SORPTION THEORIES APPLIED TO WOOD[1]

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ABSTRACT

A number of sorption theories are discussed in relation to the wood-water system. The theories are tested in terms of how well they can be made to predict moisture content through curve fitting and how well they can predict heats of adsorption. Theories discussed are the BET (Brunauer, Emmett, Teller). Hailwood and Horrobin, King, and Peirce. Even though the theories can be fitted very closely to experimental sorption data, they do not do well in predicting heat of adsorption. They do, however, all suggest the same general form of adsorption: part of the water is intimately associated with cellulose molecules and part is distinctly less intimately associated.

Keywords: sorption, isotherms, moisture content.

INTRODUCTION

Numerous theories have been derived for sorption of gases on solids, many of which can be applied to the sorption of water vapor by wood. Why has such effort been expended, and what success has been achieved? What can sorption theories tell us, and is what they tell realistic? Can they tell us anything useful about the wood-water system? This paper attempts to answer some of these questions.

The paper reviews the nature of sorption and how water is held in wood, sorption isotherms, and thermodynamics of sorption, and how it all relates to sorption theory. A description of some of the theories is presented, and finally some tests of the theories developed. This should lead us to the point where we can answer some questions on the usefulness of sorption theories.

Our present theoretical understanding does not allow us to estimate the variations of equilibrium moisture content with relative humidity and temperature from first principles. At this point mathematical models, or sorption theories, have been developed. From the most optimistic standpoint, they describe the mechanism of how water is held in wood. From the most pessimistic standpoint, they merely provide an equation that, through curve fitting of data, furnishes a means of correlating and interpolating data. Probably the truth lies somewhere between, and the theories really do give us a glimpse of the mechanism of sorption.

GENERAL NATURE OF SORPTION

Hearle and Peters (1960) and Skaar (1972) have reviewed sorption from the molecular standpoint. Water is believed to be hydrogen-bonded to the hydroxyl

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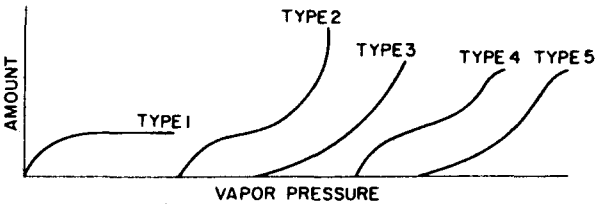


FIG. I. Types of sorption isotherms.

groups of the cellulosic and hemicellulosic portions of wood. Not all hydroxyl groups are accessible to water molecules because cellulose molecules form crystalline regions where the hydroxyl groups of adjacent molecules hold them in a parallel arrangement.

Sorption isotherms

Five general types of sorption isotherms have been identified for various gas-solid systems (Fig. 1). The Type 1 isotherm is characteristic of sorption where a layer of vapor only one molecule thick is formed on the solid. Type 2 sorption is characteristic of sorption where more than one layer of vapor is formed on the solid and where the forces of attraction between the vapor and solid are large. (Wood exhibits this type of sorption.) Type 3 sorption is similar to Type 2 except that the forces between the vapor and solid are relatively small. Types 4 and 5 characterize the case in which the ultimate amount of adsorption is limited by capillary condensation in rigid capillaries.

Sorption isotherms are generally temperature-dependent. As temperature increases, the amount of vapor adsorbed at any given vapor pressure decreases (Fig. 2). Differences of up to 5% moisture content exist at equal relative humidities between different temperatures.

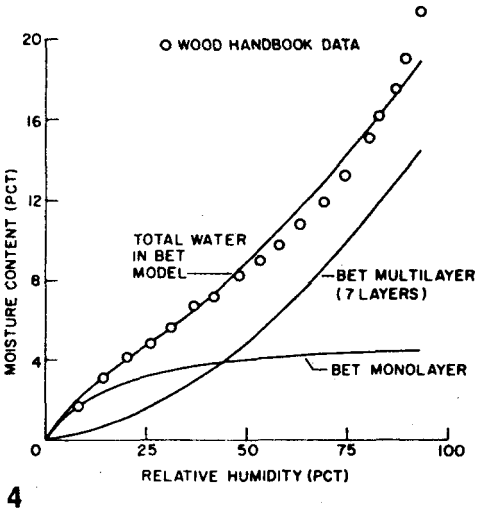
Thermodynamics of sorption

The adsorption of water by wood is an exothermic process. Most sorption theories are derived in such a way that energies of adsorption are an integral part of the theory. The principal thermodynamic quantity of interest for this purpose is the differential heat of adsorption, which is discussed in detail in Hearle and Peters (1960), Stamm (1964), and Skaar (1972).

