

A MODEL FOR SORPTION OF WATER VAPOR BY CELLULOSIC MATERIALS

Ralph M. Nelson, Jr.

Research Mechanical Engineer
United States Department of Agriculture Forest Service
Southeastern Forest Experiment Station, Southern Forest Fire Laboratory
P.O. Box 5106, Macon, GA 31208

(Received 12 January 1982)

ABSTRACT

The sorption of water vapor by cellulosic materials is modeled with an exponential relationship between the Gibbs free energy change and equilibrium moisture content. The utility and simplicity of the model are illustrated with applications to several sets of sorption data in the literature. Adsorption and desorption isotherms generally are described with an accuracy of $\pm 0.5\%$ moisture content up to relative humidities of about 90%. Effects of temperature and sorption hysteresis are examined briefly.

Keywords: Sorption isotherms, adsorption, desorption, Type II sorption.

The sorption (adsorption and desorption) of water vapor by cellulosic materials at a fixed temperature is characterized by sigmoid curves relating equilibrium moisture contents and relative humidities. These relationships are of considerable practical interest because they greatly affect the properties of materials such as wood, paper, textiles, and cellulose derivatives during the manufacturing process or in use as final products. Some of these important properties are strength, dimensional stability, machinability, adhesiveness, and decay resistance.

The nature of adsorption has been discussed extensively in the literature, and many theoretical models have been derived to explain the details of this process. Simpson (1979) has shown that a number of theories of Type II (or multilayer) adsorption can describe sorption data for wood, and that they provide reasonable mechanistic interpretations of how wood takes up water. In contrast to work on adsorption, little effort has been made to describe theoretically the equilibrium moisture contents obtained by desorption. Instead, the kinetics of this process has been of greater interest, and numerous models describing desorption rates have been proposed (Stamm 1964; Hearle and Peters 1960; Skaar 1972; and Siau 1971).

Nonlinear regression methods were used by Simpson (1971, 1973) to fit sorption data for wood to several mathematical models of Type II adsorption. He found that the equilibrium moisture content of wood can be reproduced well with these techniques. Deviations of 0.5% moisture content or less were obtained over the entire range of temperature and relative humidity. Anderson and McCarthy (1963) derived an equation for Type II adsorption on the basis of an exponential relationship between moisture content and differential heat of wetting. Combination of this exponential expression with a form of the Gibbs-Helmholtz equation from thermodynamics results in a sigmoid relationship between moisture content and relative humidity when temperature is constant. The authors show that their

isotherm accurately reproduces adsorption data for a number of fibrous materials over a range of relative humidities from 10 to 85%.

This paper describes an empirical model that can be used to characterize isotherms for Type II sorption and to present supporting evidence from data in the literature. The approach used is similar to that of Anderson and McCarthy (1963) and, indeed, a similar final result is found. The two models differ, however, in the thermodynamic variables employed and in the ease with which the model parameters can be related to measurable quantities. In subsequent sections, the thermodynamic considerations and practical applications to existing data are discussed.

THERMODYNAMIC CONSIDERATIONS

This section presents details of model development as well as a discussion of hysteresis and temperature effects on sorption and how these effects change the parameters of the model. Limitations in development of the model are described also.

Model development

The model to be developed must be regarded as empirical in that, like the Anderson-McCarthy equation, it has as its foundation an observed relationship between a thermodynamic variable and equilibrium moisture content. If the adsorption and desorption of water vapor by a cellulosic material at constant temperature are measured after reaching equilibrium with several relative humidities, the resulting isotherms generally take the sigmoid shapes referred to earlier. In a thermodynamic analysis of these isotherms, the decrease in Gibbs free energy per gram of sorbed water may be calculated from

$$\Delta G = -\frac{RT}{M} \ln \frac{p}{p_0} = -\frac{RT}{M} \ln \left(\frac{RH}{100} \right) \quad (1)$$

