp\left(\frac{-\Delta \bar{g}}{RT}\right) = \exp\left\{\frac{-\exp[\kappa_1 + \kappa_2 u]}{RT}\right\} \\ = \exp\left\{\frac{-\exp[\lambda_1 + \lambda_2 T + \lambda_3 T^2 + (\lambda_4 + \lambda_5 T + \lambda_6 T^2)u]}{RT}\right\} \quad (31)$$

4.2.3 Modified Oswin model (OC3)

The original model of Oswin [73] is a two-parameter isotherm equation. It was modified to include temperature explicitly [74] and has been applied to a variety of materials including foods [20, 33, 75, 76], wood [77], and a cellulosic membrane [78]. The abbreviation “OC3” is used for this model based on the names Oswin & Chen and the number of fitting parameters. Water activity is given by

$$a_w = \frac{1}{1 + \left(\frac{\omega_1 - \omega_2 T}{u}\right)^{\omega_3}} \quad (32)$$

where ω_1 , ω_2 , and ω_3 are positive fitting parameters.

4.2.4 Models derived from Othmer's postulate (ODE4 and ODP6)

The differential enthalpy of sorption (relative to liquid water) at low temperatures can be obtained from the slope of a log-log plot of RH for constant EMC at different temperatures vs. saturation vapor pressure of pure water. This method,

based on the work of Othmer [79, 80], has been widely used to determine the differential enthalpy of sorption of water vapor in cellulosic materials [40, 81–84]. Othmer postulated that the ratio $\Delta \bar{h}/\Delta_l^s h$ is dependent only on EMC (that is, invariant with temperature). However, Othmer's method gives appreciable errors compared to the Clapeyron equation for analysis of high-temperature sorption data because it assumes ideal gas behavior (SI Part IV).

We derive two sorption models based on this postulate (SI Part VI), using a linear equation for $\Delta_l^s h$ and two different functional forms for the EMC dependence of $\Delta \bar{h}$. The first form is an exponential decay function, which gives the following model:

$$a_w = \exp\left\{-\frac{C}{RT_{ref}} - \varepsilon_1 \exp(-\varepsilon_2 u) \left[\frac{L_0}{RT} - \frac{L_0}{RT_{ref}} + \frac{L_1}{R} \ln\left(\frac{T}{T_{ref}}\right)\right]\right\} \quad (33)$$

where ε_1 , ε_2 , C , and T_{ref} are fitting parameters and L_0 and L_1 are constants related to $\Delta_l^s h$. The abbreviation “ODE4” is used for this model based on the names Othmer & Dietenberger, the exponential form, and the number of fitting parameters.

The second form is a power-law function, which gives the following model:

$$a_w = \exp\left\{-\frac{C}{RT_{ref}} - [\zeta_1 (u + \zeta_2)^{-\zeta_3} + \zeta_4] \left[\frac{L_0}{RT} - \frac{L_0}{RT_{ref}} + \frac{L_1}{R} \ln\left(\frac{T}{T_{ref}}\right)\right]\right\} \quad (34)$$

where $\zeta_1 \dots \zeta_4$, C , and T_{ref} are fitting parameters and L_0 and L_1 are constants related to $\Delta_l^s h$. The abbreviation “ODP6” is used for this model based on the names Othmer & Dietenberger, the power-law form, and the number of fitting parameters.

The inverted forms of these models, equations for differential enthalpy of sorption and heat of wetting, and further details are given in SI Part VI.

4.3 Model optimization

Two different approaches were used for fitting experimental data and identifying model parameters. Goodness of fit was quantified using the coefficient of determination (R^2). The first approach maximized only $R^2(u)$ to test whether fitting EMC alone gives accurate predictions of other quantities, such as heat of wetting and differential enthalpy of sorption. The second approach maximized the weighted average R^2 across multiple quantities, to assess the ability of the models to simultaneously fit all the data. Weighting factors were selected to maintain good fitting of EMC values while improving the fitting of the other quantities. Weighting factors were set to 1 for sources with data at multiple temperatures, i.e., sorption data [52, 57] and heat of wetting data of Hearmon and Burcham [64]. Weighting factors were set

to 0.1 for sources with data at a single temperature, i.e., $\Delta\bar{h}$ values of Weichert [65] and calorimetry data of Volbehr [63] and Nopens et al. [35].

For both approaches, the generalized reduced gradient method was used in the Excel Solver (Microsoft Corp., Redmond, WA, USA). Different sets of initial parameter values were explored to avoid possible local minima.

5 Model evaluation results and discussion

The first approach (optimizing only EMC) yielded higher values of R^2 for the six-parameter models (CAST, GAB6, NA6, and ODP6) than the three- and four-parameter models (OC3 and ODE4). Details are provided in SI Part VII (Tables S6 and S7). Values of $R^2(u)$ and $R^2(a_w)$ for the CAST, GAB6, and ODP6 models were in the range 0.995–0.999, with the NA6 model having slightly lower values. In general, the fitting of the heat of wetting and differential enthalpy of sorption were inadequate when the models were optimized only to EMC data. Nonetheless, the CAST model gave the best results for q_{wet} and Δh for this approach, although q_{wet} was systematically underpredicted and mean relative errors for both quantities were in the range 7–27% across the different wood species and data sources. Given this finding, we focus on the second optimization approach below (simultaneously fitting u , a_w , q_{wet} , and $\Delta\bar{h}$).

Table 3 Parameter values of the CAST model fitted to sorption and calorimetric data (with u in kg kg^{−1}, T in K, and $\Delta\bar{g}$ in kJ mol^{−1})

Parameter	Beech	Spruce
β_1	46.33	304.2
β_2	777.6	1661
β_3	2.028	3.520
β_4	0.2210	0.3895
β_5	1.725	2.886
β_6	0.3664	0.2006

5.1 Overview

The optimized CAST model parameters are listed in Table 3. Values of R^2 for the various models are reported in Tables 4 and 5 based on each set of experimental data. Overall, these fitting statistics indicate that the CAST model represents the sorption data and related thermodynamic quantities exceptionally well. Although the experimental datasets for beech and spruce are taken from disparate publications spanning from 1896 to 2019, they are unified effectively by the CAST model coupled with the improved thermodynamic framework. For example, the beech data include sorption isotherm measurements from two publications covering the range 25–170 °C [52, 57], heat of wetting data from two publications [35, 64], and sorption calorimetry data directly giving the differential enthalpy [35]. It is interesting to note that the CAST model provides a close link between the spruce dataset of Volbehr [63], which is considered the first publication

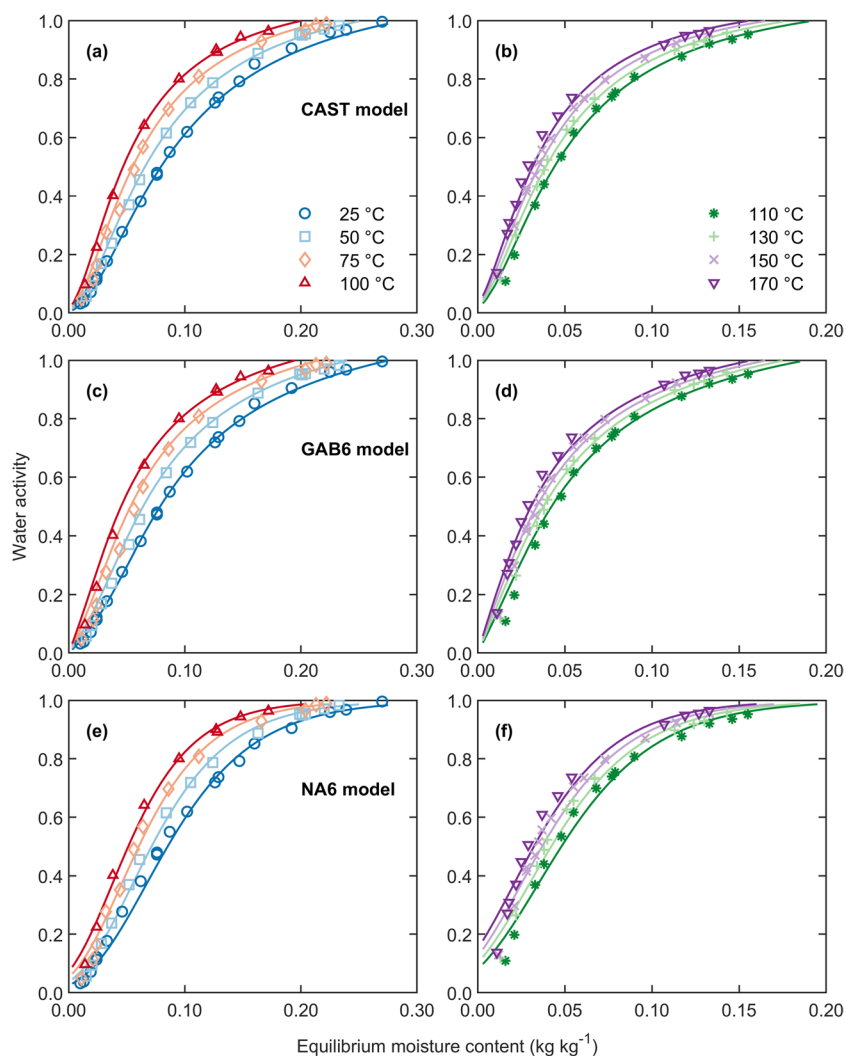
Table 4 Coefficient of determination (R^2) for various models fitted to beech data

Quantity	Data source	CAST	GAB6	NA6	OC3	ODE4	ODP6
u	Weichert [57]	0.995	0.995	0.974	0.792	0.941	0.986
	Engelhardt [52]	0.997	0.996	0.983	0.844	0.863	0.968
a_w	Weichert [57]	0.998	0.994	0.995	0.955	0.963	0.994
	Engelhardt [52]	0.994	0.988	0.977	0.891	0.880	0.970
$\Delta\bar{g}$	Weichert [57]	0.988	-	0.962	-	0.923	0.969
	Engelhardt [52]	0.975	-	0.908	-	0.715	0.903
q_{wet}	Hearmon and Burcham [64]	0.996	0.990	0.986	0.825	0.853	0.975
	Nopens et al. [35]	0.934	0.903	0.938	0.822	0.869	0.960
$\Delta\bar{h}$	Weichert [65]	0.990	0.956	0.946	0.716	0.903	0.982
	Nopens et al. [35]	0.962	0.923	0.934	0.875	0.800	0.745

Table 5 Coefficient of determination (R^2) for various models fitted to spruce data

Quantity	Data source	CAST	GAB6	NA6	OC3	ODE4	ODP6
u	Weichert [57]	0.998	0.992	0.993	0.947	0.978	0.994
a_w	Weichert [57]	0.999	0.993	0.996	0.971	0.985	0.994
$\Delta\bar{g}$	Weichert [57]	0.992	-	0.979	-	0.919	0.967
q_{wet}	Volbehr [63]	0.999	0.957	0.994	0.855	0.887	0.987
$\Delta\bar{h}$	Weichert [65]	0.998	0.959	0.995	0.929	0.925	0.914

Fig. 7 Fits of select models (solid curves) to beech data (discrete points) of Weichert [57] (left column) and Engelhardt [52] (right column)



on heat of wetting of wood, and the spruce sorption isotherm data of Weichert [57], which was recently identified as one of a select few publications giving reliable sorption data for wood at multiple temperatures [61].

Curve fits for the CAST model, GAB6 model, and NA6 model to sorption data for beech are plotted in Fig. 7, with residuals in modeled water activity plotted in Fig. 8. Curve fits for spruce sorption data are shown in SI Part VIII. The exceptional goodness of fit of the CAST model to sorption data across the wide range of temperatures is evident. Although nonrandom patterns in the residuals are evident in Fig. 8, they are less pronounced for the CAST model than the GAB6 and NA6 models. The GAB6 and NA6 models give lower R^2 values than the CAST model for both beech and spruce across all quantities, with one exception in each case. The primary disadvantage of the GAB6 model is that it does not allow analytical integration for calculating the heat of wetting. Thus, while the GAB6 model is useful for interpolation of sorption data over much of the RH range, it is not as versatile for thermodynamic modeling as the CAST

model. The NA6 model statistics for spruce are consistently good and overall better than for beech, though this model does not fit the low a_w region well, particularly with increasing temperature. This may imply that the NA6 model is better suited to a limited temperature range.

The fitting statistics for the OC3 and ODE4 models are clearly inferior to those for the CAST model, although this would be expected given that they have only three or four parameters, respectively. A drawback of the linear temperature dependence in the OC3 model is that extrapolation to higher temperatures may yield nonphysical negative values of u . The ODE4 model also gives negative u values at low a_w , particularly with increasing temperature. The ODE4 model captures the general shape of the heat of wetting and the differential enthalpy of sorption (SI Part VI) but does not reproduce the effect of temperature nearly as well as the CAST model.

Although the ODP6 model generally fits the data more accurately than the ODE4 model (with two exceptions), it does not fit sorption data well at the low and high regions

Fig. 8 Residuals in modeled water activity based on fits from Fig. 7

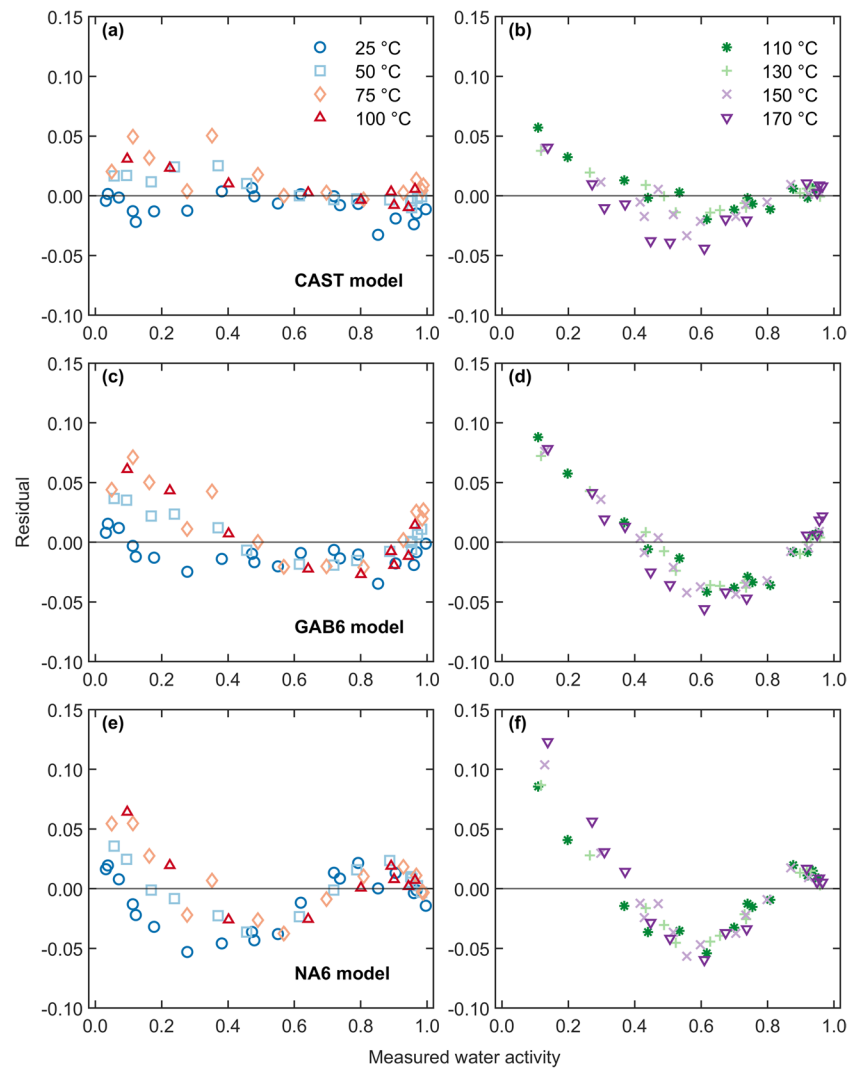
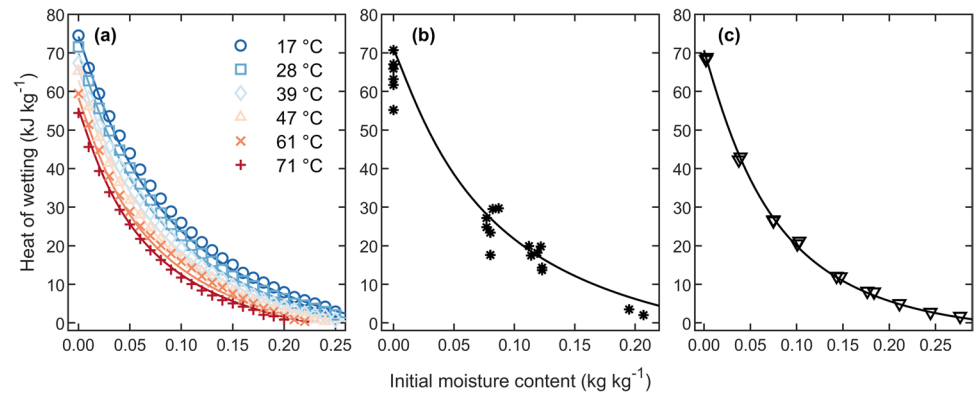


Fig. 9 Heat of wetting vs. initial moisture content from the CAST model (solid curves) fit to data (discrete points) of **a** Hearmon and Burcham [64] for beech at a series of temperatures, **b** Nopens et al. [35] for beech at 25 °C, and **c** Volbehr [63] for spruce at 0 °C



(SI Part VI). In all cases but one, the statistics for the CAST model are superior to those for the ODP6 model.

5.2 Heat of wetting

The heat of wetting given by the CAST model is plotted in Fig. 9a with experimental data for beech [64] for a series

of temperatures as a function of initial moisture content. The ability of the model to replicate the shape of the data across a wide range of moisture contents and temperatures is noteworthy. The data of Nopens et al. [35] for beech at 25 °C is plotted in Fig. 9b. Although the calorimetric data exhibit considerable scatter, the CAST model represents the shape correctly. The heat of wetting of spruce at

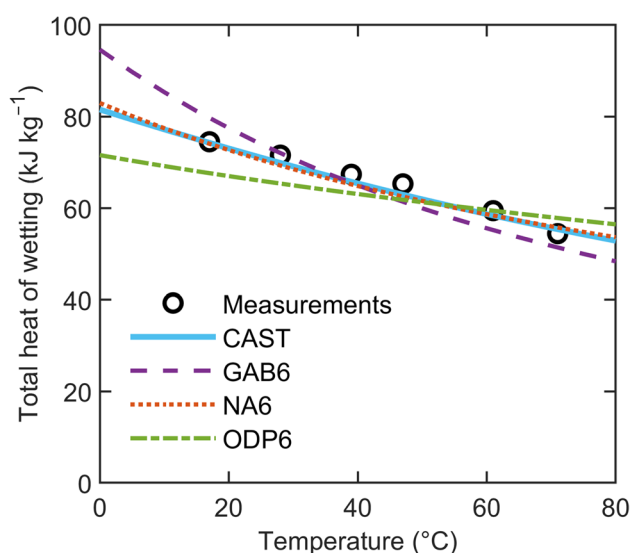


Fig. 10 Variation of the total heat of wetting of beech with temperature given by various models compared with measurements of Hearmon and Burcham [64]

0 °C [63] is plotted in Fig. 9c, with negligible deviation between model and experimental data. The CAST model thus provides exceptional agreement with both calorimetric data and sorption isotherm data across a broad range of temperatures.

The influence of temperature on the total heat of wetting for select models for beech is shown in Fig. 10. The CAST and NA6 model curves are clearly consistent with the data of Hearmon and Burcham [64]. The slopes of these curves are also consistent with calorimetric measurements for Klinki pine [66] and Hinoki [67], which found that the total heat of wetting decreases with increasing temperature at a rate of approximately -0.4 to -0.3 $\text{kJ kg}_{\text{ds}}^{-1} \text{K}^{-1}$. On the other hand, the GAB6 and ODP6 models do not fit the data as well. Given the lack of data for the influence of temperature on the heat of wetting of spruce (only 0 °C data), the model fitting of spruce data was not constrained to reproduce the

slope observed for the other wood species. The total heat of wetting of spruce measured by Volbehr [63] at 0 °C is lower than would be expected based on the temperature dependence of the other woods. This may be a result of different sample preparation methods. For spruce, the CAST model fitting yielded a temperature dependence of the total heat of wetting of $+0.10$ $\text{kJ kg}_{\text{ds}}^{-1} \text{K}^{-1}$ at 30 °C.