The energies of adsorption (cal/g water) of water on wood involve (Fig. 3): The energy released when water is adsorbed by the cell wall of wood (or the energy required to evaporate water from the cell wall of wood) is termed Q_v; the energy released when water vapor condenses to water (or the energy required to evaporate water from the liquid state) is termed Q_o, which is the heat of vaporization of water. The difference between these two quantities

$$Q_L = Q_v - Q_o$$

is the differential heat of adsorption. Q_L is the additional energy released, above the heat of vaporization of water, when water is adsorbed by wood. It is also the



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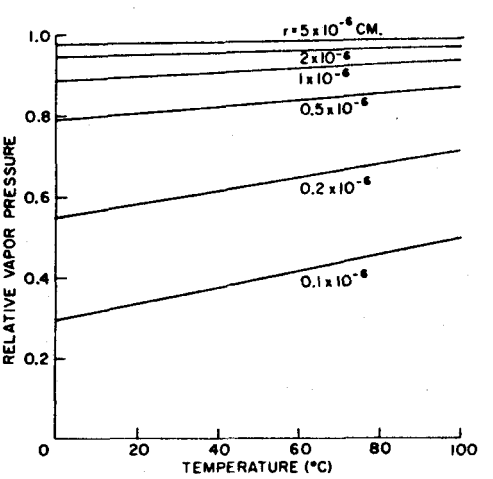

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FIG. 4. Brunauer, Emmett, and Teller sorption theory fitted with sorption data at 40 C from Wood Handbook (1974).

FIG. 5. Dependence of temperature and capillary radius on the relative vapor pressure at which capillary condensation occurs.

slope of the curve. In an exothermic reaction, such as the adsorption of water by wood, K should decrease with an increase in temperature.

SORPTION MODELS

Many theoretical ,sorption models have been offered as explanations for the adsorption phenomena observed in many polymers. The approach here will be to describe only a few, and to do so in more detail than would be possible if many models were covered. The two main criteria for choosing models for description were the extent to which the model can be tested, and how well it is known and how widely it is used. Venkateswaran (1970) has listed the equations of a number of these sorption models. Hearle and Peters (1960). Skaar (1972), and Simpson (1973) have also discussed several models.

There are several general categories of sorption theories. In one category, the theories attribute some portion of sorption to condensation of bulk liquid in capillaries as a result of the lowering of equilibrium vapor pressure over these small capillaries. Another group of theories considers sorption to occur as a result of the buildup of water molecules in layers on the adsorbent. A monolayer is laid down first, and then in some systems multiple layers are built on it. A third category of sorption theories considers the polymer-water system to be a solution.

Brunauer, Emmett, and Teller (BET) theory

The BET theory (1938) is one of the best known and most widely used sorption theories. Its greatest use is probably in estimating surface area from the adsorption of gases on solids where the gas does not swell the solid. Since the wood-water system does swell, this application of the theory is of limited value. In the BET theory, gas molecules are built up on the solid surface in layers on sorption