where R is the universal gas constant, M is the molecular weight of water, p is the equilibrium pressure of water vapor (assumed to be an ideal gas) at absolute temperature T , and p_0 is the corresponding saturation vapor pressure (Skaar 1972). Since p/p_0 equals percent relative humidity (RH) divided by 100%, ΔG is also written in terms of RH in Eq. (1). Consideration must be given to the limiting cases of Eq. (1) when RH approaches zero and 100%, corresponding to dryness and fiber saturation, respectively. Let the moisture content expressed as a fraction of the oven-dry weight be denoted by m . Then the fiber saturation point, m_s , logically should be defined as the moisture content of the material for which $\Delta G = 0$ at a specified temperature. This definition is consistent with the concept that m_s corresponds to a RH of 99.99% (or 100% for practical purposes). On the other hand, an infinite ΔG is obtained from Eq. (1) when $RH = 0$. Such a result is questionable since the Gibbs-Helmholtz equation would then require an infinite heat change, which has never been observed (Babbitt 1942). For this paper, a finite value of ΔG , say ΔG_0 , is regarded as a satisfactory estimate of ΔG as RH

approaches zero. These considerations impose the following two conditions on any sorption model which is intended to apply over the entire RH range:

$$\Delta G = \Delta G_0 \text{ when } m = 0 \quad (2)$$

$$\Delta G = 0 \text{ when } m = m_s. \quad (3)$$

Stamm and Loughborough (1935), Kelsey and Clarke (1956), and Babbitt (1942) are among the authors who have reported ΔG as a function of m for cellulosic materials. Except for m values approaching the fiber saturation point, their data suggest an exponential variation of ΔG with m , and such a relationship is used here. This constitutes a point of departure from Anderson and McCarthy (1963), who utilize a similar relationship between differential heat of wetting and moisture content. A model to consider is

$$\ln \Delta G = \ln \Delta G_0 \left(1 - \frac{m}{m_s}\right). \quad (4)$$

This model fails to satisfy Eq. (3) because $\Delta G = 1$ when $m = m_s$. It also restricts the upper limit of RH to about 97% at room temperature. On the other hand, a high degree of linearity often can be achieved in plots of $\ln \Delta G$ versus m . For example, strong linearity is evident in Figs. 1 and 2, which present plots of experimental data reported by Stamm (1964) and Kelsey and Clarke (1956) for sorption of water vapor by white spruce and klinki pine, respectively. When extrapolated to $\ln \Delta G = 0$ (or $\Delta G = 1$), the desorption curves intersect the m -axis at values close to the fiber saturation point as determined from the isotherm plots. Thus, the m value at $\Delta G = 1$, defined as m_v for both adsorption and desorption, must replace m_s in the model. The extent to which m_v represents m_s for plots of desorption data is uncertain because of extrapolation to a value of m_s in a region where moisture content is increasing rapidly with relative humidity. Nevertheless, m_v may be regarded as an approximate value of m_s for desorption. An alternative model satisfying both Eqs. (2) and (3) is

$$\ln(\Delta G + 1) = \ln(\Delta G_0 + 1) \left(1 - \frac{m}{m_s}\right). \quad (5)$$

If plots of experimental data are constructed according to Eq. (5), it is generally found that linearity is not as great as with Eq. (4), but that the deviations from linearity are not excessive. These deviations usually occur in the region of high RH where both models fail to correctly describe sorption affected by capillary-condensed water. Because of its greater linearity and relative simplicity, Eq. (4) with m_v replacing m_s will be utilized in the remainder of this paper. Failure to satisfy Eq. (3) is not considered to be of practical interest here.

Rearrangement of Eq. (4) gives, for desorption data,

$$\Delta G = (\Delta G_0)^{1-(m/m_v)} \quad (6)$$

where dimensions of ΔG are cal/g. Substitution of Eq. (1) into Eq. (6) produces the desorption isotherm

$$\frac{RH}{100} = \exp \left[-\frac{M}{RT} (\Delta G_0)^{1-(m/m_v)} \right] \quad (7)$$

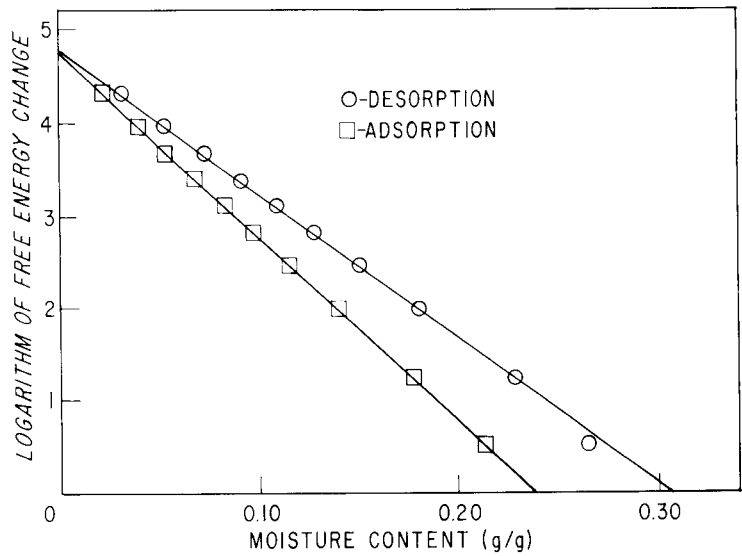


FIG. 1. Gibbs free energy change with equilibrium moisture content for sorption of water vapor by white spruce wood at 25 C. Adapted from Stamm (1964).