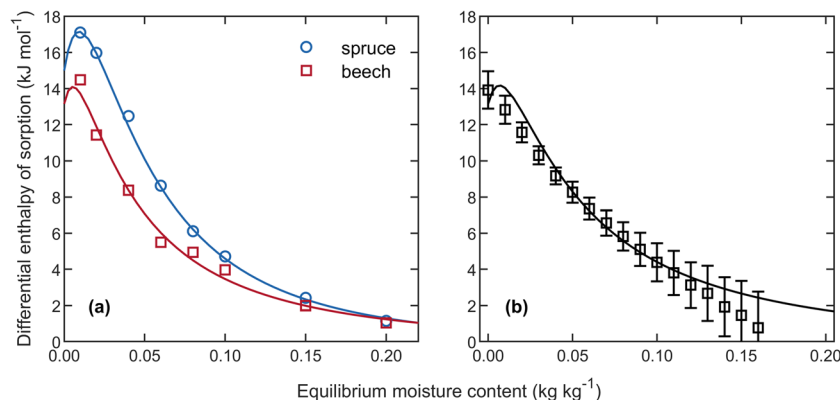
5.3 Differential enthalpy and entropy of sorption

The differential enthalpy of sorption given by the CAST model is compared in Fig. 11a with values reported by Weichert [65] for spruce and beech at 62.5 °C from analysis using the Clausius-Clapeyron equation and in Fig. 11b with sorption calorimetry data from Nopens et al. [35] for beech at 25 °C. The model correctly represents the shape of the data, and discrepancies are mostly within experimental uncertainty.

The differential enthalpy of sorption predicted by the CAST model at 25 °C is plotted vs. the differential entropy in Fig. 12, for the range of u values of beech and spruce corresponding to those measured by Weichert [57]. The linearity over most of the range indicates that the model is nearly in agreement with literature describing enthalpy-entropy compensation for water vapor sorption in various cellulosic materials [20, 85–90]. Departures from linearity in Fig. 12 are evident for larger values of $\Delta\bar{h}$ and $\Delta\bar{s}$, which correspond with $u < 0.04$ kg kg^{-1} . A linear relationship between $\Delta\bar{h}$ and $\Delta\bar{s}$ was not imposed on the CAST model because it is not clear that a fundamental theoretical basis for this exists. In a recent review of enthalpy-entropy compensation, Khrapunov [91] argued that the linear relationship may arise from correlated errors in enthalpy and entropy and recommended that these errors be quantified.

None of the studies cited above included uncertainty analysis. However, Thybring et al. [24] used the Monte Carlo method to determine the uncertainty in the differential enthalpy of sorption calculated from the data of Weichert [57] using the Clausius-Clapeyron equation. This work

Fig. 11 Differential enthalpy of sorption vs. equilibrium moisture content from the CAST model (solid curves) compared with values (discrete points) reported by **a** Weichert [65] at 62.5 °C and **b** Nopens et al. [35] at 25 °C, where error bars indicate standard deviation of three replicates



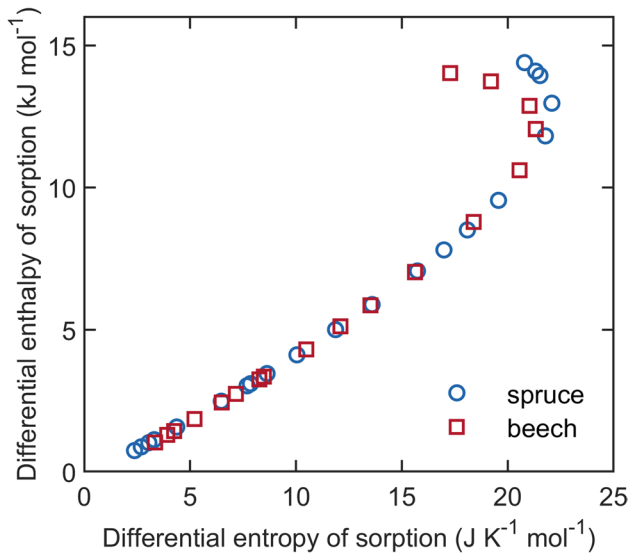


Fig. 12 Enthalpy-entropy plot for the CAST model fit to data at 25 °C [57]

showed that uncertainty in $\Delta\bar{h}$ increases appreciably with decreasing u . Although the study did not discuss enthalpy-entropy compensation, it suggests that further work is needed to assess the uncertainties in $\Delta\bar{g}$, $\Delta\bar{h}$, and $\Delta\bar{s}$ at low u and evaluate any correlation. In SI Part VI, we show that linear enthalpy-entropy compensation is a direct consequence of Othmer's postulate. But as shown previously, the models derived from Othmer's postulate do not fit the data as accurately as the CAST model.

5.4 Properties near saturation

Equilibrium moisture content curves at $a_w = 0.995$ for the various model fits to beech data are plotted as a function of temperature in Fig. 13a. The CAST model and GAB6 model show similar curves, with the NA6 model offset to slightly higher EMC. These models have the advantage of avoiding nonphysical negative u values at higher temperatures. The linear fit of Pearson et al. [62] to literature data for various wood species near 100% relative humidity is shown for comparison. This linear fit should be treated with caution given the experimental challenges with measurements at high temperature and relative humidity discussed by Pearson et al. [62], the use of extrapolation, the number of different wood species represented, and the inclusion of data that are now known to be unreliable, i.e., historic data from the Forest Products Laboratory [77].

Absorbed water in the material has thermodynamic properties very close to pure water as the water activity approaches unity. The differential enthalpy of sorption would thus be expected to approach zero. The predicted $\Delta\bar{h}$ at $a_w = 0.995$ (corresponding to high EMC) is plotted

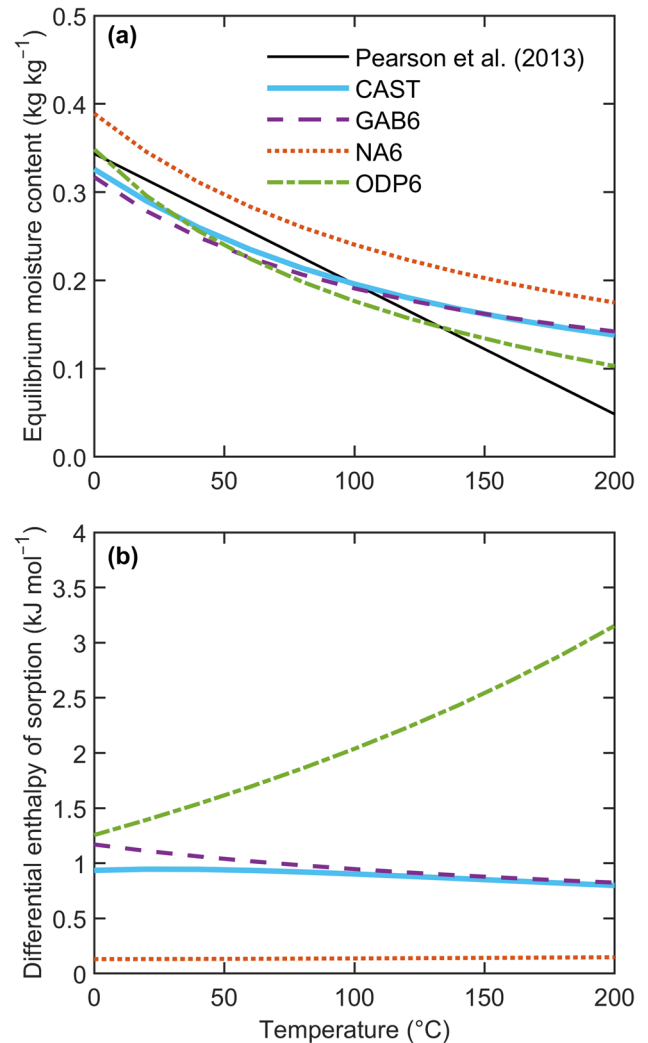


Fig. 13 **a** Equilibrium moisture content at $a_w = 0.995$ as a function of temperature from model fits to beech data, and linear fit of Pearson et al. [62] to literature data near 100% RH; **b** Differential enthalpy of sorption at $a_w = 0.995$ as a function of temperature

in Fig. 13b as a function of temperature for select models. The magnitude of $\Delta\bar{h}$ for the CAST model ($< 1 \text{ kJ mol}^{-1}$) is small relative to the magnitude at low EMC shown in Fig. 11 ($\sim 14 \text{ kJ mol}^{-1}$) and does not vary appreciably with temperature. This may reflect a cancellation of two phenomena: EMC decreases as temperature increases (Fig. 13a) while $\Delta\bar{h}$ increases as EMC decreases (Fig. 11). For applications where sorption modeling is used in simulation of coupled heat and moisture transfer, it may be advantageous for $\Delta\bar{h}$ to be small but nonzero for computational robustness. The GAB6 model curve is similar to the CAST model, whereas the NA6 model has a lower magnitude. In contrast, the ODP6 model has a higher magnitude that increases considerably with temperature.

Although the CAST model is not intended for fitting $a_w > 0.995$, it provides a convenient way of normalizing the

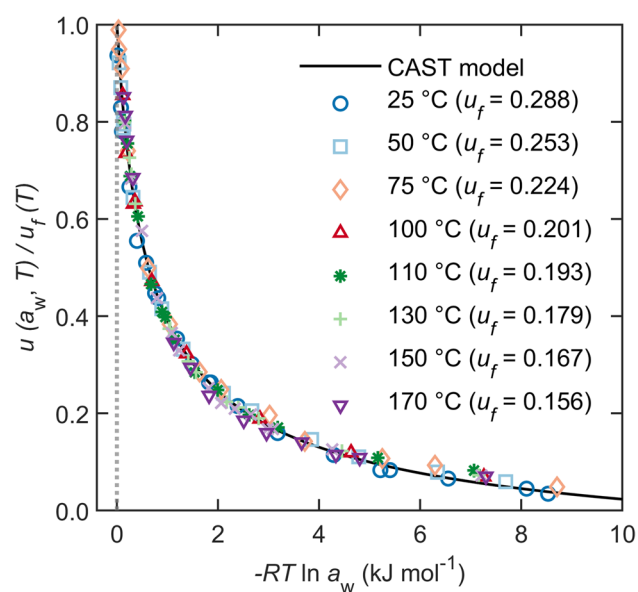


Fig. 14 Normalized equilibrium moisture content vs. differential Gibbs energy of sorption for the CAST model and beech data of Engelhardt [52] and Weichert [57]

EMC, as given by Eq. (28). The normalized EMC is plotted as a function of $\Delta\bar{g} = -RT \ln a_w$ in Fig. 14 for the CAST model and experimental beech data. Other sorption models are not included in Fig. 14 because none of them gives normalized EMC as a function of $-RT \ln a_w$ alone. The difference between $u(a_w = 0.995, T)$ shown in Fig. 13a and $u_f(T)$ is generally less than 0.008 kg kg^{-1} . This method of plotting the data yields a single curve over a range of temperatures, as shown previously by Willems [60] across several datasets for water vapor sorption in wood. However, we point out several differences. First, the experimental values in Fig. 14 are normalized by $u_f(T)$ calculated from Eq. (25) at each temperature (indicated in the legend). The constants $\beta_1 \dots \beta_6$ used for calculating $u_f(T)$ are optimized by simultaneously fitting all the experimental quantities listed in Table 2; this includes calorimetric data in addition to sorption data. In contrast, Willems [60] used a different extrapolation method for the corresponding value, denoted EMC_{max} in that work, which relied on sorption data alone; see Willems [92] for further details. Second, the universality of the relationship shown in Fig. 14 covers a wider range of temperatures; the highest temperature here is 170°C as opposed to 100°C in Willems [60]. Third, the thermodynamic water activity is used here instead of relative humidity.

6 Conclusions

This article clarifies the thermodynamics of water vapor sorption in cellulosic materials and formulates a new model that seamlessly links equilibrium sorption data with multiple

thermodynamic quantities. We overcome two main limitations of prior work: (i) reliance on the ideal gas equation and (ii) lack of consistency between different aspects of sorption theory, often reflected in discrepancies between model predictions and independently measured thermodynamic properties.

We formulate a new model known as the Comprehensive Analytical Sorption Thermodynamic (CAST) model that is consistent with the thermodynamic framework advanced in this article. An empirical relationship between the differential Gibbs energy of sorption ($\Delta\bar{g}$), equilibrium moisture content (u), and temperature (T) serves to generate analytical equations for the differential enthalpy of sorption ($\Delta\bar{h}$), the differential entropy of sorption ($\Delta\bar{s}$), and the integral heat of wetting (q_{wet}). The fundamental relationship between $\Delta\bar{g}$ and water activity (a_w) yields a six-parameter equilibrium sorption model that can be expressed as $u(a_w, T)$ or inverted to give $a_w(u, T)$. The CAST model is evaluated using sorption data and calorimetric data from the wood science literature over a wide range of temperatures. It fits the experimental data with higher accuracy than several other models, including the six-parameter modified GAB model. Although the experimental datasets are from disparate literature sources spanning many decades, they are unified effectively by the CAST model. The relatively simple analytical equations of the CAST model provide accurate values over a wide range of temperature and moisture conditions, making it simple to implement in computer simulations of heat and moisture transfer.

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Data availability No datasets were generated or analysed during the current study. This study relied on literature data for model evaluation

(Table 2). Previously published data that were digitized for this study are available upon request.

Declarations

Ethics approval and consent to participate This study did not involve human or animal participants.

Consent for publication All authors agreed with the content and gave explicit consent to submit this article.

Competing interests The authors declare no competing interests.

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Supplementary Information¹

Journal: *Adsorption*

Comprehensive Analytical Sorption Thermodynamic (CAST) model for water vapor sorption in cellulosic materials

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¹ Numbered equations, figures, and tables mentioned in this document that do not begin with the letter “S” are found in the main manuscript.

I. Empirical Equations for Properties of Water

This section specifies the empirical equations used for calculating the saturation properties of water, compressibility factor, and fugacity coefficient. In addition, it describes a linear approximation for the enthalpy of vaporization.

Saturation vapor pressure, liquid molar volume, and vapor molar volume

Wagner and Pruss (1993) provide equations for saturation properties of pure liquid water and water vapor, which can be found in the appendix to their article (International Association for the Properties of Water and Steam, September 1992 *Revised Supplementary Release on Saturation Properties of Ordinary Water Substance*). Values calculated with these equations are compared with current standard reference data (Lemmon et al. 2022; Wagner and Pruss 2002; IAPWS 2018), which we subsequently refer to as the steam table.

The saturation vapor pressure p_{gl} is given by (Wagner and Pruss 1993)

$$\ln\left(\frac{p_{gl}}{p_c}\right) = \frac{T_c}{T} (a_1\tau + a_2\tau^{1.5} + a_3\tau^3 + a_4\tau^{3.5} + a_5\tau^4 + a_6\tau^{7.5}) \quad (S1)$$

where p_c is the critical pressure (22.064 MPa), T is temperature (K), T_c is the critical temperature (647.096 K), $\tau = 1 - T/T_c$, and $\{a_1, a_2, a_3, a_4, a_5, a_6\} = \{-7.85951783, 1.84408259, -11.7866497, 22.6807411, -15.9618719, 1.80122502\}$. Eq. (S1) agrees with the steam table to within better than 0.01% between the triple point (273.16 K) and the critical point (647.096 K).

The molar volume of saturated liquid water ($\text{m}^3 \text{mol}^{-1}$) was calculated from the molar mass ($0.018015268 \text{ kg mol}^{-1}$) and the density of saturated liquid ρ_l (kg m^{-3}) given by (Wagner and Pruss 1993)

$$\frac{\rho_l}{\rho_c} = 1 + b_1\tau^{1/3} + b_2\tau^{2/3} + b_3\tau^{5/3} + b_4\tau^{16/3} + b_5\tau^{43/3} + b_6\tau^{110/3} \quad (S2)$$

where ρ_c is the critical density (322 kg m^{-3}) and $\{b_1, b_2, b_3, b_4, b_5, b_6\} = \{1.99274064, 1.09965342, -0.510839303, -1.75493479, -45.5170352, -6.74694450 \times 10^5\}$. Eq. (S2) agrees with the steam table to within 0.05% between 273.16 K and 634 K, and within 0.2% up to 647.096 K.

The molar volume of saturated water vapor was calculated from the molar mass and the density of saturated vapor ρ_{gl} (kg m^{-3}) given by (Wagner and Pruss 1993)

$$\ln\left(\frac{\rho_{gl}}{\rho_c}\right) = c_1\tau^{2/6} + c_2\tau^{4/6} + c_3\tau^{8/6} + c_4\tau^{18/6} + c_5\tau^{37/6} + c_6\tau^{71/6} \quad (S3)$$

where $\{c_1, c_2, c_3, c_4, c_5, c_6\} = \{-2.03150240, -2.68302940, -5.38626492, -17.2991605, -44.7586581, -63.9201063\}$. Eq. (S3) agrees with the steam table to within better than 0.05% between 273.16 K and 638 K, and within 0.2% up to 647.096 K.

Calculated values of the enthalpy of vaporization of water with the Clapeyron equation (Eq. 1) and Eqs. (S1)–(S3) yield the black dotted curve in Fig. 1, which agrees with the steam table to within 0.05% up to 632 K. Because of the complexity of Eq. (S1), the derivative dp_{gl}/dT was evaluated numerically rather than analytically.

Compressibility factor

The compressibility factor is defined by $Z = p_g v_g / RT$, where p_g is the water vapor pressure (Pa), v_g is the molar volume of water vapor ($\text{m}^3 \text{mol}^{-1}$), and R is the gas constant ($8.31446 \text{ J K}^{-1} \text{mol}^{-1}$). A convenient empirical approximation, as a function of pressure and temperature, is given by Eq. (2) and

Eq. (3). The empirical constants k_1 , k_2 , and k_3 (0.186, 0.233, and 2.70, respectively) were optimized to fit the enthalpy of vaporization of water using the Clapeyron equation. Approximated values of Z are compared with reference values (calculated using p_g , v_g , and T from the steam table) in Fig. S1 as a function of relative humidity (p_g/p_{gl}) for select temperatures. The error in Z using this approximation is plotted in Fig. S2 for select temperatures.

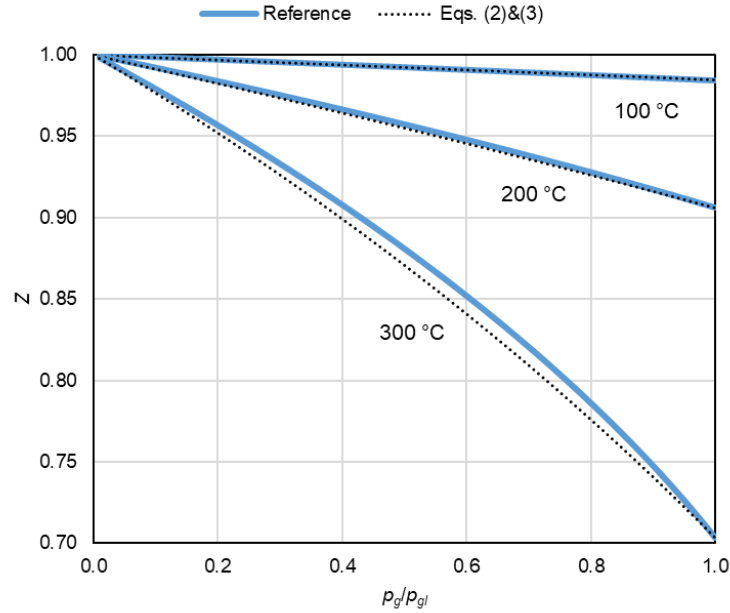


Fig. S1 Compressibility factor vs. relative humidity for select temperatures

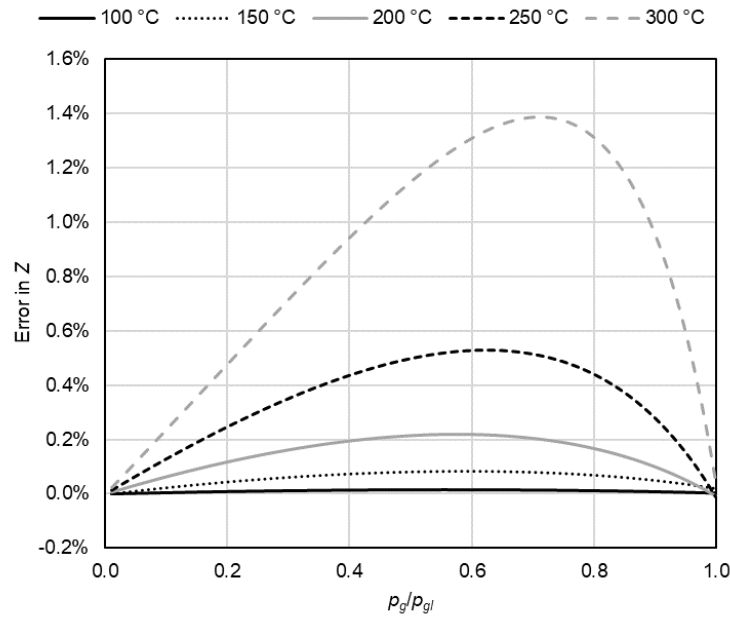


Fig. S2 Relative error in the compressibility factor calculated with Eqs. (2) and (3) as a function of relative humidity for select temperatures

Fugacity coefficient

The fugacity coefficient is defined by $\varphi = f_g/p_g$, where f_g is the water vapor fugacity and p_g is the water vapor pressure. The fugacity coefficient is related to the compressibility factor through the residual Gibbs energy ($g^R = g_g - g^\circ$) as follows (Smith et al. 2022, Eqs. 10.33–10.35):

$$\frac{g^R}{RT} = \ln \varphi = \left(\int_0^p \frac{Z-1}{p} dp \right)_T \quad (\text{S4})$$

The empirical approximation for Z given by Eqs. (2) and (3), with the integration of Eq. (S4), is consistent with the functional form of the fugacity coefficient given by Eq. (9).