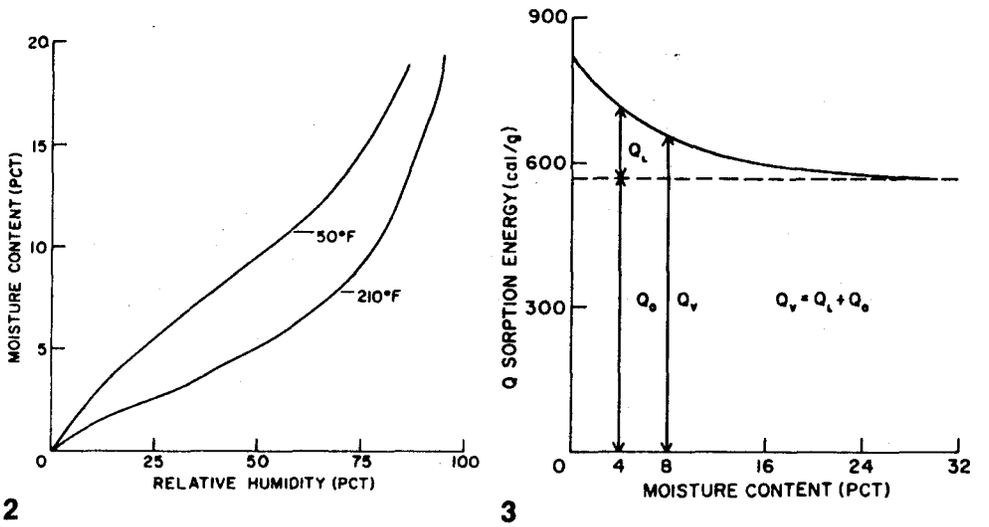


FIG. 2. Effect of temperature on the sorption isotherm of wood.
FIG. 3. Energies of adsorption of water by wood. Q_v = Energy of evaporate water from cell wall. Q_o = Heat of vaporization of water. Q_L = Differential heat of adsorption.

additional energy, above the heat of vaporization, required to evaporate water from wood.

There are two methods of determining Q_L (Skaar 1972). One method involves the use of the Clausius-Clapeyron equation and the temperature dependence of the sorption isotherm of wood. The other method involves the measurement of the heat given off during the adsorption of water by wood. This readily measured quantity is termed the integral heat of wetting W_s (cal/g wood) and is related to Q_L by:

$$Q_L = -\frac{dW_s}{dm}$$

where m is moisture content (g water/g wood).

Another relationship relevant to the thermodynamics of adsorption and how it relates to sorption theories is the Gibbs-Helmholtz equation. This equation relates the temperature dependence of the equilibrium constant of a chemical reaction to the enthalpy for the reaction. A number of the sorption theories contain parameters that are either considered equilibrium constants in the model or are analogous to one. The equation can be written:

$$\frac{d \ln K}{d(1/T)} = \frac{-\Delta H}{R} \tag{1}$$

where K is the equilibrium constant, T is temperature in °K, *H* is the heat of reaction, and R is the gas constant. The equilibrium constant can be plotted against the reciprocal of temperature and the heat of reaction calculated from the

sites. The derivation can consider any number of layers, and for the general case the final equation is:

$$m = \left(\frac{W_m Ch}{1 - h}\,\frac{1 - (n + 1)h^n + nh^{n+1}}{1 + (C - 1)h - Ch^{n+1}}\right) \tag{2}$$

and for the case of a monolayer of water vapor (n = 1):

$$m = \frac{W_m Ch}{1 + Ch} \tag{3}$$

where

m = fractional moisture content
h = relative vapor pressure
W_m = moisture content when monolayer is full
n = number of layers of molecules on a sorption site
C = constant related to the energy of adsorption

Equations (2) and (3) allow us to calculate and examine the complete isotherm once the parameters W_m, *C,* and *n* are known, and to visualize how the model predicts the way that water is held in wood. Figure 4 shows how water is partitioned in wood according to the BET model. Equation (3) predicts the moisture content from the first layer of molecules adsorbed on the sorption sites. This sorption rises rapidly with relative vapor pressure at first, but soon levels off at 4 to 5 (W,) percent moisture content. Before monomolecular sorption is complete, the second, third, etc., layers begin to form, and at high relative vapor pressures most of the total sorption is in the multilayer form. The number of layers of molecules on the sorption sites of wood turns out to be in the range of 5 to 10, according to the model.