which is a two-parameter model valid over most of the RH range. In an exact sense, the model is not valid at extremely small RH values. In the limiting case, when $m = 0$ and $T = 298$ K, Eq. (7) becomes

$$\frac{RH}{100} = \exp\left[-\frac{M\Delta G_0}{RT}\right] \approx \exp[-5.02] \approx 0.0066. \tag{8}$$

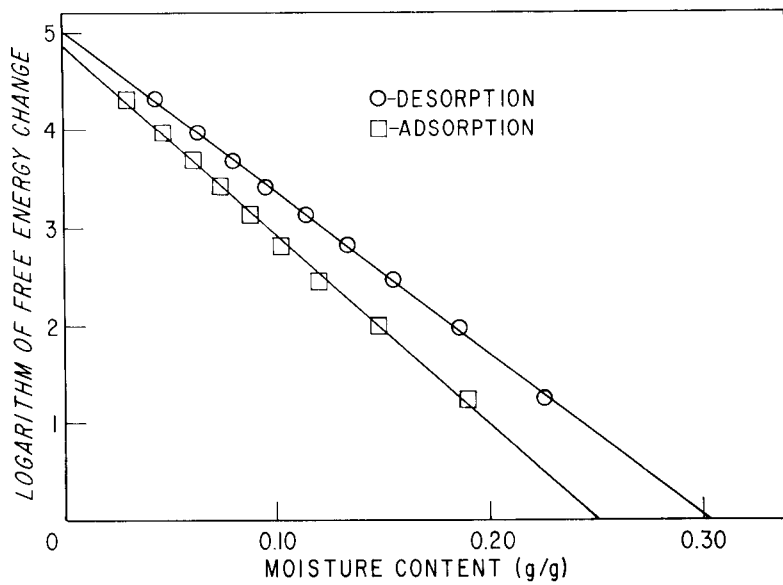


FIG. 2. Gibbs free energy change with equilibrium moisture content for sorption of water vapor by klinki pine at 25 C. Adapted from Kelsey and Clarke (1956).

In this calculation ΔG_0 is taken as 165 cal/g, which agrees with published data for wood (Stamm and Loughborough 1935). This value is consistent with a differential heat of desorption of 270 cal/g and an entropy change of 0.35 cal/g $^\circ$ K. The true value of RH is only of academic interest, however, since for practical purposes RH = 0 when m = 0.

Effects of hysteresis and temperature

Sorption hysteresis is a term that refers to the fact that the amount of water held by cellulosic materials at a given temperature and relative humidity depends on the direction from which equilibrium is approached. More water can be held following desorption than following adsorption. The quotient of the adsorption and desorption moisture contents at fixed relative humidity and temperature, referred to here as the hysteresis ratio, varies from about 0.75 to 0.90 (Stamm 1964). This variability primarily depends upon the RH level and the nature of the sorbing material.

A relationship similar in form to Eq. (7) describes RH as a function of m during adsorption except at values of RH exceeding about 90%. As for desorption, capillary condensation apparently alters the exponential relationship between ΔG and m determined by forces of attraction between the cellulosic material and water. For adsorption, however, m_v in Eq. (7) must be interpreted in a different way than for desorption. Though no immediately apparent significance can be attached to m_v as determined from plots of adsorption data, it is interesting to note that if the logarithm of Eq. (6) written for adsorption is divided by the same expression for desorption, the hysteresis ratio at the given temperature and relative humidity is approximated by the ratio of m_v values for adsorption and desorption. If the hysteresis ratio is denoted by r, the resulting equation is

$$r = \frac{\left[\frac{\ln \Delta G}{\ln \Delta G_0} - 1 \right]_a \cdot (m_v)_a}{\left[\frac{\ln \Delta G}{\ln \Delta G_0} - 1 \right]_d \cdot (m_v)_d} \quad (9)$$

where subscripts a and d refer to adsorption and desorption and the quantity $\ln \Delta G$ is the same for both processes. Accuracy of the approximation is dependent upon the degree of equality between values of ΔG_0 for adsorption and desorption. Consider Figs. 1 and 2, for example. Because values of ΔG_0 for adsorption and desorption are more nearly identical in Fig. 1 than in Fig. 2, the hysteresis ratio should be more accurately estimated for the Stamm data than for the data in Fig. 2. A check of the data in Figs. 1 and 2 shows this is indeed the case.