Reference values of φ were calculated from the steam table as follows (see Smith et al. 2022, pp. 379–382). At low pressure, the fugacity coefficient approaches unity. Here we assumed that $\varphi = 1$ at a reference vapor pressure $p_{ref} = 1$ Pa. The molar Gibbs energy of water vapor g_g (J mol⁻¹) was calculated from reference values of molar enthalpy h_g (J mol⁻¹) and molar entropy s_g (J K⁻¹ mol⁻¹) using $g_g = h_g - Ts_g$, for water vapor pressures from $p_g/p_{gl} = 0.01$ to $p_g/p_{gl} = 1$ at temperatures from 0 °C to 300 °C in 25 °C increments. The fugacity coefficient as a function of pressure and temperature was calculated as

$$\varphi_g = \frac{p_{ref}}{p_g} \exp \left[\frac{g(p_g, T) - g(p_{ref}, T)}{RT} \right] \quad (\text{S5})$$

Approximated values of φ are compared with reference values for select temperatures in Fig. S3. The error in approximated values relative to reference values is plotted in Fig. S4.

The difference in molar Gibbs energy of water vapor (relative to saturation), $g_g - g_{gl}$, was calculated from molar enthalpy and entropy values in the steam table as described above. These reference values are compared in Fig. S5 with values of $\mu_g - \mu_{gl}$ calculated from Eq. (8) using the empirical approximation for the fugacity coefficient.

The ratio of fugacity coefficients (relative to saturation), φ_g/φ_{gl} , was calculated directly from the steam table for select temperatures with the following equation:

$$\frac{\varphi_g}{\varphi_{gl}} = \frac{p_{gl}}{p_g} \exp \left(\frac{g_g - g_{gl}}{RT} \right) \quad (\text{S6})$$

This ratio is plotted as a function of relative humidity in Fig. S6, shown as light blue curves. The relationship is approximately linear, providing support for the empirical form of Eq. (9), which is shown in Fig. S6 as black curves.

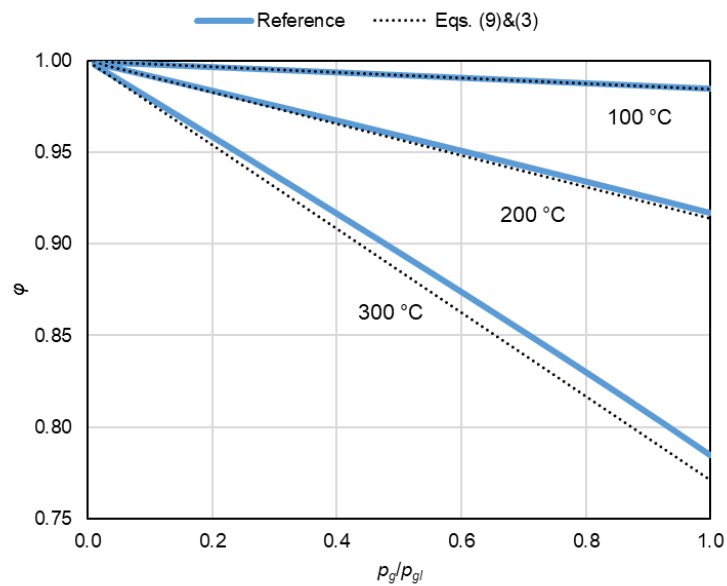


Fig. S3 Reference values of the fugacity coefficient (calculated with Eq. S5) and empirical approximation (Eqs. 9 and 3) as a function of relative humidity for select temperatures

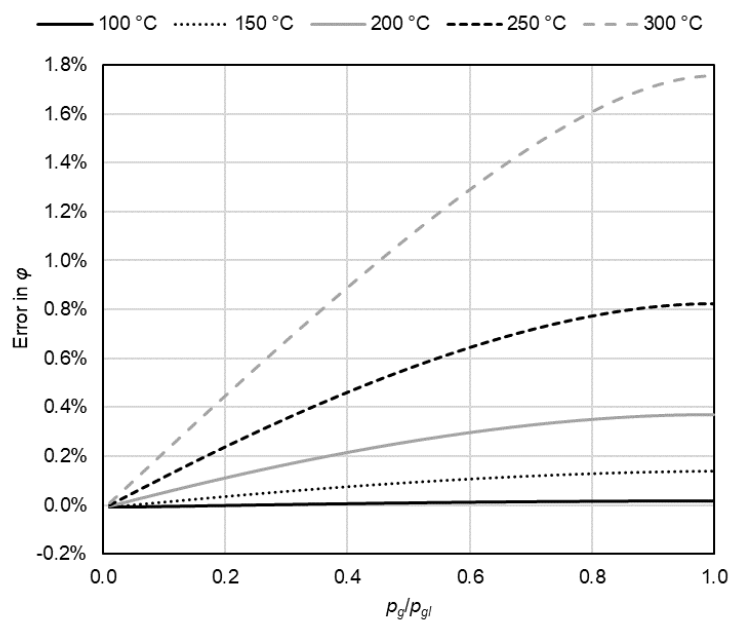


Fig. S4 Relative error in the fugacity coefficient calculated with Eqs. (9) and (3) as a function of relative humidity for select temperatures

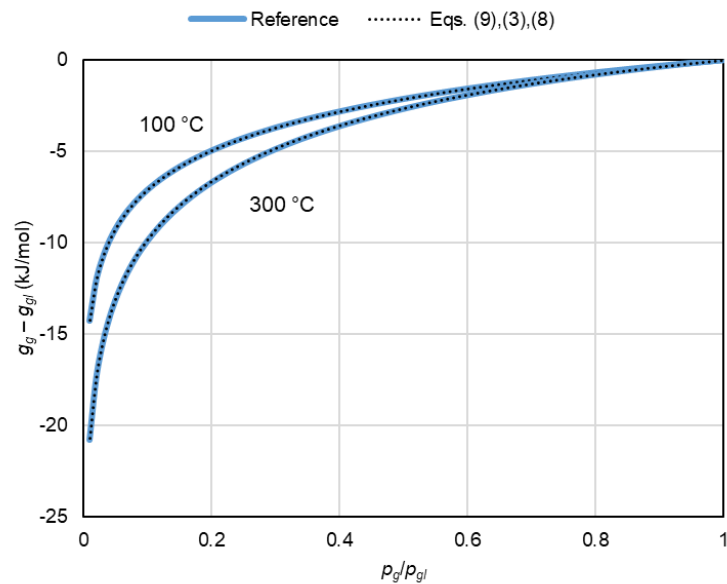


Fig. S5 Reference values of the difference in molar Gibbs energy of water vapor (calculated from the steam table) and values calculated using the empirical approximation for fugacity coefficient, as a function of relative humidity for select temperatures

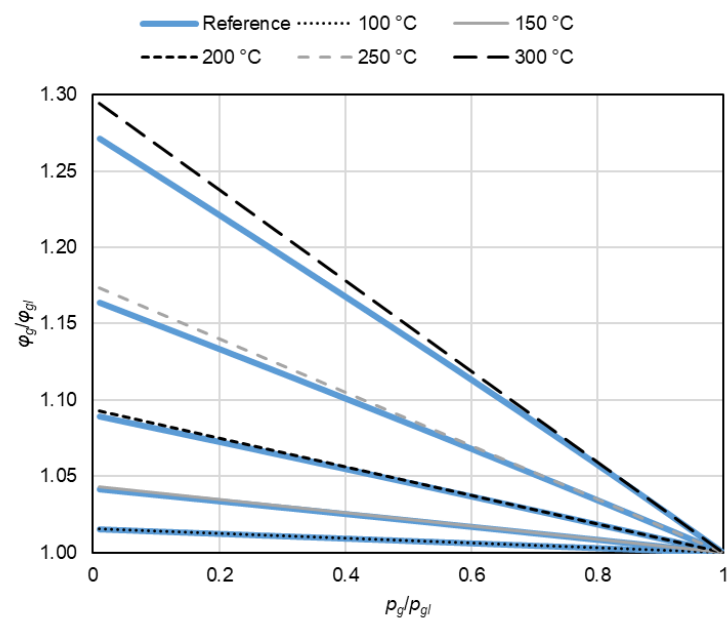


Fig. S6 Ratio of fugacity coefficients calculated with Eq. (S6) as a function of relative humidity for select temperatures (Reference blue curves) and calculated with Eqs. (9) and (3)

Linear approximation for enthalpy of vaporization

At low temperatures the enthalpy of vaporization can be approximated using a linear equation for (as suggested by Adkins 1968):

$$\Delta_l^g h \cong L_0 - L_1 T = 49.3 - 2.5RT \quad (\text{S7})$$

where L_0 and L_1 are constants and the value 49.3 is given in kJ mol^{-1} . This is shown as the blue dashed line in Fig. S7. Although it is clearly inadequate over a wide temperature range, the advantage of this equation is the relatively simple integration of the Clausius-Clapeyron equation to give the saturation vapor pressure as

$$p_{gl} \cong T^{-2.5} \exp(42.2 - 49.3/RT) \quad (\text{S8})$$

where p_{gl} is expressed in Pa and T is in K. Between 0°C and the critical point, the saturation vapor pressure from Eq. (S8) is accurate within 5.4%, but the corresponding enthalpy difference from Eq. (S7) merely approximates the Clausius-Clapeyron curve rather than the reference curve. Restricting the range from 0°C to 100°C (and optimizing the coefficients), the saturation vapor pressure is accurate within 0.1%. Thus, depending on the accuracy and temperature range desired for modeling, one can select appropriate equations from those given above.

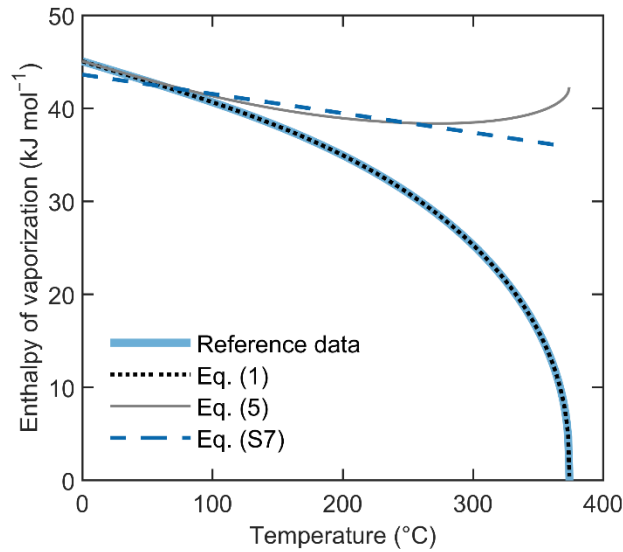


Fig. S7 Enthalpy of vaporization of water as a function of temperature from reference data, Clapeyron equation, Clausius-Clapeyron equation, and linear approximation

II. Derivation of the Differential Enthalpy of Sorption

This section provides a derivation of the differential enthalpy of water vapor sorption in a swelling solid absorbent at constant total pressure. This is a modification of the framework of Myers and Monson (2014), which describes multi-component gas adsorption in a microporous solid at constant volume. At constant total pressure, the heat given off by a reversible process corresponds to the change in enthalpy of the system. Thus, calorimetric measurements at constant total pressure (e.g., atmospheric pressure) can be directly related to enthalpy changes.

The system consists of two phases, gas and solid. The gas phase includes water vapor and any number of inert species (such as dry air). The inert species are neither adsorbed nor absorbed by the solid. The solid phase includes a solid absorbent and water molecules absorbed by the solid. The system is at constant external pressure, and both the gas phase and the solid phase may change volume. The partial pressure of water vapor p_g can be varied while the total pressure P remains constant. The system is semi-open in the sense that water vapor can be added from a reservoir. The system is closed for the solid absorbent and inert gas.

The criterion for equilibrium at constant temperature and total pressure is the equality of the chemical potential of water in the absorbed phase μ_a (J mol_w^{-1} , where the subscript “w” refers to water) and the chemical potential of water in the gas phase μ_g (J mol_w^{-1}).

Given the constraint of constant total pressure, the natural thermodynamic variables are enthalpy and Gibbs energy. The total Gibbs energy of the solid phase is G (J kg_{ds}^{-1} , where the subscript “ds” refers to dry solid), the total enthalpy of the solid phase is H (J kg_{ds}^{-1}), and the total entropy of the solid phase is S ($\text{J K}^{-1} \text{kg}_{ds}^{-1}$). These thermodynamic variables are expressed as specific extensive quantities, that is, normalized by the mass of dry solid.

Let n be the equilibrium amount of absorbed water ($\text{mol}_w \text{kg}_{ds}^{-1}$). For the solid phase with constant mass of solid absorbent, at constant total pressure, we have

$$dH = TdS + \mu_a dn \quad (\text{S9})$$

$$dG = -SdT + \mu_a dn \quad (\text{S10})$$

Differentiating Eq. (S9) with respect to n gives

$$\left(\frac{\partial H}{\partial n}\right)_{T,P} = T \left(\frac{\partial S}{\partial n}\right)_{T,P} + \mu_a \quad (\text{S11})$$

The partial derivative on the right side of Eq. (S11) can be transformed using a Maxwell relation based on the Gibbs energy (from Eq. S10; for further details on Maxwell relations, see Ott and Boerio-Goates 2000 or Smith et al. 2022). Since dG is an exact differential, it follows that

$$\left(\frac{\partial S}{\partial n}\right)_{T,P} = -\left(\frac{\partial \mu_a}{\partial T}\right)_{P,n} \quad (\text{S12})$$

Substitution of Eq. (S12) into Eq. (S11) yields

$$\left(\frac{\partial H}{\partial n}\right)_{T,P} = \mu_a - T \left(\frac{\partial \mu_a}{\partial T}\right)_{P,n} = -T^2 \left[\frac{\partial \left(\frac{\mu_a}{T}\right)}{\partial T} \right]_{P,n} \quad (\text{S13})$$

The chemical potential of absorbed water can be expressed in terms of water vapor fugacity f_g as

$$\mu_a = \mu_g = \mu^\circ + RT \ln \frac{f_g}{f^\circ} \quad (\text{S14})$$

where μ° is the chemical potential of the ideal gas reference state and $f^\circ = 1$ bar. We subsequently express f_g in bar and drop the symbol f° . The fugacity can be calculated from $f_g = \phi \cdot p_g$, where ϕ is the fugacity coefficient (see Supplementary Information Part I).

Substitution of Eq. (S14) into the partial derivative on the right side of Eq. (S13) yields

$$\left[\frac{\partial \left(\frac{\mu_a}{T} \right)}{\partial T} \right]_{P,n} = \left[\frac{\partial \left(\frac{\mu^\circ}{T} \right)}{\partial T} \right]_P + \left[\frac{\partial (R \ln f_g)}{\partial T} \right]_{P,n} \quad (\text{S15})$$

The first term on the right side of Eq. (S15) can be related to the enthalpy of the ideal gas reference state, h° (J mol_w⁻¹), through the Gibbs-Helmholtz relation (for further details see Ott and Boerio-Goates 2000 or Smith et al. 2022):

$$\left[\frac{\partial \left(\frac{\mu^\circ}{T} \right)}{\partial T} \right]_P = -\frac{h^\circ}{T^2} \quad (\text{S16})$$

Substitution of Eq. (S15) and Eq. (S16) into Eq. (S13) yields

$$\left(\frac{\partial H}{\partial n} \right)_{T,P} = h^\circ - RT^2 \left(\frac{\partial \ln f_g}{\partial T} \right)_{P,n} \quad (\text{S17})$$

The term on the left side of Eq. (S17) is called the differential enthalpy of absorbed water and given the following symbol:

$$\bar{h}_a \equiv \left(\frac{\partial H}{\partial n} \right)_{T,P} \quad (\text{S18})$$

This quantity represents the differential change in the enthalpy of the system in response to transferring δn moles of water vapor per kilogram of dry solid to the solid phase at constant temperature and total pressure. This includes contributions from both absorbent–water interactions and water–water interactions.

We now express the differential enthalpy of sorption with respect to pure liquid water, combining Eqs. (S17) and (S18) and subtracting the molar enthalpy of pure liquid water h_l (J mol_w⁻¹):

$$\Delta_l^a \bar{h} = \bar{h}_a - h_l = h^\circ - h_l - RT^2 \left(\frac{\partial \ln f_g}{\partial T} \right)_{P,n} \quad (\text{S19})$$

This equation can be simplified by relating pure liquid water to the ideal gas reference state through the chemical potential:

$$\mu_l = \mu^\circ + RT \ln \frac{f_{gl}}{f^\circ} \quad (\text{S20})$$

where f_{gl} is the fugacity of water vapor in equilibrium with pure liquid water (at saturation). Applying the Gibbs-Helmholtz relation to Eq. (S20) yields

$$\left[\frac{\partial \left(\frac{\mu_l}{T} \right)}{\partial T} \right]_P = \left[\frac{\partial \left(\frac{\mu^\circ}{T} \right)}{\partial T} \right]_P + \left[\frac{\partial (R \ln f_{gl})}{\partial T} \right]_P \quad (\text{S21})$$

This simplifies to

$$-\frac{h_l}{T^2} = -\frac{h^\circ}{T^2} + R \left(\frac{\partial \ln f_{gl}}{\partial T} \right)_P \quad (\text{S22})$$

or

$$h^\circ - h_l = RT^2 \left(\frac{\partial \ln f_{gl}}{\partial T} \right)_P \quad (\text{S23})$$

Substitution of Eq. (S23) into Eq. (S19) and changing the sign to give a positive quantity, we have

$$\Delta_a {}^l \bar{h} = h_l - \bar{h}_a = RT^2 \left[\frac{\partial \ln(f_g/f_{gl})}{\partial T} \right]_{P,n} = RT^2 \left(\frac{\partial \ln a_w}{\partial T} \right)_{P,n} \quad (\text{S24})$$

where a_w is the thermodynamic water activity.

III. Equivalence of the Clapeyron Equation and Solution Thermodynamics for the Enthalpy of Vaporization of Water

This section shows the enthalpy of vaporization of water from the Clapeyron equation is equivalent to that derived from solution thermodynamics for the limiting condition of absorbed water in a hygroscopic material approaching its maximum water content.

The Clapeyron equation can be written as

$$\Delta_a^g \bar{h} = h_g - \bar{h}_a = (v_g - \bar{v}_a)T \left(\frac{\partial p_g}{\partial T} \right)_n = \left(1 - \frac{\bar{v}_a p_g}{ZRT} \right) \frac{ZRT^2}{p_g} \left(\frac{\partial p_g}{\partial T} \right)_n \quad (\text{S25})$$

where $\Delta_a^g \bar{h}$ is the difference in enthalpy (J mol^{-1}) for absorbed water changing to water vapor, h_g is the molar enthalpy of water vapor (J mol^{-1}), $\bar{h}_a$ is the differential molar enthalpy of absorbed water (J mol^{-1}), v_g is the molar volume of water vapor ($\text{m}^3 \text{mol}^{-1}$), $\bar{v}_a = \left(\frac{\partial V_s}{\partial n} \right)_{T,p}$ is the partial molar volume of absorbed water ($\text{m}^3 \text{mol}^{-1}$), V_s is the total specific volume of the solid phase ($\text{m}^3 \text{kg}^{-1}$), T is absolute temperature (K), p_g is water vapor pressure (Pa), n is water content (mol kg^{-1}), and Z is the compressibility factor.

Solution thermodynamics has been applied to gas adsorption in microporous solids to derive the isosteric heat of adsorption (Myers 2002; Myers and Monson 2014). We provide a brief overview here for the case of a single adsorbate and refer the reader to the original papers for full details. The derivation assumes that the volume of the solid phase is constant. The natural thermodynamic variables are internal energy and Helmholtz energy, except for the reference state, which refers to the gas phase behaving ideally at constant pressure of 1 bar. For applications where the total pressure varies but volume is constant, the heat of adsorption is expressed in terms of a difference in internal energy between the gas phase and the adsorbed phase. On the other hand, for applications where total pressure is constant (such as adsorption columns), the heat of adsorption is expressed in terms of a difference in enthalpy between the gas phase and the adsorbed phase. In this case, the isosteric heat of adsorption q_{st} (J mol^{-1}) is expressed as (Myers and Monson 2014)

$$q_{st} = h_g - \bar{h}_a = RT^2 \left(\frac{\partial \ln f_g}{\partial T} \right)_n + (h_g - h^\circ) - \frac{V_s}{(\partial n / \partial p_g)_T} \quad (\text{S26})$$

The second term in this equation is known as the residual enthalpy ($h^R = h_g - h^\circ$) and can be determined from the residual Gibbs energy (Eq. S4) by the Gibbs-Helmholtz relation (Smith et al. 2022, Eq. 6.44):

$$\frac{h^R}{RT} = -T \left(\frac{\partial (g^R/RT)}{\partial T} \right)_P = -T \left(\frac{\partial \ln \phi}{\partial T} \right)_P \quad (\text{S27})$$

The last term in Eq. (S26) depends on the specific volume of the solid and the slope of the sorption isotherm, $(\partial n / \partial p_g)_T$. Because this approach is based on solution thermodynamics, the description of gas adsorption in porous materials can be adapted to water vapor sorption in cellulosic materials. For such materials, the sorption isotherm is steep as p_g approaches p_{gl} , so the last term in Eq. (S26) is expected to be negligible.