BET model with capillary Condensation

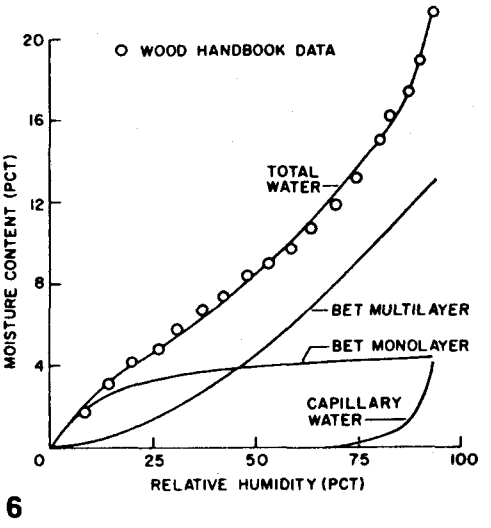
A number of modifications have been made to the BET theory. One possibility is to add a term to account for capillary condensation. Water vapor will condense in small capillaries according to the Kelvin equation:

$$r = \frac{2SM}{\rho RT \ln(1/h)} \tag{4}$$

where

r = radius of capillary
S = surface tension of liquid
M = molecular weight of the liquid
p = density of the liquid
R = gas constant (8.31×10^7 erg. $mole^{-1}$ - $°K^{-1}$)
T = temperature (°K)
h = relative vapor pressure

Equation (4) predicts that the relative vapor pressure at which capillary condensation occurs decreases with decreasing capillary radius—small capillaries fill more readily than large capillaries (Fig. 5). Using equation (4) as a basis, a model



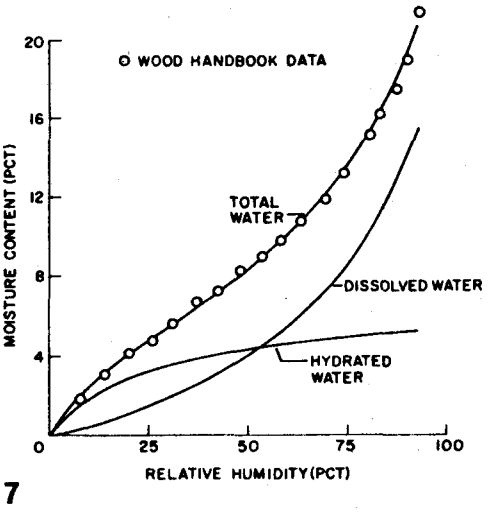


FIG. 6. Sorption model consisting of BET model and capillary condensation. Fitted with sorption data at 40 C from Wood Handbook (1974).

FIG. 7. Hailwood and Horrobin sorption model (one hydrate) fitted with sorption data at 40 C from Wood Handbook (1974).

for capillary condensed water can be derived (Simpson 1973). If all capillaries that contain water are assumed cylindrical with volume V and length ψ, then

$$r = \sqrt{V/\pi\psi} = \frac{2SM}{\rho T \ln(1/h)} \tag{5}$$

The water in these capillaries is thus the portion of total moisture content, M_c, attributable to capillary condensation. Thus,

$$M_c = \frac{V}{W_d} = \frac{\pi\psi}{W_d}\left(\frac{2SM}{RT \ln(1/h)}\right)^2 \tag{6}$$

where W, is the dry weight of wood and the density of the water is 1.

If the assumption is made that capillary Condensation is a separate sorption mechanism that operates in addition to mono- and multilayer sorption, then total sorption can be modeled as an additive combination of the BET model (Eq. (2)) and the capillary condensation model (eq. (6)). The components of this model are shown in Fig. 6. The monolayer component is much the same as the BET model alone (Fig. 4). but the multilayer component is reduced at high relative vapor pressures because the model now allows for capillary water, which becomes significant at relative vapor pressure above about 0.7.

The inclusion of capillary condensation adds another parameter, ψ/W_d to the model that has some physical significance. It is the total length of capillaries (equivalent to cylindrical capillaries) per unit weight of wood. The value of ψ/W_d for wood is in the order of 1010 centimeters per gram (cm/g), indicating a considerable network of fine capillaries where water can condense.

