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THERMODYNAMICS OF THE SWELLING OF WOOD

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Although the swelling of a number of colloidal materials has been studied intensely, little attention has been given the thermodynamic aspects of swelling. This lack of attention is perhaps because the major part of sorption and swelling data are not subject to thermodynamic calculations. Katz (2) has pointed out that thermodynamics deals only with true equilibrium conditions and hence such effects as those of sorption and swelling hysteresis and changing surface of sorption during a single cycle must be eliminated in order that the results have theoretical significance.

Katz (2) has compared the differential heats of swelling in water obtained from thermal data with the changes in free energy of swelling calculated from moisture content-vapor pressure data for cotton, wood, and casein, using the equation

$$-\Delta F = \frac{RT}{\mathrm{M}} \ln \frac{P}{P_0} \tag{1}$$

in which $-\Delta F$ is the change in free energy in gram-calories occurring when 1 g. of liquid is added to an infinite amount of swelling material at a moisture content in equilibrium with the relative vapor pressure $\frac{P}{P_0}$ R being the gas constant, T the absolute temperature, and M the molecular weight of the liquid. Since the differences between the differential heats of swelling and the changes in free energy of swelling were small, he concluded that they were within the range of experimental error and that consequently the entropy change was negligible.

Fricke and Luke (1), however, have shown that this is by no means the case. They determined both the integral heat of swelling at different moisture content values and the moisture content-relative vapor pressure relationship at two different temperatures for agar-agar, casein, and keratin

[1] Maintained at Madison, Wisconsin, by the Forest Service of the U. S. Department of Agriculture, in cooperation with the University of Wisconsin.

swelling in water. They were thus able to calculate the differential heat of swelling, using the integrated form of the Clausius-Clapeyron equation

$$\Delta H = \frac{RT_1T_2}{M(T_2 - T_1)} \ln\left(\frac{P_2}{P_1} - \frac{P_{0_2}}{P_{0_1}}\right) \tag{2}$$

in which ΔH is the change in the heat of swelling in gram-calories occurring when 1 g. of the liquid is added to an infinite amount of swelling material at a moisture content in equilibrium with the vapor pressure P_2 at the temperature T_2 and the vapor pressure P_1 at the temperature T_1, P_0, and P_{0_1} being the corresponding saturation vapor pressures and the other symbols having the same significance as in equation 1. In these calculations as well as in those for obtaining $-\Delta F$ the averages between desorption and adsorption moisture contents corresponding to each relative vapor pressure were used as an approximate means of eliminating the effects of hysteresis. The values for ΔH calculated in this way agreed very well with the values obtained from the thermal measurements, thus substantiating the validity of the theoretical equation. Values of $-\Delta F$ calculated from the vapor pressure data were in all cases less than the corresponding values of ΔH, showing that a definite entropy change ΔS accompanies swelling; thus

$$\Delta S = \frac{\Delta H - (-\Delta F)}{T} \tag{3}$$

Katz (3) has recently admitted the validity of Fricke and Lüke's findings, and suggests that the increase in entropy occurring during swelling is due to an orientation or compression of the water molecules, which become adsorbed on the surface of the swelling material, or to an association of these molecules.

In connection with a study of the seasoning of wood, the Forest Products Laboratory recently had occasion to collect moisture content—relative vapor pressure—temperature data on the drying of wood. As these data were obtained under conditions which practically eliminate hysteresis effects, it seemed worth while to subject them to thermodynamic analysis.

The equilibrium moisture content determinations were made in four specially designed drying chambers, each of which had a capacity of about 16 cu. ft. The chambers were equipped with electrically driven blowers which moved the air uniformly through the drying compartments at a rate of about 100 ft. per minute. The wet- and dry-bulb temperatures in each kiln were under the control of a thermostat of the vapor tension type. The drying conditions in the chambers were read frequently through glass windows.

The dry-bulb temperature oscillated on an average about $^1/_4$°F. above and below the desired value, while the wet-bulb temperature had a total positive and negative amplitude of about $^1/_2$°F. The wet- and dry-bulb cycles would sometimes be out of phase 180°, with the result that the wet-bulb depression was sometimes $^3/_4$°F. greater or less than desired. The maximum amplitude of relative vapor pressure oscillations at the higher temperatures was from 1.5 to 3.0 per cent for different vapor pressures, and at the lower temperatures from 4.0 to 8.0 per cent.

From twenty-five to forty strips of green flat-sawed Sitka spruce were used in determining the equilibrium moisture content for a given temperature and relative vapor pressure. The strips were cut about 3 mm. thick and weighed from 100 to 125 g. each when in an oven-dry condition. The specimens were suspended from lead stoppers located in the roof of the chambers and were weighed *in situ* during the drying process to 0.05 g.