The general effect of increasing temperatures on sorption of water vapor by cellulosic materials is to decrease the amount of water held when other factors remain constant. However, even this effect is not always present since at high RH values the higher-temperature isotherms for soda-boiled cotton of Urquhart and Williams (1924) and for some of the wood data of Kelsey (1957) cross those of lower temperature. Furthermore, cellulosic materials degrade rapidly at high temperatures and relative humidities, making the interpretation of sorption data even more complex.

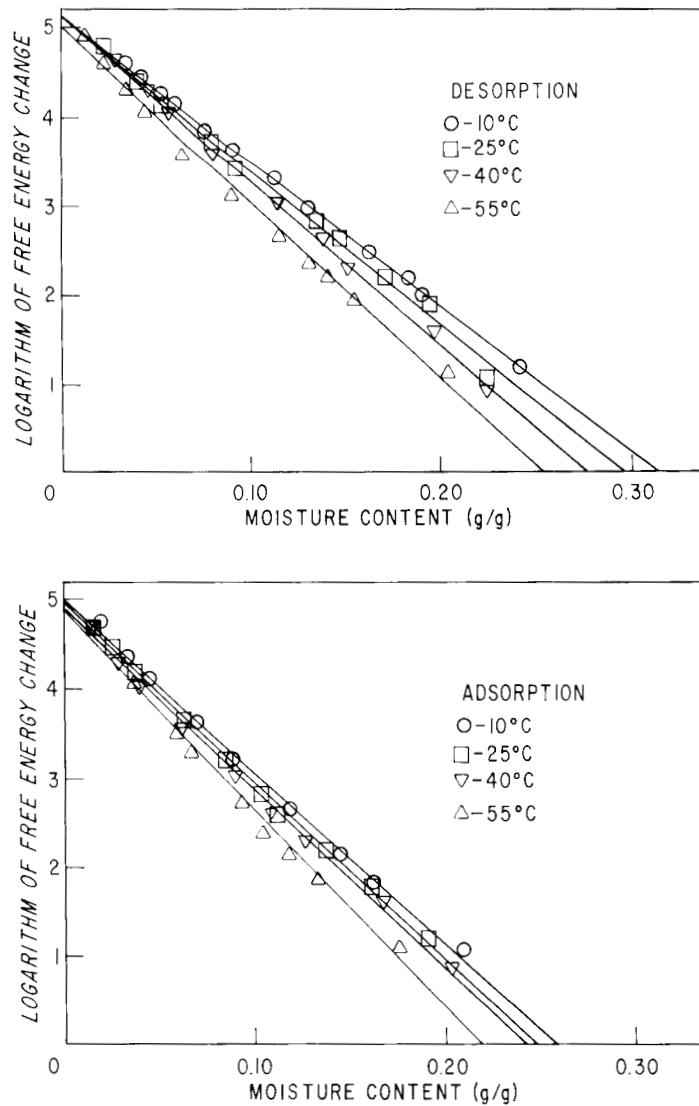


FIG. 3. The effect of temperature on Gibbs free energy change as a function of equilibrium moisture content for klinki pine (Kelsey 1957).

According to Eq. (7), nonexplicit effects of hysteresis and temperature on sorption can be accounted for by their influence on ΔG_0 and m_v . Existing data (Stamm and Loughborough 1935) suggest that ΔG_0 is independent of temperature, but that m_s (and thus m_v) is temperature-dependent. A detailed study of these effects is beyond the scope of this paper, and no attempt will be made to generalize ΔG_0 and m_v in such a way that they can be used for purposes of prediction. Only a brief inquiry into how these parameters vary will be reported here.