A further indication of the intimacy with which water permeates fine structure

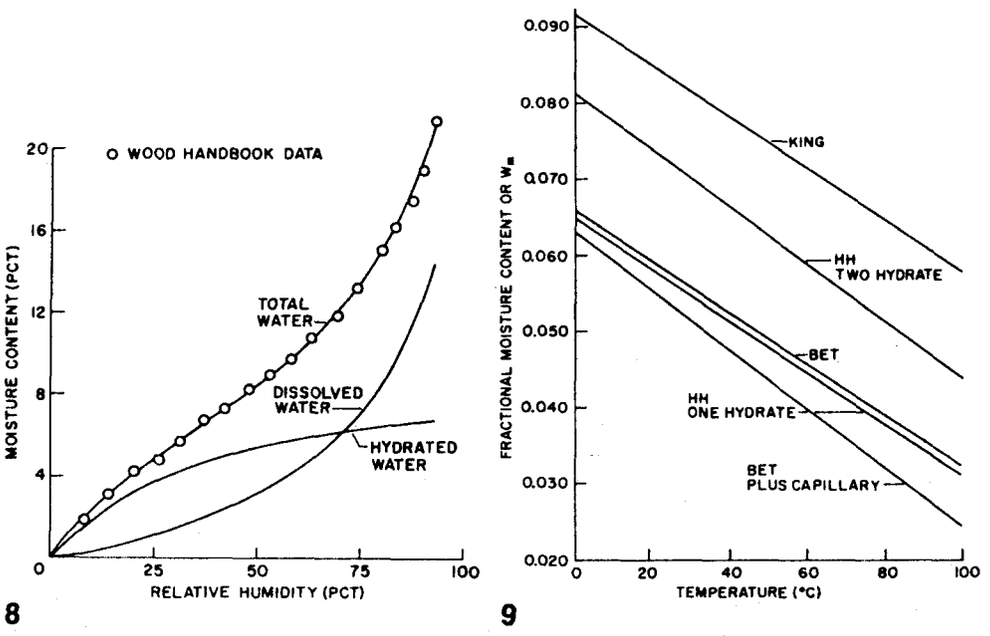


FIG. 8. Hailwood and Horrobin sorption model (two hydrates) fitted with sorption data at 40 C from Wood Handbook (1974).

FIG. 9. Monolayer or hydrated water in wood at relative vapor pressure of I.

of wood comes from the term W_m in the BET equation. W, is the moisture content that corresponds to complete filling of the monolayer, and has been used to estimate surface area. Stamm (1964) described this analysis for swelling systems. The effective contact area A can be calculated from:

$$A = aNW_m/M \tag{7}$$

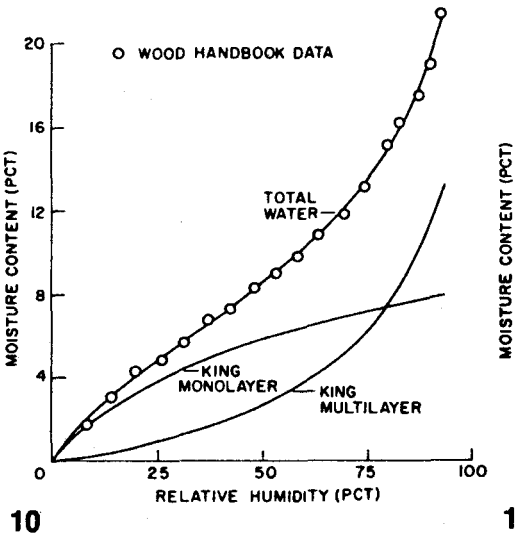
where

a = area of a water molecule
N = Avogadro's number (6.02×10^{23})
M = molecular weight of water

The value of A for wood is in the order of 200 square meters per gram, again indicating that there must be an enormous contact area between water and wood.