Substitution of Eq. (S27) into Eq. (S26), using $f_g = \phi p_g$, and neglecting the last term in Eq. (S26), we obtain

$$q_{st} \cong \frac{RT^2}{\varphi} \left[\left(\frac{\partial \varphi}{\partial T} \right)_n - \left(\frac{\partial \varphi}{\partial T} \right)_p \right] + \frac{RT^2}{p_g} \left(\frac{\partial p_g}{\partial T} \right)_n \quad (\text{S28})$$

Using the empirical function for fugacity coefficient (Eq. 9), the partial derivatives are evaluated as

$$\left(\frac{\partial \varphi}{\partial T} \right)_n = (\varphi - 1) \left(\frac{1}{K(T)} \frac{\partial K(T)}{\partial T} + \frac{1}{p_g} \frac{\partial p_g}{\partial T} \right) \quad (\text{S29})$$

and

$$\left(\frac{\partial \varphi}{\partial T} \right)_p = (\varphi - 1) \left(\frac{1}{K(T)} \frac{\partial K(T)}{\partial T} \right) \quad (\text{S30})$$

Substituting Eqs. (S29) and (S30) into Eq. (S28), we obtain

$$q_{st} \cong \left(\frac{\varphi - 1}{\varphi} + 1 \right) \frac{RT^2}{p_g} \left(\frac{\partial p_g}{\partial T} \right)_n = Z \frac{RT^2}{p_g} \left(\frac{\partial p_g}{\partial T} \right)_n \quad (\text{S31})$$

The simple result on the right side of Eq. (S31) stems from the functional forms selected for the fugacity coefficient (Eq. 9) and the compressibility factor (Eq. 2). This only requires the fugacity coefficient to be a linear function of pressure, and therefore Eq. (S31) may apply also to other gases. Calculation of the enthalpy of vaporization of water using Eq. (S31) yields the green curve in Fig. S8, which compares well with the steam table over much of the temperature range but deviates at higher temperatures. Comparing Eq. (S31) with the Clapeyron equation (Eq. S25), we establish the relationship

$$\Delta_a^g \bar{h} = h_g - \bar{h}_a \cong \left(1 - \frac{\bar{v}_a p_g}{ZRT} \right) q_{st} \quad (\text{S32})$$

This adjustment to the formulation of Myers and Monson (2014) for the isosteric heat of adsorption, when applied to the limiting condition of vaporization of pure water, achieves accuracy relative to the steam table to within 0.05% up to 318 °C, which is identical to the Clapeyron equation (Eq. S25) shown as the red curve in Fig. S8. The adjustment factor in Eq. (S32) accounts for the molar volume of the liquid phase, which was neglected in the approach leading to Eq. (S31). This confirms the equivalence of the Clapeyron equation and the solution thermodynamics description of gas adsorption in porous solids (Myers and Monson 2014) adapted for water vapor sorption in a hygroscopic material approaching its maximum water content.

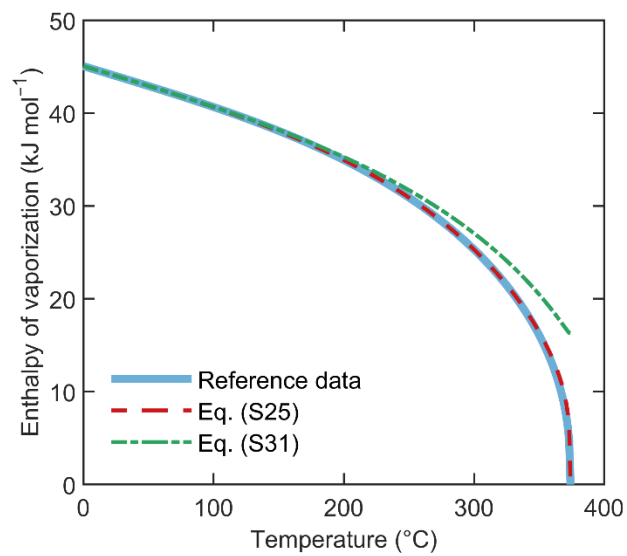


Fig. S8 Enthalpy of vaporization of water as a function of temperature calculated by various methods

IV. Comparative Analysis of the Differential Enthalpy of Sorption Using High Temperature Data

This section compares three methods for calculating the differential enthalpy of sorption using isotherm data at multiple temperatures. The dataset of Engelhardt (1979) for beech wood was selected because it covers a range of temperatures from 110 °C to 170 °C with a wide range of relative humidity values. Known reference values for the properties of water (Lemmon et al. 2022; Wagner and Pruss 2002; IAPWS 2018) or interpolated values are used to the extent possible to avoid potential bias from approximations.

The Clapeyron equation gives the enthalpy of vaporization of pure water to high accuracy below the critical point (see Fig. 1). The application of the Clapeyron equation to mixtures in general is described by Ott and Boerio-Goates (2000), and its application to gas adsorption at surfaces is described by Smith et al. (2022). Because water vapor sorption in cellulosic materials involves equilibrium between two phases, the Clapeyron equation is applicable.

The wood–water mixture is characterized by water vapor pressure p_g (Pa), temperature T (K), and composition, expressed as equilibrium moisture content u (mass ratio of water to dry solid, $\text{kg}_w \text{kg}_{ds}^{-1}$). The Clapeyron equation for this system is

$$h_g - \bar{h}_a = (v_g - \bar{v}_a)T \left(\frac{\partial p_g}{\partial T} \right)_u \quad (\text{S33})$$

where h_g is the molar enthalpy of water vapor (J mol^{-1}), $\bar{h}_a$ is the differential molar enthalpy of absorbed water (J mol^{-1}), v_g is the molar volume of water vapor ($\text{m}^3 \text{mol}^{-1}$), and $\bar{v}_a$ is the partial molar volume of absorbed water ($\text{m}^3 \text{mol}^{-1}$). The analysis yields the differential enthalpy change $\Delta_a^g \bar{h} = h_g - \bar{h}_a$, for a series of u and T values. Because of its exact formulation, the Clapeyron equation is considered the benchmark in this analysis.

In addition to the Clapeyron equation, the sorption data are analyzed using the thermodynamic framework developed in Section 2 of the main manuscript as well as the Othmer equation (Othmer 1940), which has been widely applied to water vapor sorption in cellulosic materials at low temperatures.

Methods

Interpolation of sorption isotherm data

Engelhardt (1979) published water vapor sorption data for beech wood (*Fagus sylvatica* L.) as a plot of (a_w^i, u) pairs at temperatures of 110 °C, 130 °C, 150 °C, and 170 °C, where a_w^i is relative humidity ($a_w^i = p_g/p_{gl}$). The plotted data points from the original publication were digitized and are replotted in Fig. S9. In addition, Engelhardt (1979) provided a measured sorption curve for beech at 20 °C (though discrete points were not provided); this curve closely matches the beech data of Weichert (1963) at 25 °C as shown in Fig. S10.

Linear interpolation was used to arrive at (T, a_w^i) pairs for a series of constant u values starting at 0.016 $\text{kg}_w \text{kg}_{ds}^{-1}$ (the lowest measured value across all temperature values) and increasing in increments of 0.01 $\text{kg}_w \text{kg}_{ds}^{-1}$ from 0.02 to 0.13 $\text{kg}_w \text{kg}_{ds}^{-1}$. (The highest measured value common to all temperatures was 0.133 $\text{kg}_w \text{kg}_{ds}^{-1}$.) The (T, a_w^i) pairs were transformed into (T, p_g) pairs for the series of constant u values based on reference values for $p_{gl}(T)$.

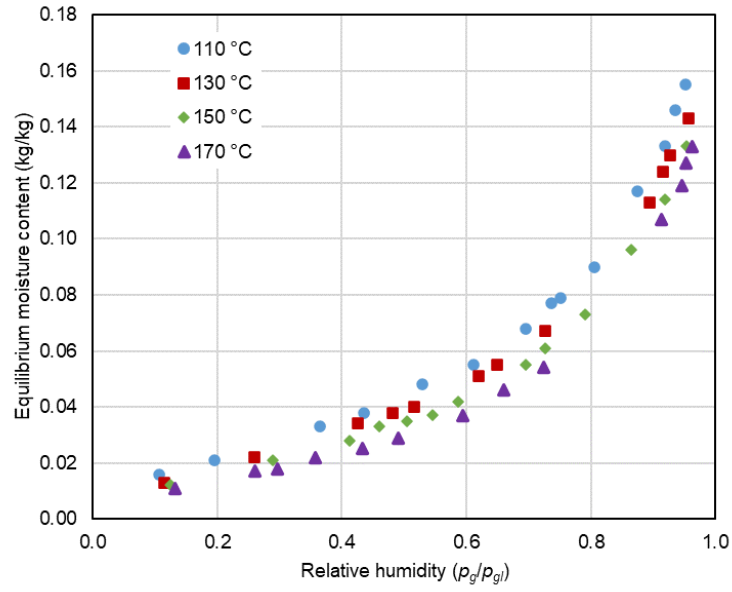


Fig. S9 Water vapor sorption data for beech at high temperatures, digitized from Engelhardt (1979)

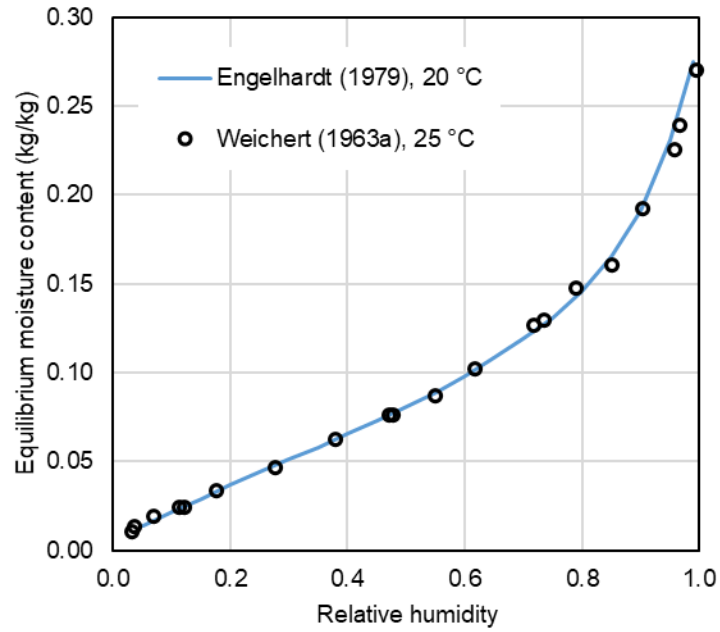


Fig. S10 Comparison of water vapor sorption data for beech digitized from a continuous curve at 20 °C (Engelhardt 1979) and from discrete points at 25 °C (Weichert 1963a)

Molar volume of water vapor

The compressibility factor Z was calculated from reference values of p_g and v_g at each temperature for the range of pressures from $p_g/p_{gl} = 0.01$ to $p_g/p_{gl} = 1$. For each (T, p_g) pair, the corresponding value of Z was found by interpolation. The molar volume of water vapor was then calculated as

$$v_g = \frac{ZRT}{p_g} \quad (\text{S34})$$

Partial molar volume of absorbed water

The partial molar volume of absorbed water in wood is the change in total volume of the mixture upon an infinitesimal increase in the number of moles of absorbed water, holding temperature, pressure, and amount of wood constant. Data for the partial molar volume of absorbed water in beech wood at high temperatures is not available. In this analysis, we make the approximation $\bar{v}_a \cong v_l$ and take the molar volume of pure liquid water from reference data. Measurements of hygro-expansion of wood cell walls at room temperature indicate that the partial molar volume of absorbed water is considerably less than that of liquid water at low moisture contents (e.g., Stamm and Seborg 1935). This effect is examined by repeating the calculations with the approximation $\bar{v}_a \cong v_l/2$.

Partial derivative of water vapor pressure with respect to temperature at constant EMC

This analysis calculates the partial derivative of water vapor pressure with respect to temperature at constant u by fitting an empirical equation to the (T, p_g) data for a given u and taking the analytical derivative. Given the limited temperature range, the water vapor pressure was approximated using a modified form of the Antoine equation:

$$\ln p_g = d_1 - \frac{d_2}{T - d_3} \quad (\text{S35})$$

where d_1 , d_2 , and d_3 are empirical constants. This equation was first fitted to reference values of the saturation vapor pressure of pure water between 100 °C and 180 °C, and agreement within 0.01% was achieved with $\{d_1, d_2, d_3\} = \{23.1309, 3773.18, 47.98\}$. The analytical derivative of Eq. (S35) is

$$\left(\frac{\partial \ln p_g}{\partial T}\right)_u = \frac{1}{p_g} \left(\frac{\partial p_g}{\partial T}\right)_u = \frac{B}{(T - C)^2} \quad (\text{S36})$$

The values of d_1 and d_2 were optimized for each series of (T, p_g) pairs at constant u , keeping the value $d_3 = 47.98$ constant (which was identified for the saturation vapor pressure of pure water). Example curve fits of Eq. (S35) to the (T, p_g) data for a series of u values are shown in Fig. S11.

The accuracy of the simple analytical derivative in Eq. (S36) was verified by calculating the enthalpy of vaporization of pure water using Equation (S33). Calculated values were within 0.03% of reference values for temperatures between 110 °C and 170 °C.

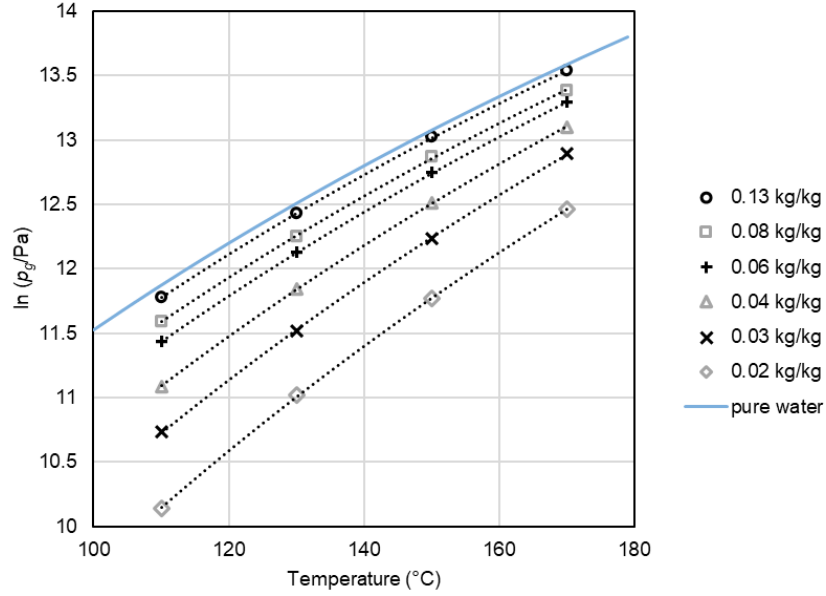


Fig. S11 Natural logarithm of equilibrium water vapor pressure vs. temperature. Points were interpolated from the data of Engelhardt (1979) at select EMCs. Dotted curves are fit to the points using Eq. (S35); note that Eq. (S35) uses Kelvin temperature rather than Celsius temperature (which is displayed in the figure for convenience). Solid curve is based on reference values for pure water at saturation.

Clapeyron equation

The total differential enthalpy change $\Delta_a^g \bar{h}$ was calculated using the following equation, based on Eq. (S33):

$$\Delta_a^g \bar{h} = h_g - \bar{h}_a \cong T(v_g - v_l) \left(\frac{\partial p_g}{\partial T} \right)_u \quad (\text{S37})$$

This equation incorporates the methods and approximations discussed above.

Thermodynamic framework approach

This approach involves summing three components to obtain the total differential enthalpy change (see Fig. 4):

$$\Delta_a^g \bar{h} = (h_g - h_{gl}) + (h_{gl} - h_l) + (h_l - \bar{h}_a) \quad (\text{S38})$$

The first term on the right side was found by interpolation based on reference values of molar enthalpy of water vapor for pressures from $p_g/p_{gl} = 0.01$ to $p_g/p_{gl} = 1$ at temperatures corresponding to the sorption data (383.15 K, 402.15 K, 423.15 K, and 443.15 K).

The second term on the right side of Eq. (S38) is the enthalpy of vaporization of pure water, which was taken directly from reference values at each temperature.

The third term on the right side of Eq. (S38) is calculated as

$$\Delta_a {}^l \bar{h} = h_l - \bar{h}_a = RT^2 \left(\frac{\partial \ln \frac{f_g}{f_{gl}}}{\partial T} \right)_u \quad (\text{S39})$$

where f_g is the fugacity of water vapor in equilibrium with absorbed water in wood and f_{gl} is the fugacity of water vapor in equilibrium with pure liquid water. Reference values of the fugacity coefficient were calculated according to the method described in Part I (Eq. S5) at temperatures corresponding to the sorption data. For each (T, p_g) pair, the corresponding value of ϕ_g was found by interpolation.

The partial derivative in Eq. (S39) was calculated as

$$\left(\frac{\partial \ln \frac{f_g}{f_{gl}}}{\partial T} \right)_u = \left(\frac{\partial \ln \frac{\phi_g p_g}{\phi_{gl} p_{gl}}}{\partial T} \right)_u = \left(\frac{\partial \ln p_g}{\partial T} \right)_u - \frac{d \ln p_{gl}}{dT} + \left(\frac{\partial \ln \frac{\phi_g}{\phi_{gl}}}{\partial T} \right)_u \quad (\text{S40})$$

The first term on the right side was calculated using Eq. (S36), identical to the approach used for the Clapeyron equation. The second term was calculated using the same approach based on the fit to the saturation vapor pressure. The third term was calculated using either a linear fit or parabolic fit to the natural logarithm of the ratio of fugacity coefficients vs. temperature.

Othmer equation

For comparison, the data of Engelhardt (1979) were analyzed using the method of Othmer (1940), which can be expressed as

$$\ln p_g = \frac{\Delta_a {}^g \bar{h}}{\Delta_l {}^g \bar{h}} \ln p_{gl} + \text{constant} \quad (\text{S41})$$

where $\Delta_l {}^g \bar{h}$ is the enthalpy of vaporization of pure water vapor. This equation relies on the assumption that water vapor behaves as an ideal gas. For each series of u values, the ratio of enthalpies was determined from a linear regression of $\ln p_g$ vs. $\ln p_{gl}$. An example is shown in Fig. S12. The total differential enthalpy change $\Delta_a {}^g \bar{h}$ was calculated as the product of the slope of the regression and the reference value of the enthalpy of vaporization of pure water for each temperature.

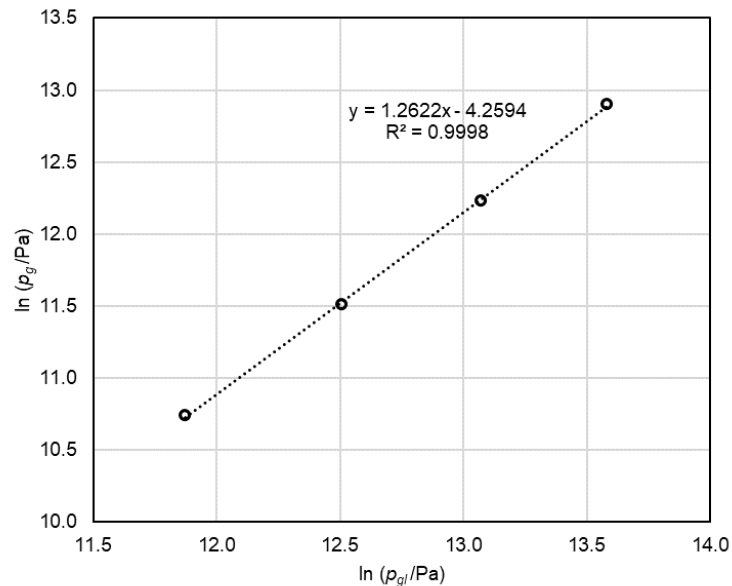


Fig. S12 Natural logarithm of equilibrium water vapor pressure vs natural logarithm of pure water saturation vapor pressure with linear regression. Points were interpolated from the data of Engelhardt (1979) at $u = 0.03 \text{ kg}_w \text{ kg}_{ds}^{-1}$

Results and discussion

The total differential enthalpy change $\Delta_a^g \bar{h}$ calculated using the Clapeyron equation is plotted in Fig. S13 as a function of EMC for each temperature. As expected, the magnitude decreases with increasing u and increasing T . The approximation $\bar{v}_a \cong v_l/2$ (instead of $\bar{v}_a \cong v_l$) changed the calculated enthalpy by only 0.08 kJ mol^{-1} (0.2%) or less.