Figures 3 and 4 show plots of experimental data for temperature-dependent water vapor sorption by klinki pine (Kelsey 1957) and cotton thermally stabilized

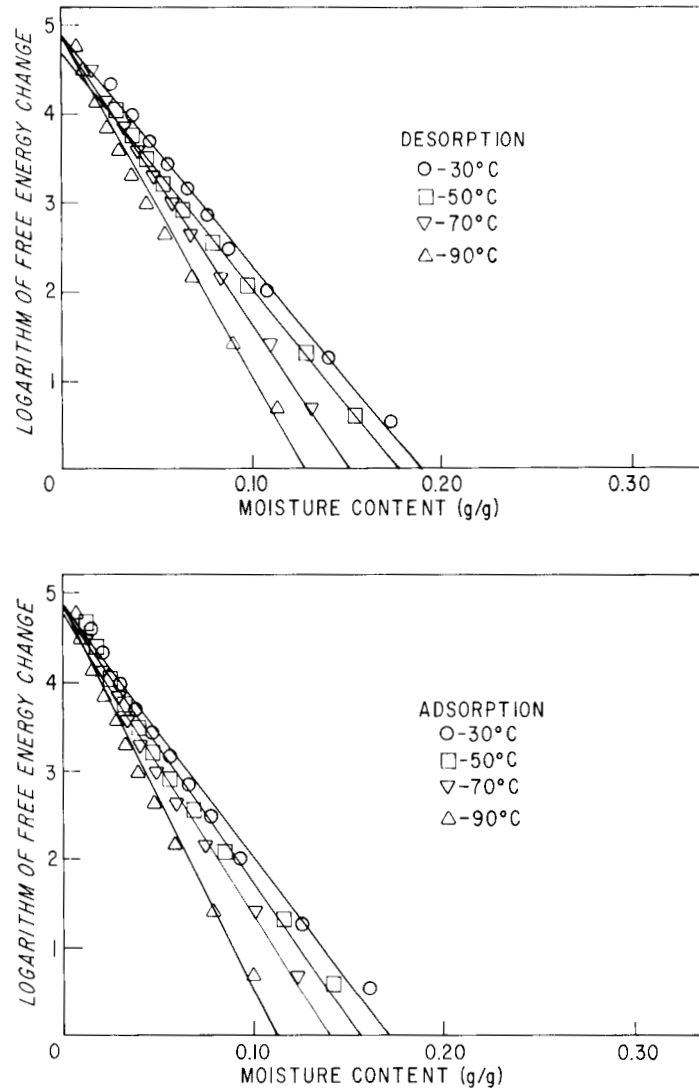


FIG. 4. The effect of temperature on Gibbs free energy change as a function of equilibrium moisture content for thermally stabilized cotton (Jeffries 1960).

at 90 C (Jeffries 1960). Figure 4 shows that overall linearity of $\ln \Delta G$ with m for cotton is relatively poor, but that the variables are roughly linear until $\ln \Delta G$ falls below about 2.5. This value corresponds to relative humidities between about 70 and 75% at temperatures from 30 to 90 C. These data show that the linearity of $\ln \Delta G$ with m is not always valid over the entire range of m . Nevertheless, useful approximations of sorption isotherms can still be made, as will be demonstrated later. The two data sets were analyzed by least squares regression to determine values of A and B in the equation

$$\ln \Delta G = A + Bm \quad (10)$$

TABLE 1. Summary of regression results for data of Kelsey (1957) and Jeffries (1960). Values of ΔG_0 and m_v can be determined from: A and B.

Parameter	Temperature (°C)	Adsorption	Desorption	Ratio (Ads./Des.)
Kelsey Data (Wood)				
A	10	4.957	5.122	0.968
B	10	-19.132	-16.306	1.173
m_v	10	0.259	0.314	0.825
A	25	4.915	5.106	0.962
B	25	-19.786	-17.266	1.146
m_v	25	0.248	0.296	0.838
A	40	4.848	5.119	0.947
B	40	-19.920	-18.482	1.078
m_v	40	0.243	0.277	0.877
A	55	4.834	5.005	0.966
B	55	-21.997	-19.695	1.117
m_v	55	0.220	0.254	0.866
Jeffries Data (Cotton)				
A	30	4.807	4.870	0.987
B	30	-28.086	-26.721	1.092
m_v	30	0.171	0.189	0.905
A	50	4.805	4.689	1.026
B	50	-30.750	-26.491	1.161
m_v	50	0.156	0.177	0.881
A	70	4.758	4.844	0.982
B	70	-34.119	-31.997	1.066
m_v	70	0.136	0.151	0.921
A	90	4.862	4.828	1.007
B	90	-43.235	-37.743	1.146
m_v	90	0.112	0.128	0.875