Hailwood and Horrobin (HH) theory

Hailwood and Horrobin (1946) developed a sorption theory that considers a polymer-water system to be a solution. Water adsorbed by polymer is assumed to exist in two states: Water in solution with the polymer (dissolved water) and water combined with units of the polymer to form hydrates. The theory is based on the equilibria between polymer. hydrated polymer, and the dissolved water. There are two types of equilibria: One between the dissolved water and the water vapor of the surroundings, and any number of equilibria between the hydrated water and dissolved water. The general form of the model can be written:



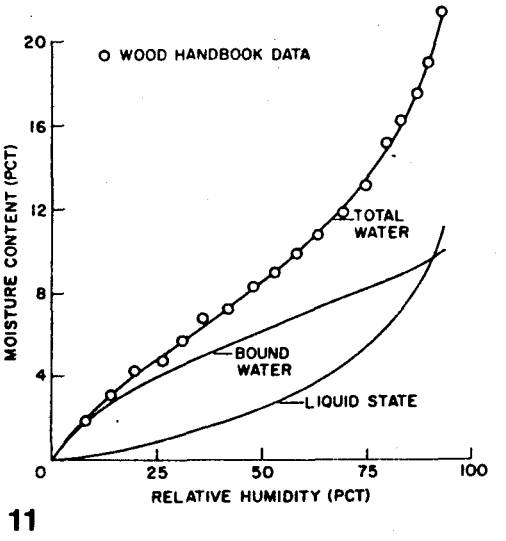


FIG. 10. Sorption model of King fitted with sorption data at 40 C from Wood Handbook (1974).
FIG. 11. Sorption model of Peirce fitted with sorption data at 40 C from Wood Handbook (1974).

$$m = \frac{18}{M_p}\left[\frac{Kh}{1 - Kh} + \frac{\sum_{i=1}^{n} i(Kh)^i K_1K_2 \ldots K_i}{1 + \sum_{i=1}^{n} (Kh)^i K_1K_2 \ldots K_i}\right] \tag{8}$$

where

m = fractional moisture content
h = relative vapor pressure
M_p = molecular weight of polymer unit that forms a hydrate
K = equilibrium constant between dissolved water and surrounding water vapor
$K_1, K_2 \ldots K_i$ = equilibria constant between dissolved water and hydrates

For the case of one hydrate, the model is:

$$m = \frac{18}{M_p}\left(\frac{Kh}{1 - Kh} + \frac{K_1Kh}{1 + K_1Kh}\right) \tag{9}$$

For two hydrates:

$$m = \frac{18}{M_p}\left(\frac{Kh}{1 - Kh} + \frac{K_1Kh + 2K_1K_2K^2h^2}{1 + K_1Kh + K_1K_2K^2h^2}\right) \tag{10}$$

The sorption isotherms from the one- and two-hydrate models are shown in Figs. 7 and 8. The model is very similar to the BET model in the partitioning of water. The hydrated water of the HH model is comparable to the monolayer of the BET theory (W_m of BET comparable to hydrated water component at $h = 1$), and the dissolved water of the HH model is comparable to the multilayer water

TABLE 1. *Moisture content deviation between fitted isotherms and actual sorption data for wood (Wood Handbook. 1974).*

Sorption model	Equation number	Worst deviation (Pct moisture content)	Average deviation (Pct moisture content)
BET	1	3.2	0.5
BET + capillary	1 and 5	0.9	0.2
HH—one hydrate	8	0.8	0.1
HH—two hydrates	9	0.5	0.1
King	10	0.8	0.1
Peirce	11	1.0	0.3

of the BET model (compare Figs. 4 and 7). The values of W_m of the BET models and the amount of hydrated water at h = 1 in the HH models are shown in Fig. 9 as a function of temperature for wood sorption data of the Wood Handbook (USDA 1974). All of the models predict similar amounts of this water that is intimately associated with wood in hydrate or monolayer form.

King theory

King (1960) derived a sorption model whose final equation is of a form similar to the HH one-hydrate model, but is derived from considering sorption similar to the BET model, that is. monolayer adsorption and multilayer adsorption. The final equation of the model can be written as (Simpson 1973):

$$m = \frac{18}{M_p}\left(\frac{BK_1p_0}{1 + K_1p_0} + \frac{DK_2p_0}{1 - K_2p_0}\right) \tag{11}$$

where

m = fractional moisture content
P_0 = vapor pressure
M_p = molecular weight of polymer unit
B = constant proportional to the number of sorption sites in a monolayer
D = constant proportional to the number of sorption sites in a multilayer
K_1 = equilibrium constant between monolayer water and external vapor pressure
K_2 = equilibrium constant multilayer water and external vapor pressure

The model partitions water into two major portions similar to the BET and HH theories: Water that is directly associated with wood and water that is somewhat removed from direct association (Fig. 10). The amount of monolayer water at saturation is slightly higher than the BET and HH models (Fig. 9).