The differential enthalpy of sorption $\Delta_a^l \bar{h}$ (relative to pure liquid water) obtained using the thermodynamic framework approach is plotted in Fig. S14 for the lowest and highest temperatures. In this case temperature did not have a strong effect; differences at a given EMC were $< 0.3 \text{ kJ mol}^{-1}$.

The values of $\Delta_g^a \bar{h}$ calculated with the Clapeyron equation and the thermodynamic framework agreed closely, as shown in Fig. S15. Differences between these two approaches were within 0.08 kJ mol^{-1} , or less than 0.2%.

In contrast, the Othmer equation yields $\Delta_g^a \bar{h}$ values that deviate substantially from those calculated with the Clapeyron equation, despite the highly linear log-log plots (Fig. S12). The differences in $\Delta_g^a \bar{h}$ between the Clapeyron equation and the Othmer equation are plotted in Fig. S16. As expected, the differences increase with temperature, as departures from ideal gas behavior become more pronounced at higher temperatures. Differences are as large as 2.9 kJ mol^{-1} ($> 5\%$). The perhaps counterintuitive result that the enthalpy differences are largest for the lowest EMC values can be explained by the fact that the Othmer equation treats water vapor as an ideal gas across the full range of pressures. Departures from ideal gas behavior increase with pressure, so differences are more pronounced for vapor pressures far from saturation, which corresponds with lower EMC values.

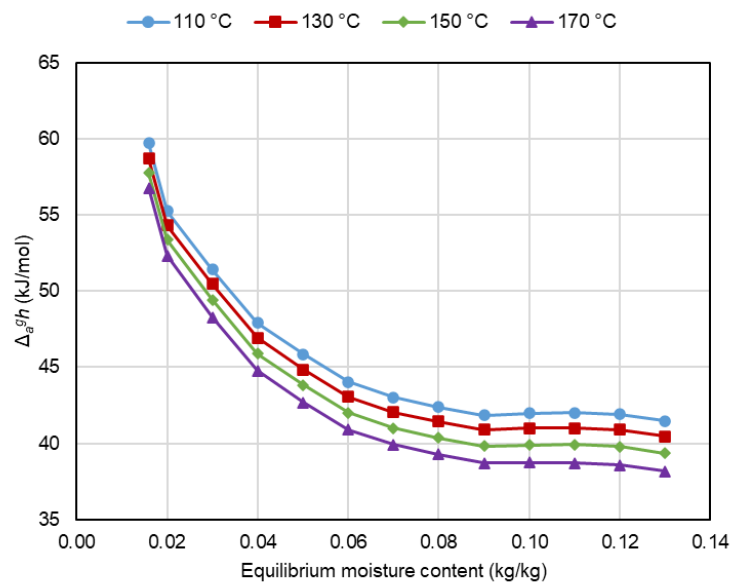


Fig. S13 Total differential enthalpy change from the Clapeyron equation (Eq. S37) applied to sorption data of Engelhardt (1979)

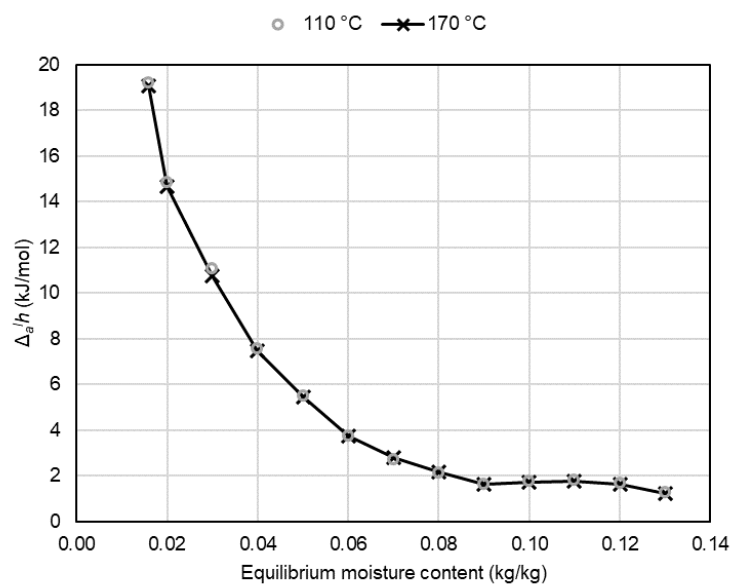


Fig. S14 Differential enthalpy of sorption (relative to pure liquid water) from the thermodynamic framework (Eq. S39) applied to sorption data of Engelhardt (1979)

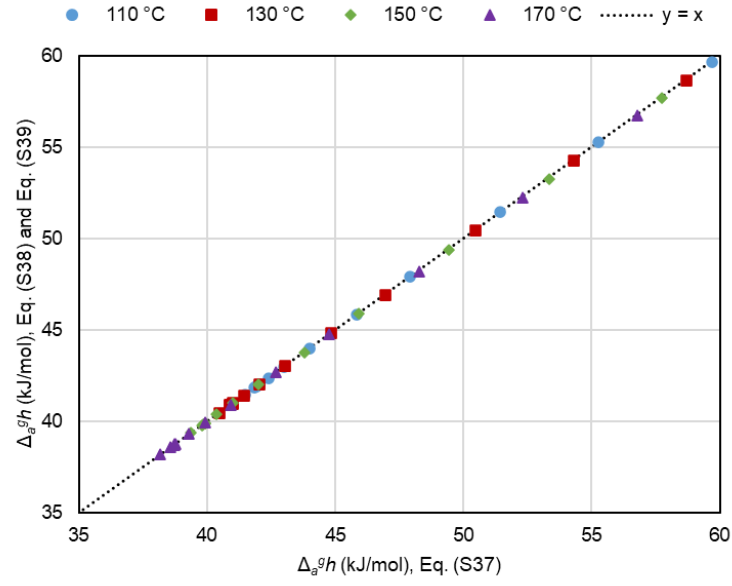


Fig. S15 Comparison of $\Delta_a^g \bar{h}$ calculated with the thermodynamic framework (Eq. S38 and Eq. S39) and the Clapeyron equation (Eq. S37)

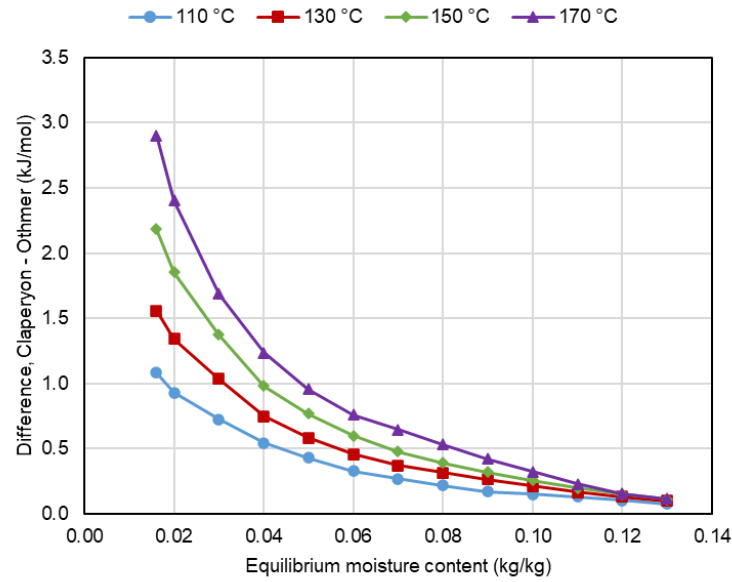


Fig. S16 Difference between $\Delta_a^g \bar{h}$ values calculated using the Clapeyron and Othmer equations

V. Influence of External Pressure on Sorption

Prior work has described the swelling pressure involved when water is absorbed by the cell wall of wood (e.g., Barkas 1949; Tarkow and Turner 1958; Skaar 1988; Bertinetti et al. 2013; Arzola-Villegas et al. 2019). Swelling is internally constrained to an extent by the structure and mechanical properties of the various cell wall layers with differing microfibril angles. The extent of swelling for a given change in moisture content depends on external conditions such as total gas pressure, applied compressive stress, or applied tensile stress. The interaction between external constraints and swelling pressure influences the equilibrium between water vapor and absorbed water in the cell wall. For example, at a given temperature and relative humidity, wood under compression has a lower EMC than unrestrained wood, whereas wood under tension has a higher EMC (Barkas 1949; Skaar 1988).

The thermodynamic framework on which the CAST model is formulated assumes that the system is at constant pressure. Under this condition, the change in enthalpy of the system is equal to the heat released by a process such as vapor sorption or wetting with liquid water. Measurements of the heat of wetting taken from the literature were conducted at atmospheric pressure, so this condition is met. However, water vapor sorption measurements taken from the literature cover a range of pressures, from partial vacuum (Weichert 1963) to pressures well above atmospheric pressure at higher temperatures (Engelhardt 1979). This range can be summarized as follows:

- Lowest pressure (Weichert 1963; 25 °C, 3.2% RH): 1.01 mbar
- Highest pressure (Engelhardt 1979; 170 °C, 96.3% RH): 7.63 bar

The relationship between swelling, moisture content, vapor pressure, and external pressure can be expressed quantitatively for a hygroscopic gel through a form of the Porter equation (Skaar 1988; Eq. 2.88):

$$\left(\frac{\partial V}{\partial u}\right)_{p_g} = v_g \left(\frac{\partial p_g}{\partial P}\right)_u \quad (\text{S42})$$

where V is the specific volume of the gel (ratio of the swollen volume to the dry mass, $\text{m}^3 \text{kg}^{-1}$), u is moisture content (ratio of the mass of water to the dry mass of the gel, kg kg^{-1}), p_g is water vapor pressure (Pa), v_g is specific volume of water vapor ($\text{m}^3 \text{kg}^{-1}$), and P is total external pressure (Pa). The left-hand side is equivalent to the apparent specific volume of absorbed water, v_a ($\text{m}^3 \text{kg}^{-1}$). The water vapor pressure p_g can be expressed as the product $a_w^i p_{gl}$ where a_w^i is the relative humidity (conventional water activity) and p_{gl} is the saturation water vapor pressure (Pa). Eq. (S42) can thus be rewritten as

$$\left(\frac{\partial a_w^i}{\partial P}\right)_u = \frac{v_a}{p_{gl} v_g} \quad (\text{S43})$$

As a first approximation, the specific volume of absorbed water is roughly equivalent to the specific volume of pure liquid water ($v_a \cong v_l$). Further, for small changes in relative humidity (Δa_w^i), the specific volume of water vapor is roughly constant. Thus, the change in relative humidity for a change in external pressure at constant moisture content can be approximated as

$$\Delta a_w^i \cong \frac{v_l}{p_{gl} v_g} \Delta P \quad (\text{S44})$$

The effect of an extreme external pressure on the sorption isotherm of spruce is illustrated in Fig. S17. The ~ 0 bar curve is the CAST model fit to the data of Weichert (1963a) at 25 °C, where the experiments were conducted in vacuum with water vapor pressures between 0.001 and 0.03 bar. The curve for a 500-

bar external pressure was calculated using Eq. (S44). This curve closely resembles that given by Skaar (1988; Fig. 2.26).

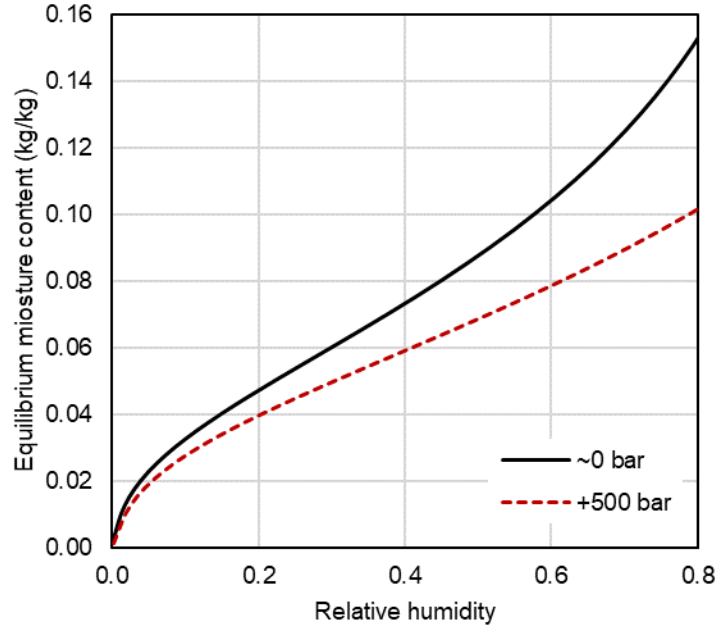


Fig. S17 Influence of external pressure on the sorption isotherm of spruce calculated with Eq. (S44)

The effect of adjusting the beech sorption data of Weichert (1963a) between 25 °C and 100 °C from the original experimental conditions to atmospheric pressure (1 bar) is shown in Fig. S18. In all cases, the relative humidity changes by less than 0.001, which is much smaller than the measurement uncertainty.

Similarly, the effect of adjusting the beech sorption data of Engelhardt (1979) between 110 °C and 170 °C from the original experimental conditions to the highest total pressure (7.63 bar at 170 °C, 96% RH) is shown in Fig. S19. The maximum change in RH at each temperature is summarized in Table S1.

Although Engelhardt (1979) did not report measurement uncertainty, the uncertainty in RH measurements of Weichert (1963a) at 100 °C was estimated as ± 0.0186 (Zelinka et al. 2020). The maximum values in Table S1 are less than 20% of this measurement uncertainty.

Table S1 Maximum change in relative humidity at each temperature when adjusting total pressure from original experimental conditions to 7.63 bar for beech data of Engelhardt (1979)

Temperature (°C)	Maximum Δa_w^i
110	0.0036
130	0.0029
150	0.0018
170	0.0011

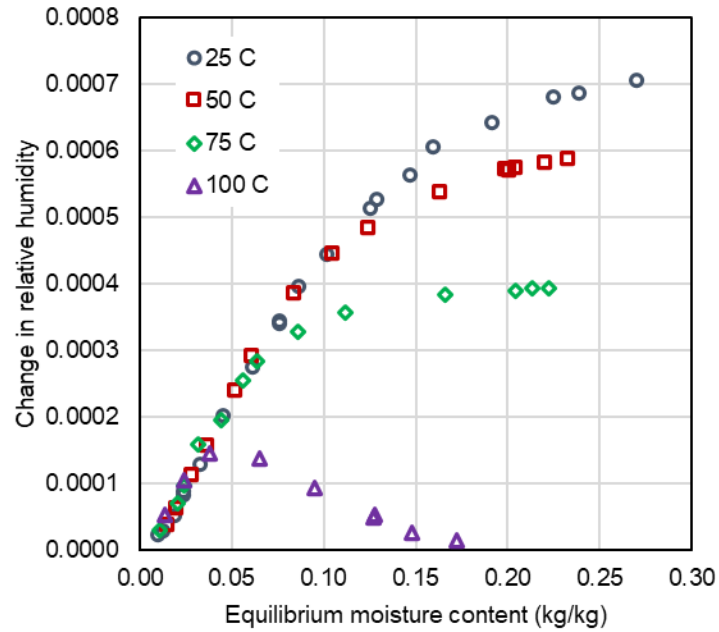


Fig. S18 Change in relative humidity when adjusting total pressure from original experimental conditions to 1 bar, as a function of equilibrium moisture content and temperature, for beech (Weichert 1963a) calculated with Eq. (S44)

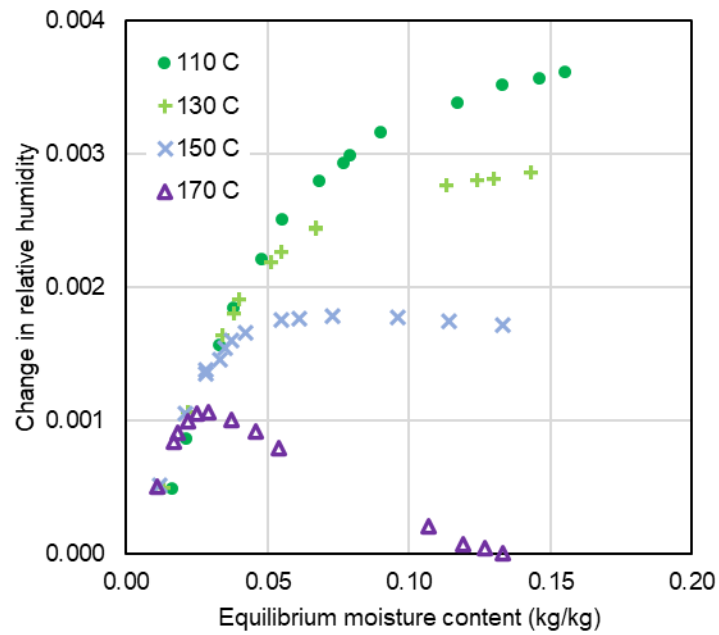


Fig. S19 Change in relative humidity when adjusting total pressure from original experimental conditions to 7.63 bar, as a function of equilibrium moisture content and temperature, for beech (Engelhardt 1979) calculated with Eq. (S44)

The effect of these changes in relative humidity (for adjustment in total external pressure) on the calculated differential enthalpy of sorption for the data of Engelhardt (1979) is summarized in Table S2. The small changes in RH result in small changes in $\Delta_a {}^l \bar{h}$ of 0.09 kJ mol⁻¹ or less.

Table S2 Effect of change in relative humidity when adjusting total pressure from original experimental conditions to 7.63 bar on differential enthalpy of sorption for beech data of Engelhardt (1979) at 110 °C and select equilibrium moisture contents

u (kg kg ⁻¹)	Original $\Delta_a {}^l \bar{h}$ (kJ mol ⁻¹)	Adjusted $\Delta_a {}^l \bar{h}$ (kJ mol ⁻¹)
0.02	14.84	14.80
0.04	7.57	7.50
0.06	3.73	3.65
0.08	2.12	2.04
0.10	1.75	1.67
0.13	1.28	1.19

In summary, the experimental sorption data taken from the literature for the purpose of evaluating the CAST model were not strictly measured at constant total pressure. However, the differences in external pressure are shown here to have negligible effects on the sorption isotherms and the differential enthalpy of sorption.

VI. Evaluation of Other Sorption Models

This section provides details on additional equilibrium sorption models that are fitted to the same data described in Section 4 of the manuscript and compared with the CAST model. In most cases, beech was selected for plots because of the broader temperature range covered by the data.

Modified Guggenheim-Anderson-de Boer model (GAB6)

Equilibrium moisture content is given by

$$u = \frac{\gamma_1 \gamma_2 \gamma_3 a_w}{(1 - \gamma_3 a_w)[1 + (\gamma_2 - 1)\gamma_3 a_w]} \text{ with } \gamma_1 = \delta_1 e^{\delta_2/T}; \gamma_2 = \delta_3 e^{\delta_4/T}; \gamma_3 = \delta_5 e^{\delta_6/T} \quad (\text{S45})$$

where $\gamma_1 \dots \gamma_3$ and $\delta_1 \dots \delta_6$ are fitting parameters. Eq. (S45) can be transformed to a quadratic equation in a_w and solved to give

$$a_w = \frac{2 - \gamma_2(1 - \gamma_1/u) - \sqrt{[\gamma_2(1 - \gamma_1/u) - 2]^2 - 4(1 - \gamma_2)}}{2\gamma_3(1 - \gamma_2)} \quad (\text{S46})$$

The quadratic equation has two solutions, one of which corresponds to relevant values ($0 \leq a_w \leq 1$); this solution has a minus sign (rather than plus sign) in front of the square root in Eq. (S46).

The differential enthalpy of sorption given by the GAB6 model as a function of u and T was calculated using Eq. (14) of the manuscript, numerically evaluating the partial derivative $\left(\frac{\partial \ln a_w}{\partial T}\right)_u$ using Eqs. (S46) and (S45). Alternatively, the analytical derivative could be used (Vázquez et al. 2011) but is cumbersome. The heat of wetting was calculated by numerical integration.

The parameters of the GAB6 model fitted to beech and spruce data are given in Table S3, and R^2 values are listed in Tables 4 and 5 of the manuscript. The quality of the GAB6 model fit for beech sorption data (a_w and u) is shown in Figs. 7 and 8 of the manuscript. Heat of wetting is shown here in Fig. S20; differential enthalpy of sorption is shown in Fig. S21; and enthalpy-entropy plots are shown in Fig. S22.