where $A = \ln \Delta G_0$ and $B = -(A/m_v)$ in accordance with the logarithmic form of Eq. (6). Values of A, B, m_v , and their ratios (adsorption to desorption) are presented in Table 1. As discussed earlier, m_v for desorption approximates the fiber saturation point occurring in a reproducible sorption cycle. An m_v for adsorption estimates the product of m_v for desorption and the hysteresis ratio. The question of whether the differences shown in Table 1 are statistically significant has not been considered here. Such a study should be based on extensive data and would extend beyond the scope of this paper.

The data in Table 1 indicate that for wood A decreases slightly with increasing temperature, but that a similar trend is less evident for cotton. The small change in A for wood may occur because prior to sorption the wood had not been stabilized at a temperature equal to or exceeding the highest experimental temperature. Factor B increases in the negative direction with increasing temperature, as would be expected if m_s (or m_v) decreases with temperature. The larger B values for cotton reflect the smaller moisture contents associated with sorption

in this material due to fewer available sites and higher temperatures. Kelsey (1957) gives a value of 1.65 for the ratio of sites available for sorption in wood to those in cellulose. At 25 to 30 C, Table 1 shows this ratio to be about 1.50 for averaged values of m_v for adsorption and desorption. This ratio decreases to about 1.42 in the neighborhood of 50 C.

Limitations

In addition to error due to the assumptions made in model development, certain limitations may introduce further error into isotherms constructed with the present method. Some of these factors, which are believed to be of secondary importance, are: species variability, internal or external stresses, fiber plasticization and degradation caused by exposure to heat, and size of sorption step (Wengert and Mitchell 1979). It is noted also that the model has not been tested with sorption data for extracted or partially decayed materials.

APPLICATION OF THE MODEL

This section describes application of the model isotherm to experimental data. Illustrations of the results are presented through use of the model to represent data presented earlier.

Procedures

Equation (7) shows that two parameters must be known to describe a set of adsorption or desorption data at a fixed temperature. These parameters are ΔG_0 and m_v , and are known *a priori* only in a general way. For example, there is evidence that $\Delta G_0 \approx 165$ cal/g and $m_v \approx 0.30$ for wood. An isotherm constructed on the basis of this information alone would probably be a good representation of desorption for several species of wood at room temperature. If one wants to be more specific, and has knowledge of ΔG_0 and a single data point (preferably at a relative humidity smaller than 85%), a linear relationship between $\ln \Delta G$ and m , and hence a sorption isotherm, can be determined from Eqs. (1) and (10). However, more useful applications of the model may be made when two or more moisture content-relative humidity data points (below 85% relative humidity) are available along with the constant temperature at which the data points are defined. In such cases, Eqs. (1) and (10) can be used either to mathematically represent a number of experimental data points or to supply missing data (when only two or three data points are available) without specific knowledge of ΔG_0 , m_v , or the hysteresis ratio. First, the temperature and relative humidity data are used in Eq. (1) to obtain values of ΔG . Next, these values and their corresponding moisture contents are substituted into Eq. (10) to produce equations that can be solved for the parameters A and B. If only two data points are available, the resulting set of algebraic equations can be solved. If a number of data points are available, A and B can be determined either by inspection of a plot of the data according to Eq. (10) or by linear regression techniques. With A and B known, ΔG_0 and m_v can be computed from the relationships

$$A = \ln \Delta G_0 = -Bm_v \quad (11)$$

and used in Eq. (7) either for the purpose of curve fitting or calculating missing

data. Alternatively, A and B can be used in Eq. (10) and then combined with Eq. (1) to accomplish the same tasks.

A more complex situation arises if the data set to be described involves effects of hysteresis and temperature. Little specific information is available on how ΔG_0 and m_v vary with temperature and from one cellulosic material to another. The effect of hysteresis presumably is best accounted for through use of a hysteresis ratio to correct a known m_v value for desorption to a corresponding value for adsorption by simple multiplication. Hysteresis ratios are expected to depend on temperature, relative humidity, and nature of the material undergoing sorption (Skaar 1979). Clearly, information similar to that in Table 1 can be of help. However, further research will be required to determine the applicability of the simple model described here to temperature-dependent sorption data.