TABLE 7. *Heats of adsorption predicted by sorption models.*

Sorption model	Heat of adsorption (cal/g)	Sorption model	Heat of adsorption (cal/g)
BET	−67	HH—two hydrates	−79.7
BET + capillary	−82	King	−110
HH—one hydrate	21.3	Peirce	−144

Peirce theory

Peirce (1929) developed a sorption theory based on two types of water—"a" phase and "b" phase—held in a polymer. The "a" phase is water bound intimately to the polymer, and the "b" phase is water less tightly held by forces similar to those in a liquid state. Peirce's model can be written as (Skaar 1972):

$$1 - h = (1 - KWm_a)\exp(-BWm_b) \tag{12}$$

where

h = relative vapor pressure
m_a = fractional moisture content of "a" water
m_b = fractional moisture content of "b" water
W and B = constants
K = constant that can be considered an equilibrium constant between "a" water and polymer

The moisture contents m_a and m_b can be written:

$$m_a = \frac{1 - \exp(-Wm)}{W} \tag{13}$$

$$m_b = \frac{Wm + \exp(-Wm) - 1}{W} \tag{14}$$

where *m* is total fractional moisture content. When Eq. (13) and (14) are substituted into Eq. (12), the total isotherm can be calculated.

Peirce's model is shown for wood in Fig. 11. Again, the model depicts the same general sorption as the BET, HH, and King models, i.e., water intimately bound to wood and a less tightly held component.

TESTS OF SORPTION THEORIES

One of the first demands of a sorption theory is that it gives an experimentally correct sorption isotherm. From a strictly mathematical standpoint, it is relatively easy to develop a sorption isotherm that, with the use of several adjustable coefficients, can be made to fit experimental data quite well. However, the test of goodness-of-fit of experimental isotherms is not a sufficient test of a theory, and a more sensitive test requires a consideration of the energy of adsorption.

Fit of experimental data

Although fitting sorption models with experimental data is an insufficient test of the validity of a model, it is worth examining as a possibly useful way to correlate and interpolate experimental data. Figures 4, 6, 7, 8, 10, and 11 and Table I indicate the degree of fit of the experimental models to sorption data for wood (Wood Handbook 1974). These data involve a series of isotherms from 0 to 100 C, and have been fitted by nonlinear regression to a number of sorption models (Simpson 1973). With the exception of the BET, all models reviewed in this paper give an excellent representation of the isotherm. Deviations between actual data and the fitted isotherms are 1% moisture content or less. The BET

model (Fig. 4, Eq. (2)) fits poorly at high relative vapor pressures, where deviations are as high as 3.2% moisture content.

Heat of adsorption tests

A far more critical test of the sorption models is their ability to predict observed values of the heat of adsorption of water by wood. The parameter *C* of the BET model is defined as:

$$C = k \exp(-(Q_v - Q_o)/RT) \tag{15}$$

where

k = constant (assumed to have a value of 1)
Q_v and Q_o = as defined previously
R = gas constant
T = temperature

Thus, the differential heat of adsorption, $Q_L = Q_v - Q_o$, can be calculated from values of *C* determined by fitting data to the BET model. In the BET model only adsorption of the first layer results in a heat of adsorption. The values of Q_L calculated from Eq. (15) at, for example, 50 C are 67 and 82 calories per gram (cal/g), respectively, for the data from the Wood Handbook fitted to the BET model of Eq. (2) and the BET plus capillary model of Eq. (2) and (6). Heats of adsorption determined either calorimetrically or by the Clansius-Clapeyron equation are in the range of 260 to 280 cal/g (Volbehr 1896; Kelsey and Clarke 1956; Skaar 1972).