Table S3 Parameters of the GAB6 model (with u in kg kg⁻¹ and T in K)

Parameter	Beech	Spruce
δ_1	7.593×10^{-3}	0.04920
δ_2	618.0	45.91
δ_3	0.2444	9.236×10^{-3}
δ_4	939.1	2111
δ_5	0.8950	0.5221
δ_6	-36.82	126.1

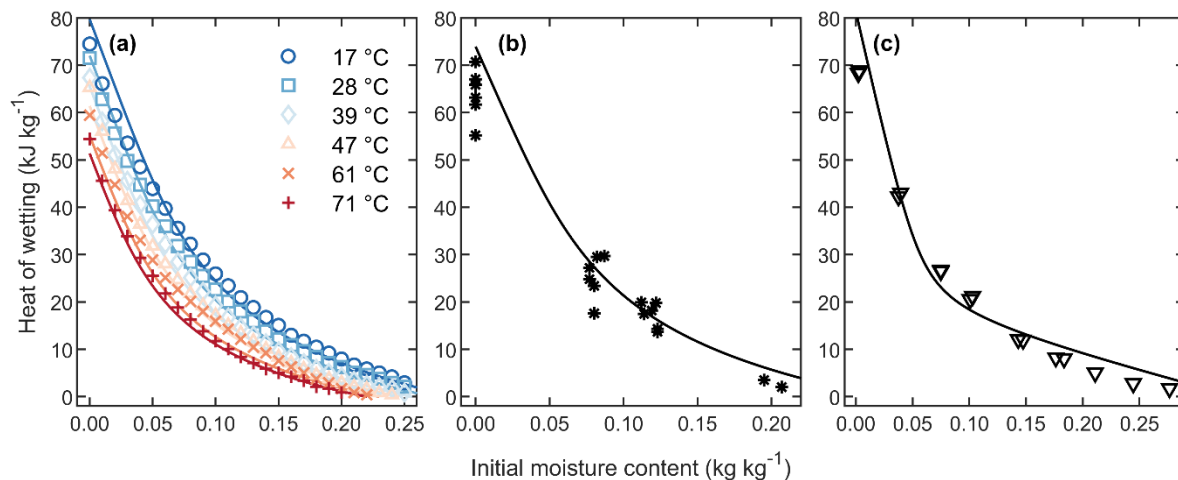


Fig. S20 Heat of wetting vs. initial moisture content from the GAB6 model (solid curves) fit to data (discrete points) of (a) Hearmon and Burcham (1956) for beech at a series of temperatures, (b) Nopens et al. (2019) for beech at 25 °C, and (c) Volbehr (1896) for spruce at 0 °C

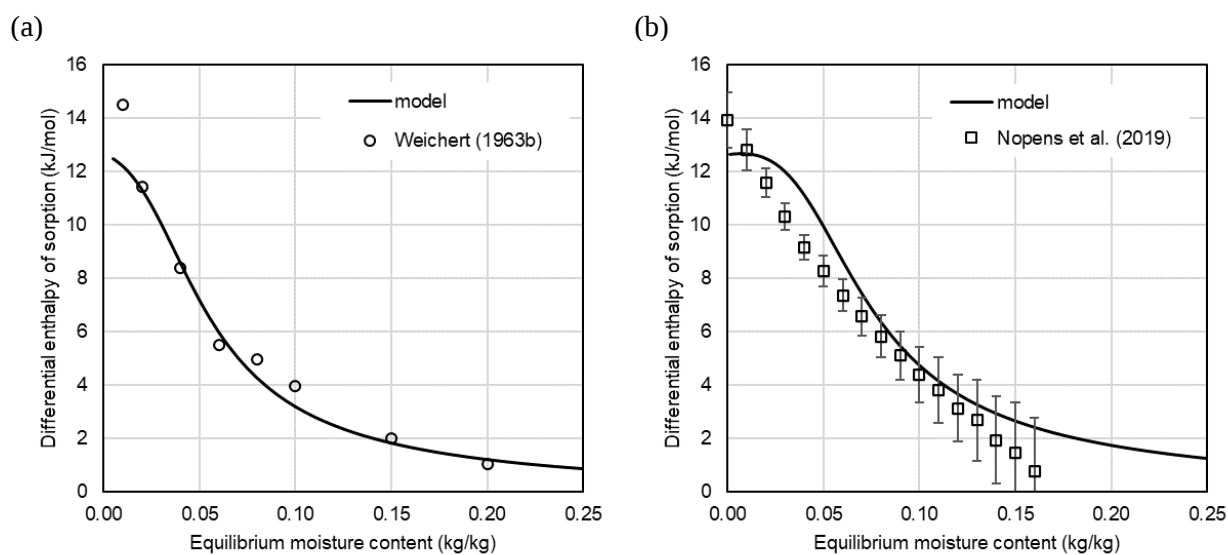


Fig. S21 Differential enthalpy of sorption vs. equilibrium moisture content of beech from the GAB6 model compared with values reported by Weichert (1963b) at 62.5 °C (a) and Nopens et al. (2019) at 25 °C (b), where error bars indicate standard deviation of three replicates

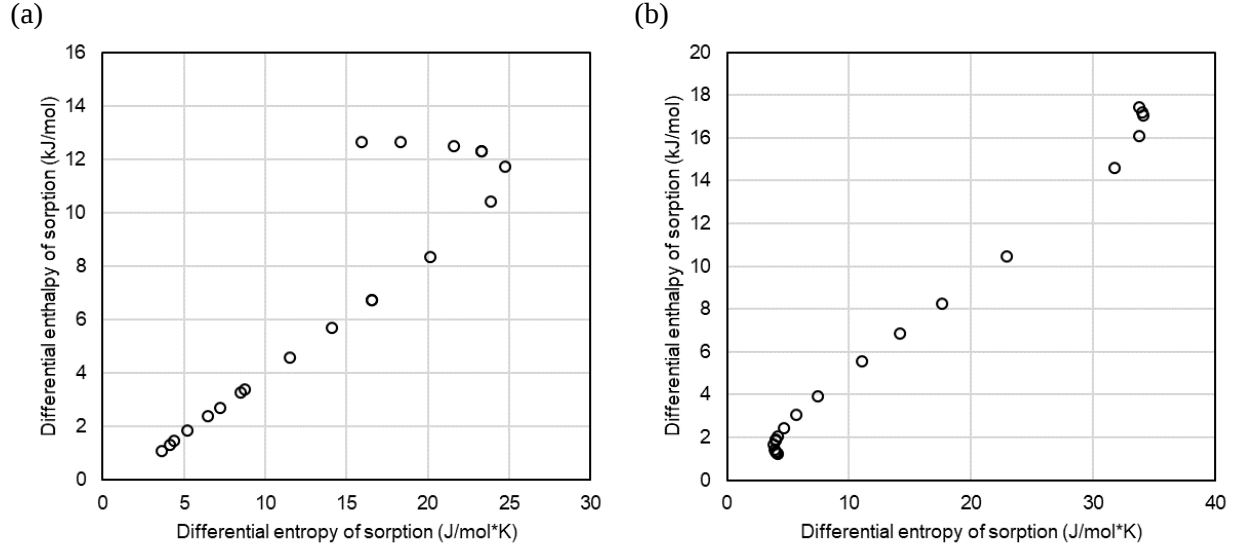


Fig. S22 Enthalpy-entropy plots for the GAB6 model fitted to data at 25 °C (Weichert 1963a) for (a) beech and (b) spruce

Modified Nelson model (NA6)

The differential Gibbs energy of sorption is given by

$$\Delta\bar{g} = \exp(\kappa_1 + \kappa_2 u), \text{ with } \kappa_1 = \lambda_1 + \lambda_2 T + \lambda_3 T^2; \kappa_2 = \lambda_4 + \lambda_5 T + \lambda_6 T^2 \quad (\text{S47})$$

where κ_1 , κ_2 , and $\lambda_1 \dots \lambda_6$ are fitting parameters. Water activity is expressed as

$$a_w = \exp\left(\frac{-\Delta\bar{g}}{RT}\right) = \exp\left[\frac{-\exp(\kappa_1 + \kappa_2 u)}{RT}\right] \quad (\text{S48})$$

This equation can be inverted to give u as a function of a_w and T :

$$u = \frac{\ln(-RT \ln a_w) - \kappa_1}{\kappa_2} \quad (\text{S49})$$

The differential enthalpy of sorption is determined by applying the Gibbs-Helmholtz relation to Eq. (S47), which gives the following:

$$\Delta\bar{h} = \Delta\bar{g} \left[1 - T \left(\frac{d\kappa_1}{dT} + u \frac{d\kappa_2}{dT} \right) \right] \quad (\text{S50})$$

where

$$\frac{d\kappa_1}{dT} = \lambda_2 + 2\lambda_3 T \text{ and } \frac{d\kappa_2}{dT} = \lambda_5 + 2\lambda_6 T \quad (\text{S51})$$

The heat of wetting is calculated by integrating $\Delta\bar{h}$ (at constant temperature). The upper integration limit is defined by $\Delta\bar{g}(u_f) \rightarrow 0$, which implies $u_f \rightarrow \infty$:

$$q_{wet} = \frac{1}{M_w} \int_{u_i}^{\infty} \Delta\bar{h} du = \frac{\exp(\kappa_1 + \kappa_2 u_i)}{M_w \kappa_2} \left[T \left(u_i \frac{d\kappa_2}{dT} + \frac{d\kappa_1}{dT} - \frac{1}{\kappa_2} \frac{d\kappa_2}{dT} \right) - 1 \right] \quad (\text{S52})$$

The parameters of the NA6 model fitted to beech and spruce data are given in Table S4, and values of R^2 are given in Tables 4 and 5 of the manuscript. The fitting of water activity and equilibrium moisture

content is shown in Figs. 7 and 8 of the manuscript. Heat of wetting is shown in Fig. S23; differential enthalpy of sorption is shown in Fig. S24; and Fig. S25 presents enthalpy-entropy plots.

Table S4 Parameters of the NA6 model (with u in kg kg^{-1} , T in K, and $\Delta\bar{g}$ in kJ mol^{-1})

Parameter	Beech	Spruce
λ_1	2.057	1.461
λ_2	2.126×10^{-3}	7.586×10^{-3}
λ_3	-5.378×10^{-6}	-1.484×10^{-5}
λ_4	15.82	-18.68
λ_5	-0.1453	0.06430
λ_6	8.858×10^{-5}	-2.380×10^{-4}

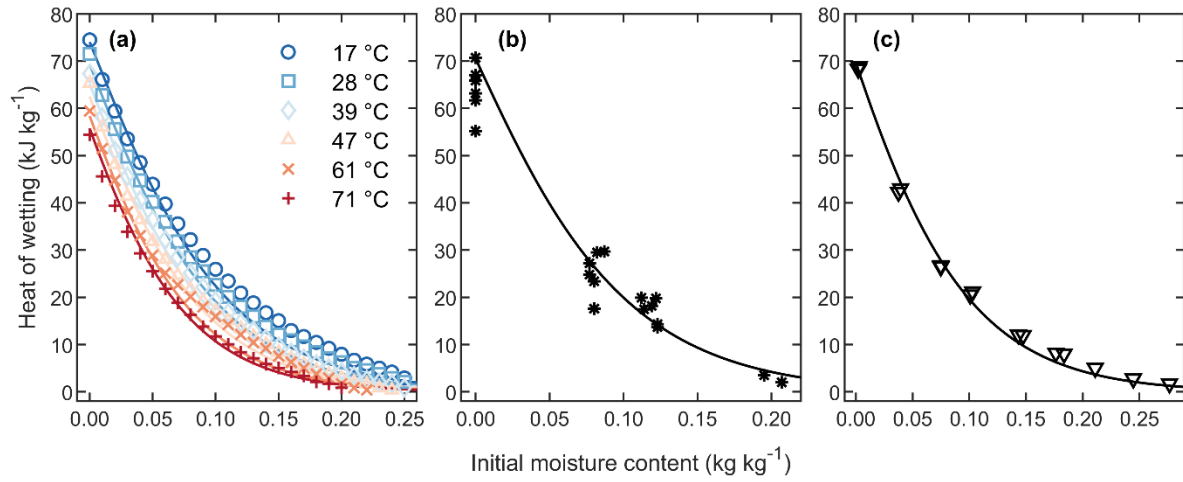


Fig. S23 Heat of wetting vs. initial moisture content from the NA6 model (solid curves) fit to data (discrete points) of (a) Hearmon and Burcham (1956) for beech at a series of temperatures, (b) Nopens et al. (2019) for beech at 25 °C, and (c) Volbehr (1896) for spruce at 0 °C

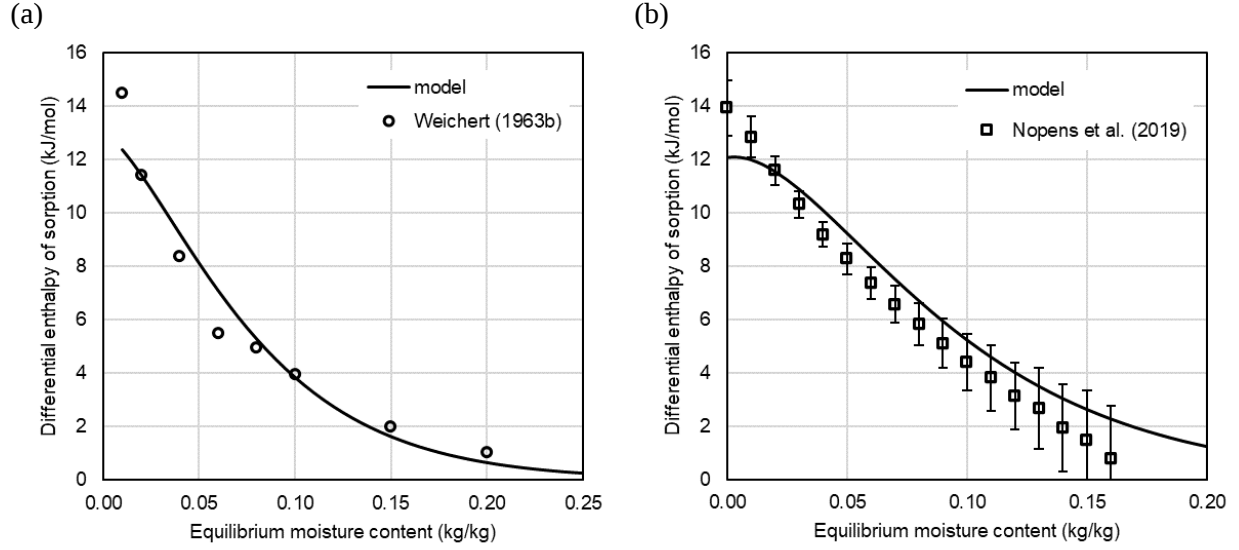


Fig. S24 Differential enthalpy of sorption vs. equilibrium moisture content of beech from the NA6 model compared with values reported by Weichert (1963b) at 62.5 °C (a) and Nopens et al. (2019) at 25 °C (b), where error bars indicate standard deviation of three replicates

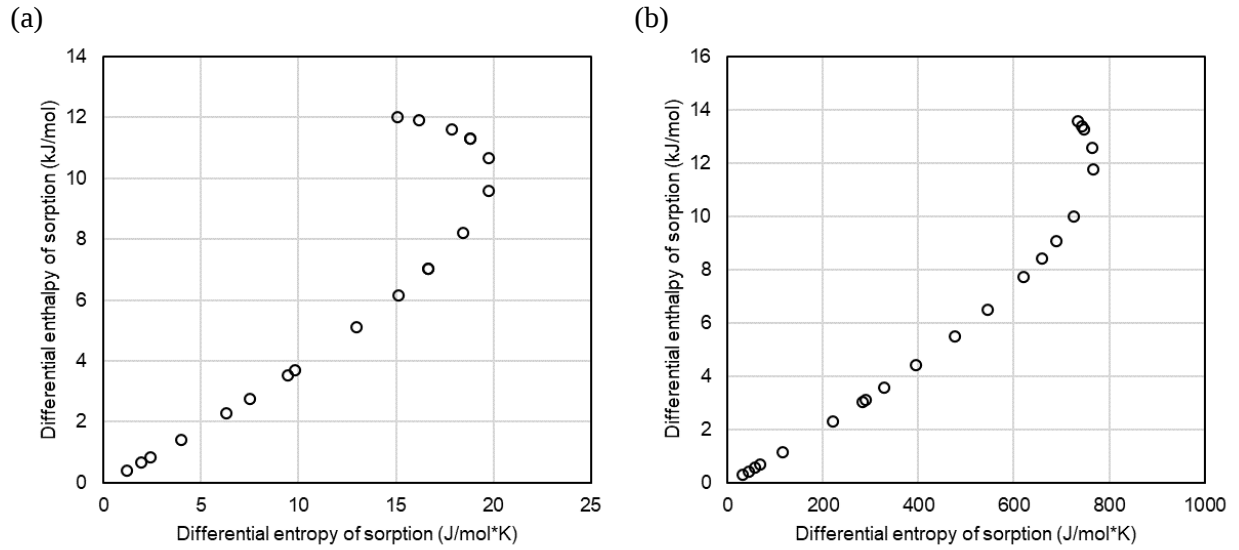


Fig. S25 Enthalpy-entropy plots for the NA6 model fitted to data at 25 °C (Weichert 1963a) for (a) beech and (b) spruce

Modified Oswin model (OC3)

Water activity is given by

$$a_w = \frac{1}{1 + \left(\frac{\omega_1 - \omega_2 T}{u} \right)^{\omega_3}} \quad (\text{S53})$$

where ω_1 , ω_2 , and ω_3 are positive constants. In prior publications, these parameters were defined using temperature in degrees Celsius. Here we express temperature in kelvins, which merely shifts the value of ω_1 . Eq. (S53) can be inverted to give equilibrium moisture content:

$$u = (\omega_1 - \omega_2 T) \left(\frac{a_w}{1-a_w} \right)^{(1/\omega_3)} \quad (\text{S54})$$

The differential enthalpy of sorption as a function of u and T can be calculated analytically with Eq. (14) by differentiating Eq. (S53):

$$\Delta \bar{h} = \frac{RT^2 \omega_2 \omega_3 (\omega_1 - \omega_2 T)^{(\omega_3 - 1)}}{u^{\omega_3} + (\omega_1 - \omega_2 T)^{\omega_3}} \quad (\text{S55})$$

The heat of wetting was calculated by numerical integration.

The parameters of the OC3 model fitted to data for beech and spruce are given in Table S5, and values of R^2 are given in Tables 4 and 5 of the manuscript. Given the linear temperature dependence in this model, to avoid nonphysical negative values of u (Eq. S54) at higher temperatures, we imposed the following constraint while optimizing model parameters: $u(a_w = 0.995, T = 473 \text{ K}) \geq 0.05 \text{ kg kg}^{-1}$. Water activity is plotted versus equilibrium moisture content in Fig. S26; heat of wetting is shown in Fig. S27; differential enthalpy of sorption is shown in Fig. S28; and enthalpy-entropy plots are shown in Fig. S29.