Results

Figures 3 and 4 represent experimental sorption data for which the linearity of $\ln \Delta G$ with m is not pronounced. Figures 5 and 6 show the corresponding isotherms calculated from Eq. (7) with ΔG_0 and m_v determined from values of A and B in Table 1. The experimental data points are plotted for comparison. For the Kelsey data in Fig. 5, the calculated moisture contents generally are smaller than the experimental values at the low- and high-humidity ends of the isotherms. They slightly overestimate the data in the middle of the relative humidity range. The curves for cotton in Fig. 6 are similar. This behavior is to be expected from careful examination of Figs. 3 and 4, and is due to representing the nonlinear data with a single straight line determined by a regression model. Failure of the model isotherms to pass through the origin in Figs. 5 and 6 is caused by introduction into Eq. (7) of a finite, rather than infinite, value for ΔG as RH approaches zero. This deviation from the mathematical relationship expressed by Eq. (1) causes negative values of m that are not shown in the figures. However, for practical purposes, $m = 0$ when $\text{RH} = 0$. The maximum standard error of the estimate for data in Fig. 3 is 0.0108; for Fig. 4, this value is 0.0228. Corresponding average standard errors of the estimate are 0.0065 and 0.0140.

In cases when linearity is more pronounced, better agreement between the model and experiment is achieved. Because of the strong linearity in the data of Figs. 1 and 2, the constants A and B from Eq. (10) were not determined by regression, but from lines placed through the data by visual estimation. Thus, isotherms in the form of Eq. (7) can be written by inspection for the data in Fig. 1 (with M/RT equal to 0.0304) as

$$\frac{\text{RH}}{100} = \exp[-.0304(\exp[4.77])^{1-(m/.307)}] \quad (12)$$

and

$$\frac{\text{RH}}{100} = \exp[-.0304(\exp[4.75])^{1-(m/.239)}] \quad (13)$$

for desorption and adsorption, respectively. Similar isotherms for the data in Fig. 2 are

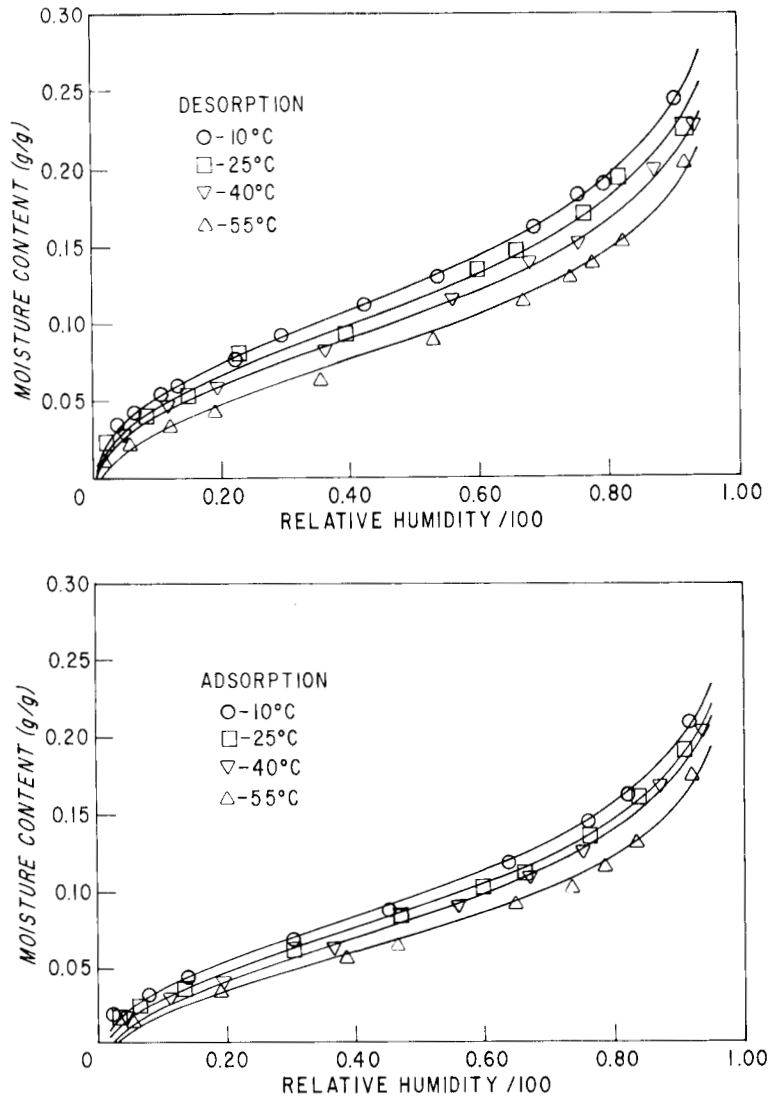


FIG. 5. Comparison of experimental and calculated isotherms for sorption data of Kelsey (see Fig. 3).