The remainder of the models reviewed in this paper can be tested for agreement of heats of adsorption by assuming the temperature-dependence of the equilibrium constants of the models follows a relationship similar to Eq. 1. The adsorption of water vapor by wood is an exothermic reaction, and as such, an equilibrium constant should decrease with an increase in temperature (or the constant should increase with the reciprocal of temperature). In a plot of the logarithm of the equilibrium constant versus the reciprocal of absolute temperature, the heat of adsorption is proportional to the slope and for an exothermic reaction should have a negative value. The equilibrium constants of the sorption models reviewed here have all been determined as a function of temperature (Simpson 1973). The heats of adsorption calculated from these constants are shown in Table 2. Agreement with measured heats of adsorption is not good. The closest agreement (Peirce model) is in error by a factor of two, and the one hydrate Hailwood and Horrobin model predicts an endothermic reaction instead of an exothermic reaction.

Mechanical property tests

One of the extensions of Peirce's model is the prediction that the relative modulus of rigidity should be linearly related to the amount of "a" water (Peirce 1929; Meredith 1957). Meredith (1957) has shown this to be true for a number of natural polymers. This relationship can be tested for modulus of elasticity in bending from the known variation of this property with total moisture content (Wood Handbook 1974), and is shown in Fig. 12 where the relative modulus (ratio

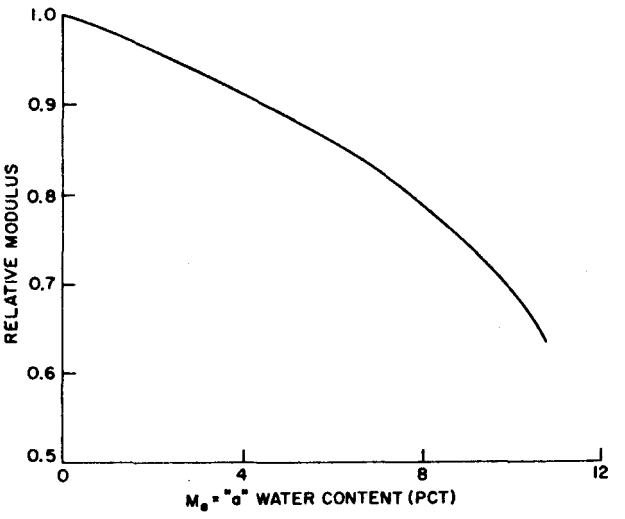


FIG. 12. Effect of "a" water content of Peirce model on relative modulus of elasticity in bending on Douglas-fir at 70 F.

of modulus at moisture content m to modulus at zero moisture content) is plotted against "a" water content (calculated from Eq. (13)). The results are not linear as predicted by the theory.

Are sorption theories useful?

The sorption models discussed represent some of the most widely known theories-ones that have been applied to wood in the past, and ones that can be compared with actual sorption data. One test of the theories is how well they can predict the heat of adsorption. Values of heat of adsorption that are predicted by the models are in error by 50% or more, and in some cases the models predict endothermic reactions that are known to be exothermic. All models incorporate simplifying assumptions that are necessary in order to derive a mathematical model. Perhaps it is too much to expect these simplified models to accurately predict the energy associated with adsorption. For example, one of the simplifying assumptions in the BET model, that all of the energy of adsorption is in monolayer adsorption, probably precludes it from accurately predicting the heat of adsorption. All of the theories discussed here paint the same general picture of adsorption: part of the water is intimately associated with cellulose molecules (monolayer, hydrated, bound water) and part is distinctly less intimately associated (multilayer, dissolved, liquid). This general view has become the accepted concept of how water is held in wood (and many other polymers).

The models reviewed here can be fitted with nonlinear-regression techniques to experimental data, and most of them with excellent results. If there is one practical use of these models at present, it is their excellent ability to correlate, interpolate, and compactly store a large amount of sorption data for wood. The analysis of Simpson (1973) shows that moisture content can be calculated with deviations of no more than $^1/_2$% moisture content over the entire moisture content

and temperature range. This accurate and compact storage of sorption data can be very useful in many kinds of mathematical or computer modeling.

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