Table S5 Parameters of the OC3 model (with u in kg kg^{-1} and T in K)

Parameter	Beech	Spruce
ω_1	0.1893	0.2043
ω_2	3.590×10^{-4}	4.056×10^{-4}
ω_3	3.069	3.223

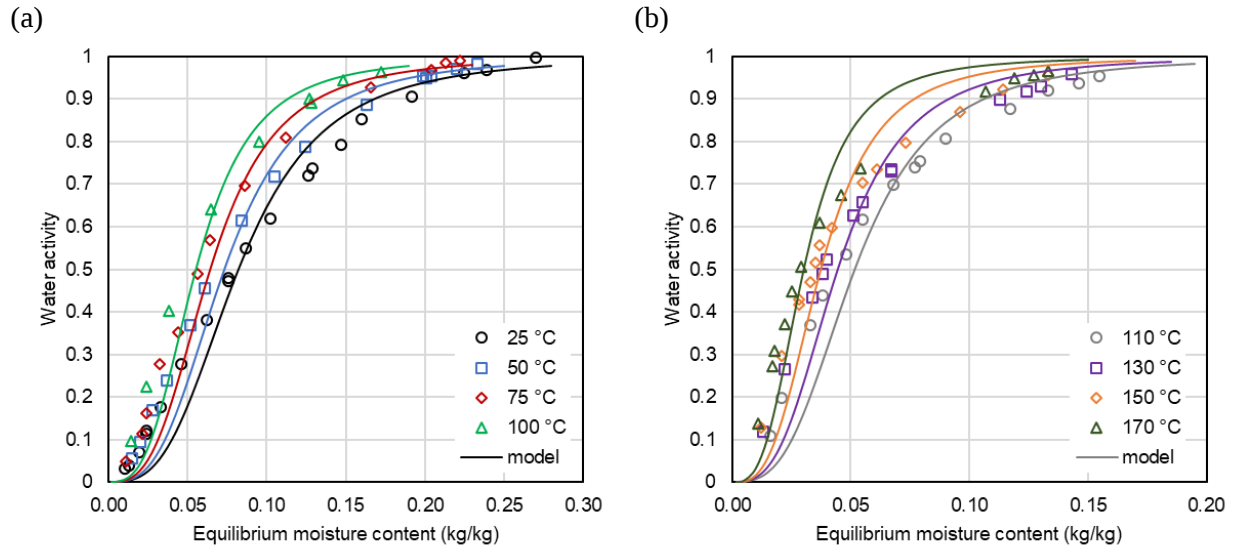


Fig. S26 Water activity vs. equilibrium moisture content for the OC3 model (curves) fitted to beech data (discrete points) of (a) Weichert (1963a) and (b) Engelhardt (1979)

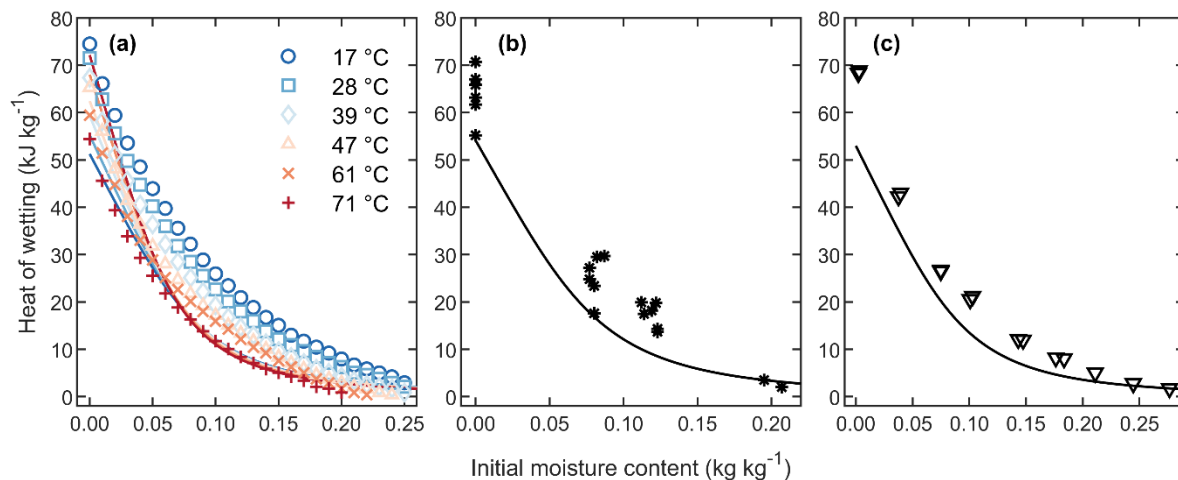


Fig. S27 Heat of wetting vs. initial moisture content from the OC3 model (solid curves) fit to data (discrete points) of (a) Hearmon and Burcham (1956) for beech at a series of temperatures, (b) Nopens et al. (2019) for beech at 25 °C, and (c) Volbehr (1896) for spruce at 0 °C

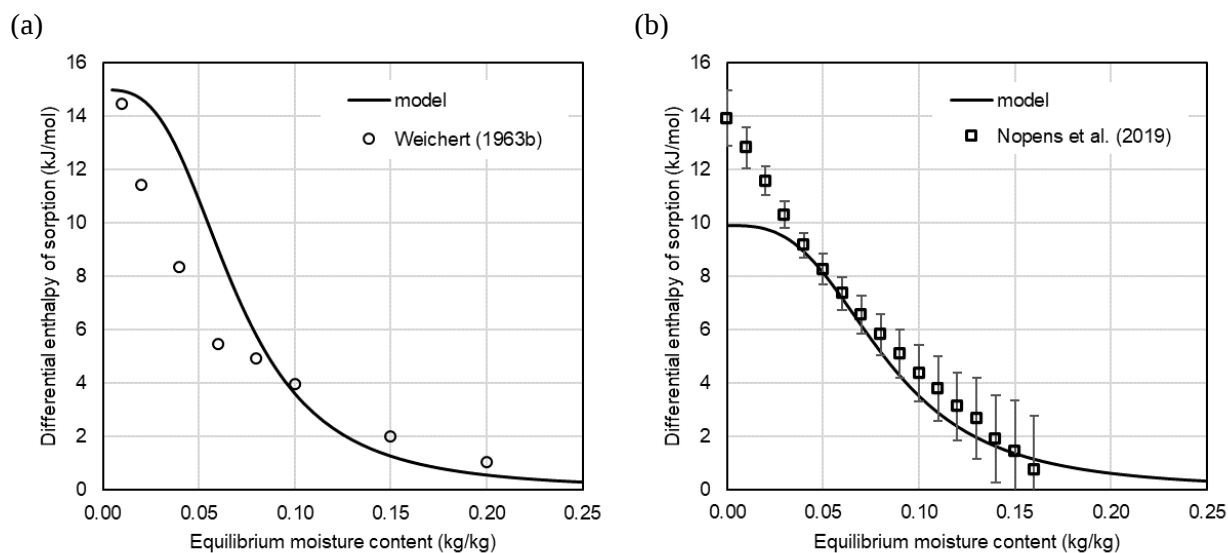


Fig. S28 Differential enthalpy of sorption vs. equilibrium moisture content of beech from the OC3 model compared with values reported by (a) Weichert (1963b) at 62.5 °C and (b) Nopens et al. (2019) at 25 °C, where error bars indicate standard deviation of three replicates

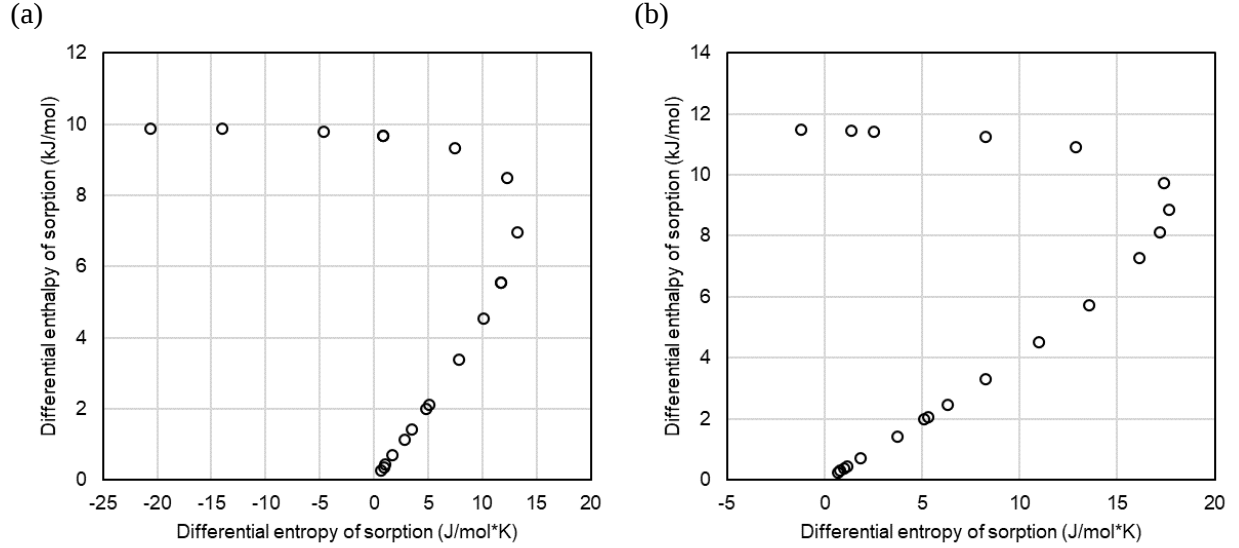


Fig. S29 Enthalpy-entropy plots for the OC3 model fitted to data at 25 °C (Weichert 1963a) for (a) beech and (b) spruce

Models derived from Othmer's postulate (ODE4 and ODP6)

Othmer (1940) observed a linear relationship between the vapor pressure of a given substance (p_g) and that of a reference substance (p_{ref}) over a wide range of temperatures on a log-log plot. Using the Clausius-Clapeyron equation, Othmer equated the slope of this line to the ratio of the enthalpy of vaporization of the substance of interest (Δh) to the enthalpy of vaporization of the reference substance (Δh_{ref}):

$$\frac{d \ln p_g}{d \ln p_{ref}} = \frac{\Delta h}{\Delta h_{ref}} \quad (\text{S56})$$

Othmer's equation provides a way to determine the enthalpy of vaporization of the substance of interest based on measurements of its vapor pressure over a range of temperatures and known properties of the reference substance. Water was a convenient reference substance in many of Othmer's examples, given that its saturation vapor pressure and enthalpy of vaporization are well characterized.

Othmer and Sawyer (1943) showed that this relationship also applies to vapor sorption for a range of different sorbates and sorbents, including water vapor sorption in paper. For water vapor sorption in a sorbent, the differential enthalpy of sorption relative to liquid water (rather than water vapor), can be obtained by modifying Eq. (S56):

$$\frac{d \ln a_w}{d \ln p_{gl}} = \frac{\Delta \bar{h}}{\Delta_l^g h} \quad (\text{S57})$$

Application of this method relies on the Clausius-Clapeyron equation (which assumes ideal gas behavior and negligible molar volume of absorbed water). It is further assumed that the ratio $\Delta \bar{h} / \Delta_l^g h$ is dependent only on equilibrium moisture content (that is, invariant with temperature). We refer to this as Othmer's postulate and define this ratio as

$$r(u) = \frac{\Delta \bar{h}}{\Delta_l^g h} \quad (\text{S58})$$

to indicate that it is a function of u alone. Two different functional forms for $r(u)$ are considered below. Recalling the linear approximation for the enthalpy of vaporization of water from Eq. (S7), the differential enthalpy of sorption can be expressed as

$$\Delta \bar{h} = r(u)(L_0 - L_1 T) \quad (\text{S59})$$

This equation provides a way to generate equilibrium sorption models as shown below through application of the Gibbs-Helmholtz relation. Eq. (S59) can be restated as

$$\Delta \bar{h} = \left[\frac{\partial(\Delta \bar{g}/T)}{\partial(1/T)} \right]_{P,u} = r(u)(L_0 - L_1 T) \quad (\text{S60})$$

Integration of Eq. (S60) gives the following:

$$\frac{\Delta \bar{g}(u,T)}{T} = \frac{C}{T_{ref}} + r(u) \left[\frac{L_0}{T} - \frac{L_0}{T_{ref}} + L_1 \ln \left(\frac{T}{T_{ref}} \right) \right] \quad (\text{S61})$$

where C and T_{ref} are integration constants. Substituting the relationship between differential Gibbs energy of sorption and water activity (see Eq. (12) in the manuscript), this leads to an equilibrium sorption model of the following form:

$$a_w = \exp \left\{ -\frac{C}{RT_{ref}} - r(u) \left[\frac{L_0}{RT} - \frac{L_0}{RT_{ref}} + \frac{L_1}{R} \ln \left(\frac{T}{T_{ref}} \right) \right] \right\} \quad (\text{S62})$$

This equation can be inverted to give u as a function of a_w and T , as shown below for two forms of $r(u)$.

Eq. (S59) implies a linear relationship between the differential enthalpy and entropy as shown below. Solving Eq. (S59) for $r(u)$, substituting into Eq. (S61) to eliminate $r(u)$, and solving for $\Delta \bar{h}$ gives

$$\Delta \bar{h} = A(T)\Delta \bar{g}(u,T) - B(T) \quad (\text{S63})$$

where

$$A(T) = \frac{(L_0 - L_1 T) T_{ref}}{L_0(T_{ref} - T) + L_1 T T_{ref} \ln(T/T_{ref})} \quad (\text{S64})$$

and

$$B(T) = \frac{(L_0 - L_1 T) T C}{L_0(T_{ref} - T) + L_1 T T_{ref} \ln(T/T_{ref})} \quad (\text{S65})$$

Substitution of the definition $\Delta \bar{g} = \Delta \bar{h} - T\Delta \bar{s}$ into Eq. (S63) gives a linear relationship between the differential enthalpy and entropy of sorption:

$$\Delta \bar{h}(u,T) = \frac{A(T)}{A(T)-1} T\Delta \bar{s}(u,T) + \frac{B(T)}{A(T)-1} \quad (\text{S66})$$

If the enthalpy of vaporization can be considered independent of temperature ($L_1 = 0$), then Eq. (S66) reduces to

$$\Delta \bar{h}(u) = T_{ref}\Delta \bar{s}(u) + C \quad (\text{S67})$$

This equation is known as enthalpy-entropy compensation theory. Much of the literature that has analyzed water vapor sorption data using this theory has done so over a limited temperature range. The change in the enthalpy of vaporization of pure water over the typical range of experimental data is relatively small. For example, it varies by only 4% between 20 °C and 60 °C. Thus, any changes in $A(T)$ and $B(T)$ could go

undetected in such experiments. The linear relationship between differential enthalpy and differential entropy of sorption in Eq. (S66) was derived from Othmer's postulate, linear temperature dependence of the enthalpy of vaporization of water, the Gibbs-Helmholtz relation, and the definition of the Gibbs energy.

Several different functional forms for $r(u)$ have been proposed in the literature. Some of these may provide a good fit to experimental data but have either of two limitations as an equilibrium sorption model. First, when $r(u)$ is substituted into Eq. (S62), certain functional forms do not facilitate inversion to give u as a function of a_w . Second, certain forms of $r(u)$ cannot be integrated analytically to give the heat of wetting. Below we consider two forms that overcome these limitations.

Exponential model (ODE4)

Several authors have indicated that the heat of wetting and the differential enthalpy of sorption can be approximated with an exponential decay function (e.g., Anderson and McCarthy 1963; Weisser 1985; Skaar 1988; Nopens et al. 2019), which we express as

$$r(u) = \varepsilon_1 \exp(-\varepsilon_2 u) \quad (\text{S68})$$

where ε_1 and ε_2 are fitting parameters. The differential enthalpy of sorption is given by

$$\Delta \bar{h} = \varepsilon_1 \exp(-\varepsilon_2 u) (L_0 - L_1 T) \quad (\text{S69})$$

where L_0 and L_1 are given in Eq. (S7). Integration (at constant temperature) gives the heat of wetting:

$$q_{wet} = \frac{1}{M_w} \int_{u_i}^{u_f} \Delta \bar{h} du = -\frac{\varepsilon_1 (L_0 - L_1 T)}{M_w \varepsilon_2} [\exp(-\varepsilon_2 u_f) - \exp(-\varepsilon_2 u_i)] \quad (\text{S70})$$

Substituting Eq. (S68) into Eq. (S62) gives an equilibrium sorption model:

$$a_w = \exp \left\{ -\frac{C}{RT_{ref}} - \varepsilon_1 \exp(-\varepsilon_2 u) \left[\frac{L_0}{RT} - \frac{L_0}{RT_{ref}} + \frac{L_1}{R} \ln \left(\frac{T}{T_{ref}} \right) \right] \right\} \quad (\text{S71})$$

This equation can be inverted to give the following:

$$u = \frac{1}{\varepsilon_2} \ln \left\{ \varepsilon_1 \left[\frac{L_0/T - L_0/T_{ref} + L_1 \ln(T/T_{ref})}{-R \ln a_w - C/T_{ref}} \right] \right\} \quad (\text{S72})$$

The optimized fitting parameters are listed in Table S6, and values of R^2 are given in Tables 4 and 5 of the manuscript. The fitting of water activity and equilibrium moisture content for beech is shown in Fig. S30, heat of wetting in Fig. S31, and differential enthalpy of sorption in Fig. S32. Linear enthalpy-entropy compensation is shown for beech and spruce in Fig. S33.

Table S6 Parameters of the ODE4 model (with u in kg kg⁻¹, T in K, and $\Delta \bar{h}$ in kJ mol⁻¹)

Parameter	Beech	Spruce
ε_1	0.4465	0.5945
ε_2	15.81	19.57
C	-0.6008	-0.07993
T_{ref}	593.7	510.2

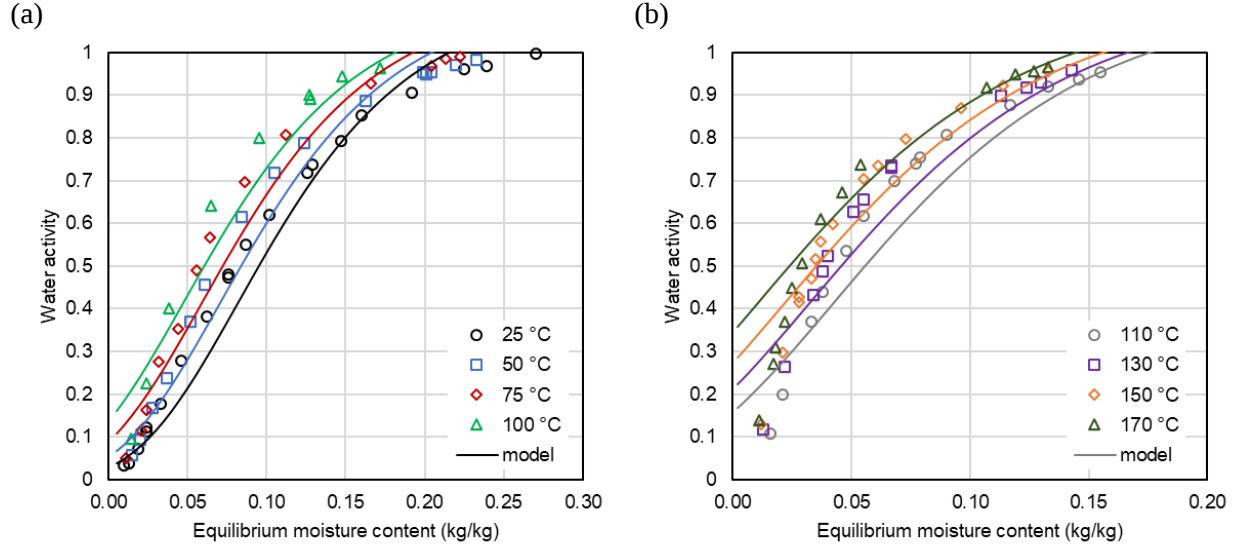


Fig. S30 Water activity vs. equilibrium moisture content for the ODE4 model (curves) fitted to beech data (discrete points) of (a) Weichert (1963a) and (b) Engelhardt (1979)

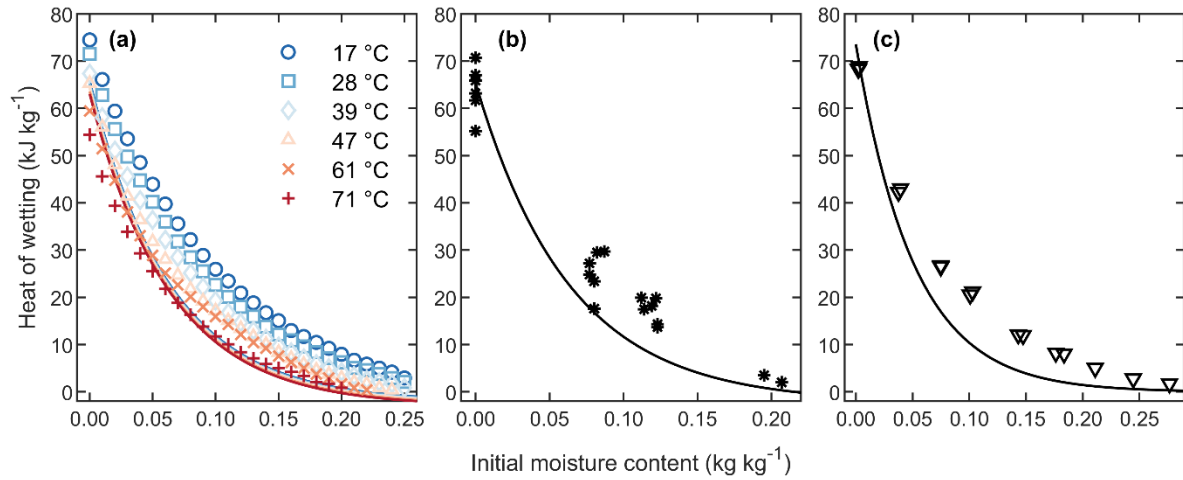


Fig. S31 Heat of wetting vs. initial moisture content from the ODE4 model (solid curves) fit to data (discrete points) of (a) Hearmon and Burcham (1956) for beech at a series of temperatures, (b) Nopens et al. (2019) for beech at 25 °C, and (c) Volbehr (1896) for spruce at 0 °C

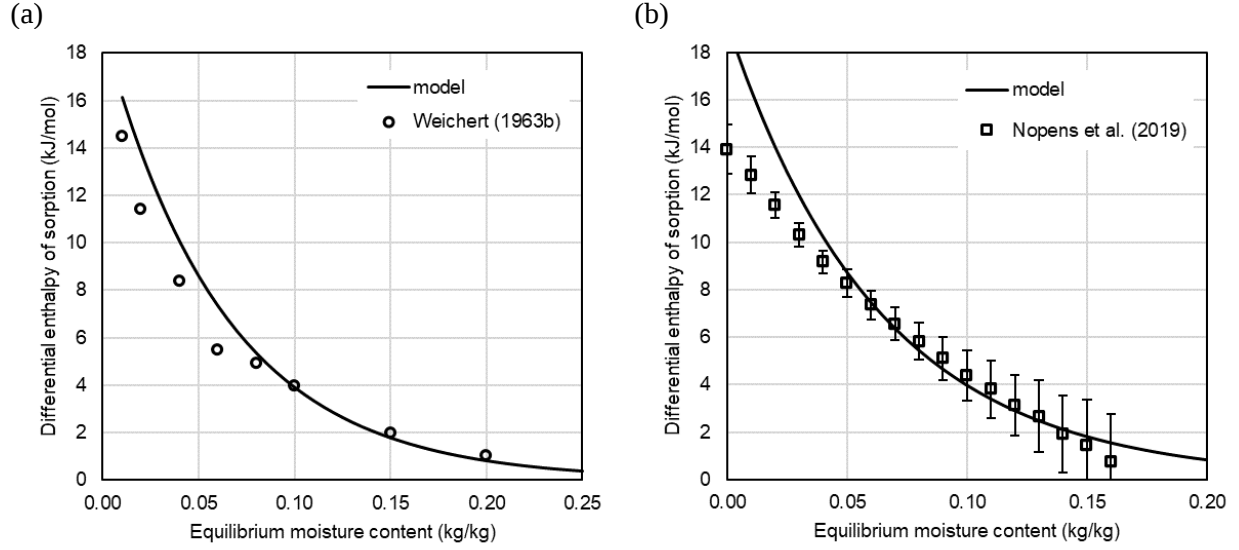


Fig. S32 Differential enthalpy of sorption vs. equilibrium moisture content of beech from the ODE4 model compared with values reported by (a) Weichert (1963b) at 62.5 °C and (b) Nopens et al. (2019) at 25 °C, where error bars indicate standard deviation of three replicates