$$\frac{RH}{100} = \exp[-.0304(\exp[5.0])^{1-(m/.304)}] \quad (14)$$

and

$$\frac{RH}{100} = \exp[-.0304(\exp[4.85])^{1-(m/.251)}]. \quad (15)$$

The computed isotherms are shown in Figs. 7 and 8 with the actual data plotted for comparison. Except for RH approaching zero, the agreement is excellent, as expected.

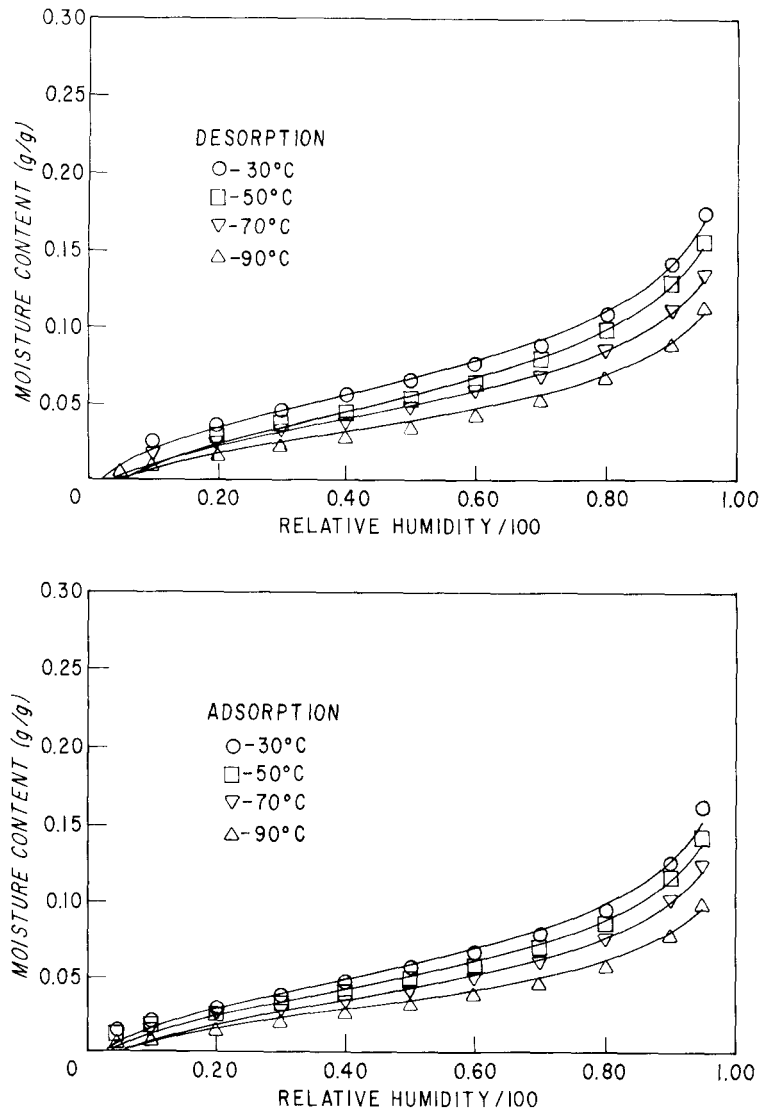


FIG. 6. Comparison of experimental and calculated isotherms for sorption data of Jeffries (see Fig. 4).

DISCUSSION

Figures 5 to 8 demonstrate that the relationship given in Eq. (7) can represent water vapor sorption by cellulosic materials for relative humidities between about 5 and 90%. As with other sorption models, complexities caused by capillary condensation invalidate the model at higher humidities.

The model presented in this paper is similar to two of the mathematical models of adsorption discussed by Simpson (1973). These are the isotherms of Anderson and McCarthy (1963) and Bradley (1936). The primary difference between the present model and that of Anderson and McCarthy is the variable (Gibbs free