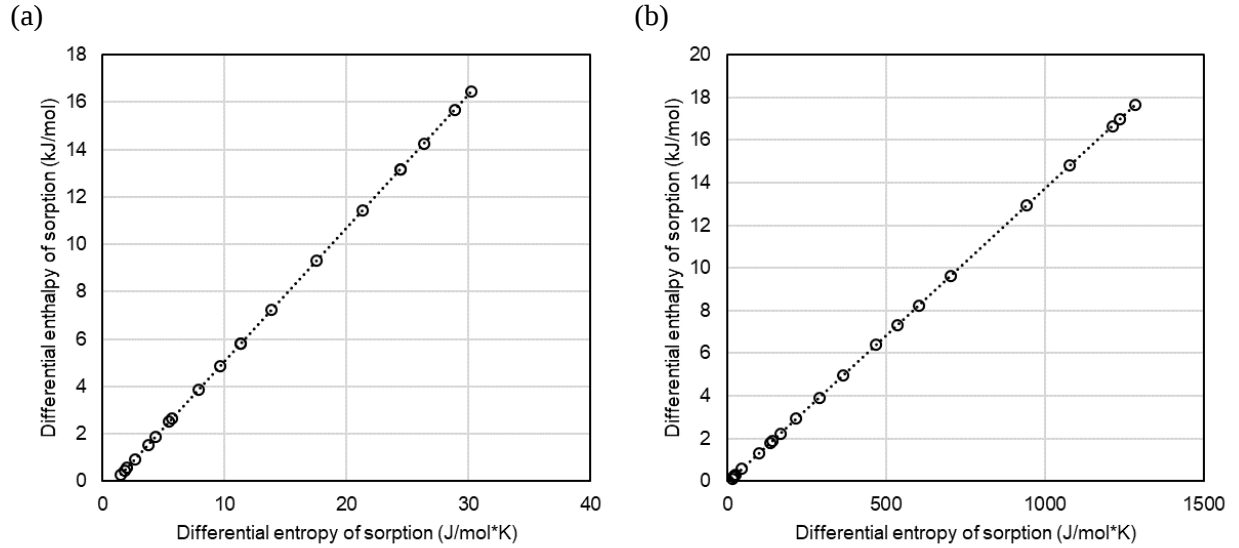


Fig. S33 Enthalpy-entropy plots for the ODE4 model fitted to data at 25 °C (Weichert 1963a) for (a) beech and (b) spruce

Power-law model (ODP6)

To improve upon the exponential model for $r(u)$, we propose a modified power function:

$$r(u) = \zeta_1(u + \zeta_2)^{-\zeta_3} + \zeta_4 \quad (\text{S73})$$

where $\zeta_1 \dots \zeta_4$ are fitting parameters. The differential enthalpy of sorption is given by

$$\Delta \bar{h} = [\zeta_1(u + \zeta_2)^{-\zeta_3} + \zeta_4](L_0 - L_1 T) \quad (S74)$$

Integration (at constant temperature) gives the heat of wetting:

$$q_{wet} = \frac{1}{M_w} \int_{u_i}^{u_f} \Delta \bar{h} du = \frac{(L_0 - L_1 T)}{M_w} \left[\frac{\zeta_1}{1 - \zeta_3} (u_f + \zeta_2)^{1 - \zeta_3} + \zeta_4 u_f - \frac{\zeta_1}{1 - \zeta_3} (u_i + \zeta_2)^{1 - \zeta_3} - \zeta_4 u_i \right] \quad (S75)$$

Substituting Eq. (S73) into Eq. (S62) gives an equilibrium sorption model:

$$a_w = \exp \left\{ -\frac{C}{RT_{ref}} - [\zeta_1(u + \zeta_2)^{-\zeta_3} + \zeta_4] \left[\frac{L_0}{RT} - \frac{L_0}{RT_{ref}} + \frac{L_1}{R} \ln \left(\frac{T}{T_{ref}} \right) \right] \right\} \quad (S76)$$

This equation can be inverted to give the following:

$$u = \zeta_1^{1/\zeta_3} \left[\frac{-R \ln a_w - C/T_{ref}}{L_0/T - L_0/T_{ref} + L_1 \ln(T/T_{ref})} - \zeta_4 \right]^{-1/\zeta_3} - \zeta_2 \quad (S77)$$

The optimized fitting parameters are listed in Table S7, and values of R^2 are given in Tables 4 and 5 of the manuscript. The fitting of water activity and equilibrium moisture content for beech is shown in Fig. S34, heat of wetting in Fig. S35, and differential enthalpy of sorption in Fig. S36. Linear enthalpy-entropy compensation is shown in Fig S37.

Table S7 Parameters of the ODP6 model (with u in kg kg⁻¹, T in K, and $\Delta \bar{h}$ in kJ mol⁻¹)

Parameter	Beech	Spruce
ζ_1	3.042×10^{-3}	3.728×10^{-4}
ζ_2	0.04208	0.1178
ζ_3	1.582	3.458
ζ_4	0.01534	0.01152
C	-2.626	-0.8457
T_{ref}	912.6	607.0

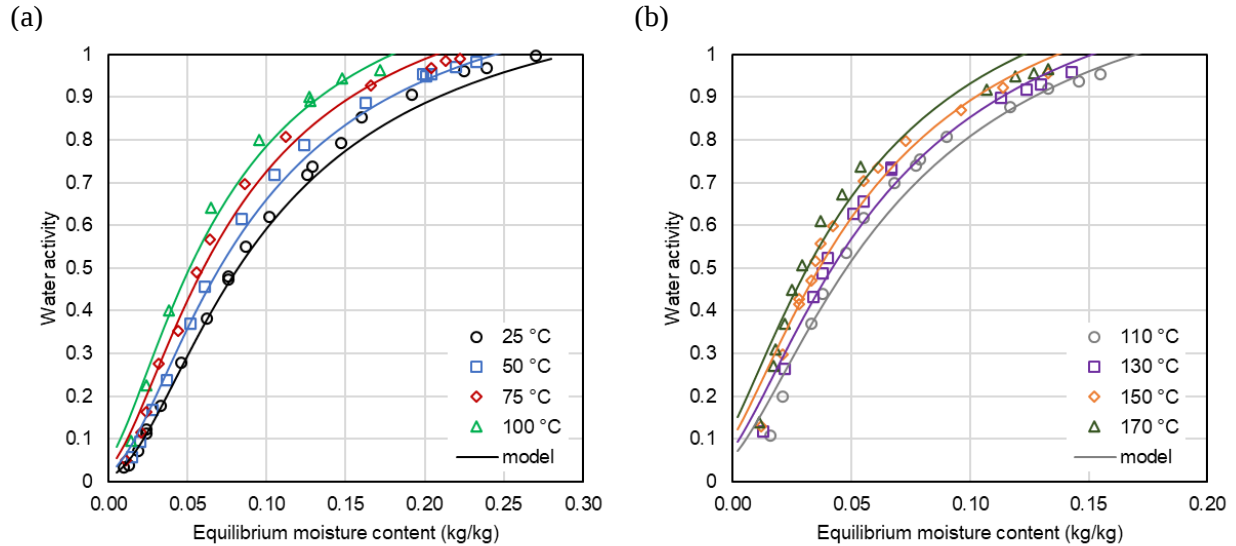


Fig. S34 Water activity vs. equilibrium moisture content for the ODP6 model (curves) fitted to beech data (discrete points) of (a) Weichert (1963a) and (b) Engelhardt (1979)

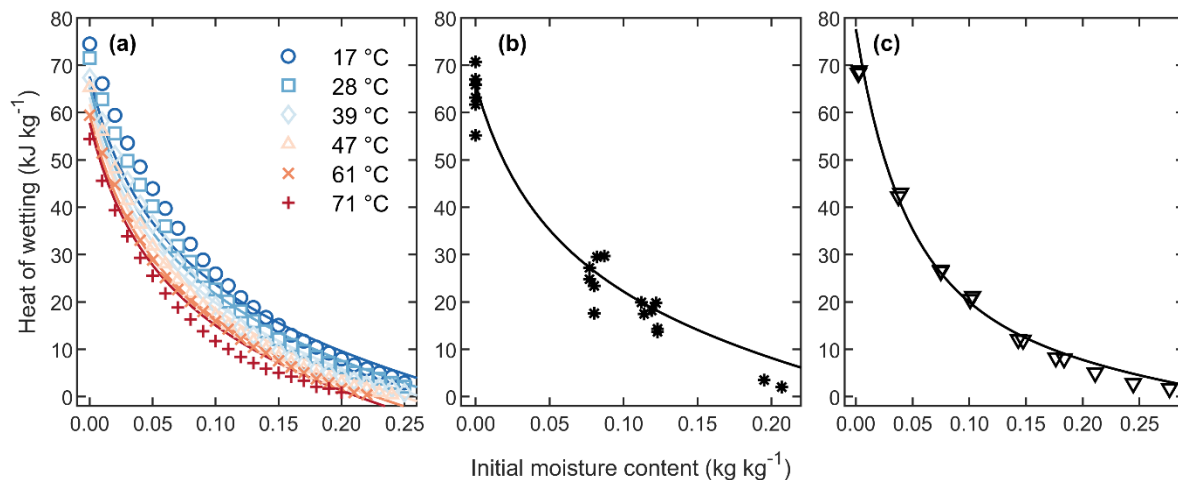


Fig. S35 Heat of wetting vs. initial moisture content from the ODP6 model (solid curves) fit to data (discrete points) of (a) Hearmon and Burcham (1956) for beech at a series of temperatures, (b) Nopens et al. (2019) for beech at 25 °C, and (c) Volbehr (1896) for spruce at 0 °C

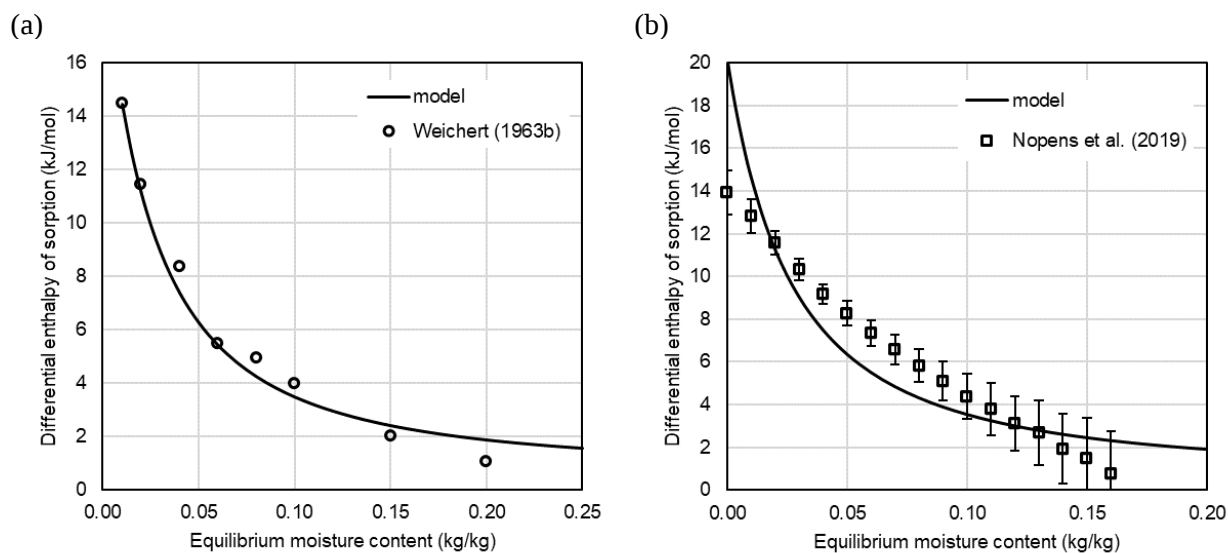


Fig. S36 Differential enthalpy of sorption vs. equilibrium moisture content of beech from the ODP6 model compared with values reported by (a) Weichert (1963b) at 62.5 °C and (b) Nopens et al. (2019) at 25 °C, where error bars indicate standard deviation of three replicates

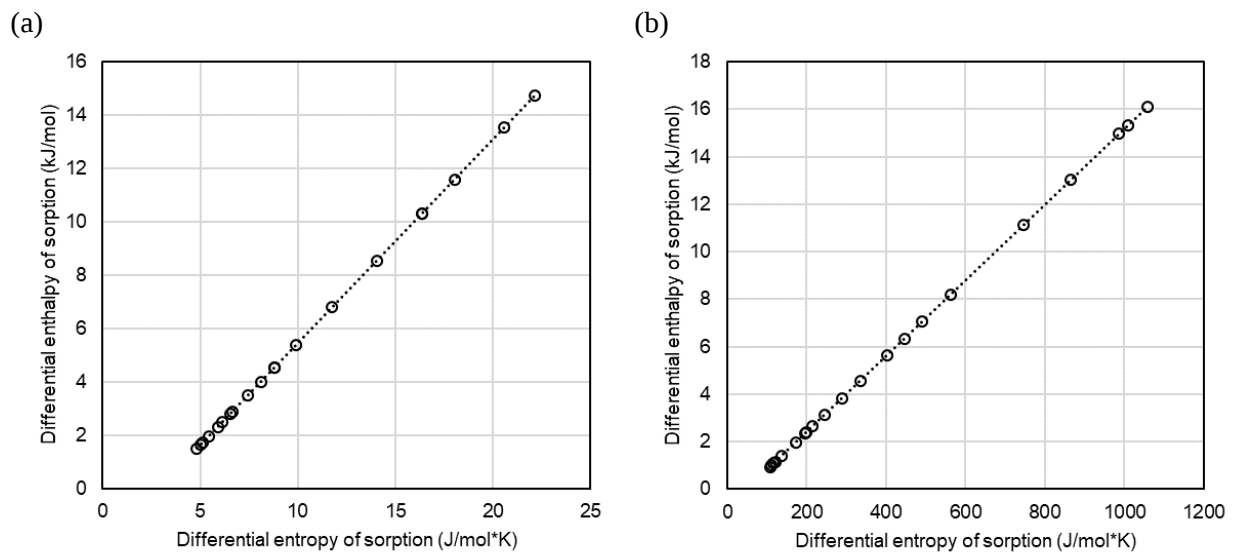


Fig. S37 Enthalpy-entropy plots for the ODP6 model fitted to data at 25 °C (Weichert 1963a) for (a) beech and (b) spruce

VII. Model Optimization Based Only on Equilibrium Moisture Content

The first optimization method maximized the coefficient of determination (R^2) only for EMC, as described in Section 4.3 of the manuscript. The results for all quantities across all models are listed in Table S8 for beech and Table S9 for spruce.

Table S8 Coefficient of determination (R^2) for various models optimized only for equilibrium moisture content of beech

Quantity	Data source	CAST	GAB6	NA6	OC3	ODE4	ODP6
u	Weichert (1963a)	0.997	0.996	0.981	0.876	0.964	0.996
	Engelhardt (1979)	0.998	0.998	0.984	0.924	0.965	0.997
a_w	Weichert (1963a)	0.997	0.997	0.992	0.948	0.982	0.995
	Engelhardt (1979)	0.997	0.994	0.974	0.643	0.942	0.998
$\Delta\bar{g}$	Weichert (1963a)	0.981	-	0.961	-	0.923	0.920
	Engelhardt (1979)	0.992	-	0.903	-	0.831	0.990
q_{wet}	Hearmon and Burcham (1956)	0.880	0.945	0.867	0.210	0.638	0.768
	Nopens et al. (2019)	0.922	0.644	0.691	< 0.1	0.656	0.830
$\Delta\bar{h}$	Weichert (1963b)	0.932	0.865	0.735	0.652	< 0.1	0.123
	Nopens et al. (2019)	0.772	0.444	< 0.1	< 0.1	< 0.1	< 0.1

Table S9 Coefficient of determination (R^2) for various models optimized only for equilibrium moisture content of spruce

Quantity	Data source	CAST	GAB6	NA6	OC3	ODE4	ODP6
u	Weichert (1963a)	0.998	0.997	0.994	0.955	0.984	0.998
a_w	Weichert (1963a)	0.998	0.999	0.995	0.946	0.989	0.997
$\Delta\bar{g}$	Weichert (1963a)	0.994	-	0.983	-	0.964	0.970
q_{wet}	Volbehr (1896)	0.951	< 0.1	< 0.1	0.730	0.834	0.771
$\Delta\bar{h}$	Weichert (1963b)	0.979	0.964	0.978	0.957	0.538	< 0.1

VIII. Supplementary Model Results for Spruce Sorption Data

Curve fits to spruce sorption data for models having six parameters are shown in Fig. S38. These model fits were based on the second optimization method, which maximized the coefficient of determination (R^2) across all experimental data (not just EMC) with weighting factors described in Section 4.3 of the manuscript.

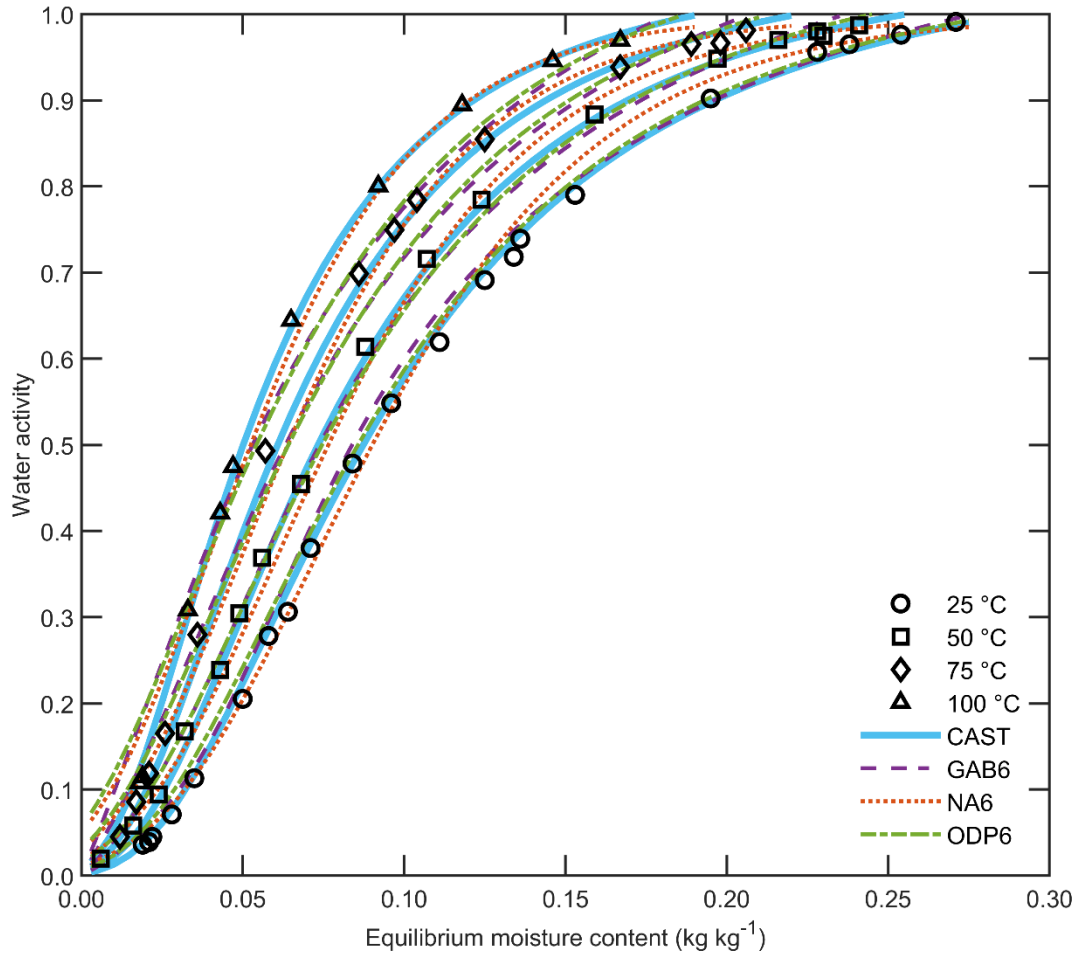


Fig. S38 Water activity vs. equilibrium moisture content for various models (curves) fit to spruce data (discrete points) of Weichert (1963a)

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