The hysteresis phenomenon encountered in desorption and adsorption measurements made on very small specimens under the most carefully controlled vapor pressure conditions was largely eliminated in these measurements. The specimens used were sufficiently large to permit the setting up of moisture gradients across the sections during the process of drying. This combined with the oscillations in vapor pressure permit alternate desorption and adsorption to take place, thus tending to establish an intermediate moisture content equilibrium. The appreciable reduction in hysteresis obtained in this way is illustrated in figure 1 by the oscillating vapor pressure—desorption curve. The normal desorption and the adsorption curves shown in figure 1 were obtained by Seborg and Stamm (5) by using very small cross sections of wood suspended from quartz helical balances in thermostatically controlled (25° ± 0.02°C.) tubes through which air humidified over saturated salt solutions was passed. These carefully controlled conditions tend to promote the maximum hysteresis effect. All the available drying data obtained under industrial control conditions on other softwood species also gave curves which fell within this hysteresis loop. The oscillating vapor pressure—desorption curve approaches more nearly the normal desorption curve at high relative vapor pressures and the adsorption curve at low relative vapor pressures. This would be expected on the basis of Urquhart and Williams' (8) explanation of the hysteresis loop. In the initial desorption the maximum number of the hydroxyl groups of the amylene oxide chains of cellulose are satisfied by water. When the material approaches the dry state these hydroxyl groups are drawn closer and closer together as a result of shrinkage, and they finally mutually satisfy each other. On adsorption part of these hydroxyl groups are not freed for water adsorption, thus accounting for the decreased moisture equilibrium values. Oscillating vapor pressure conditions at high relative vapor pressures hence have only a

slight tendency to cause the hydroxyl groups of the cellulose mutually to satisfy each other, whereas this tendency becomes appreciable at low relative vapor pressures.

The dotted line in figure 1 connecting the origin with the saturation point represents the sorption conditions that would be attained if Henry's law were followed. This line is tangent at the origin to the curve for hysteresis-free sorption, showing that Henry's law is obeyed at infinitesimal concentrations.

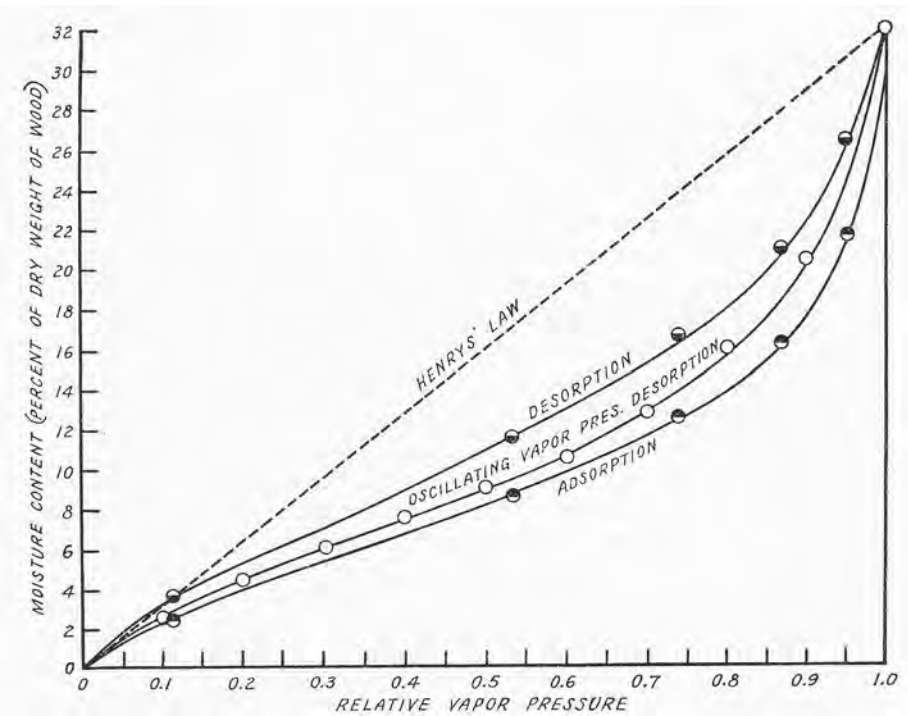

FIG. 1. MOISTURE CONTENT—RELATIVE VAPOR PRESSURE RELATIONSHIP FOR SITKA SPRUCE UNDER NORMAL DESORPTION AND ADSORPTION CONDITIONS AND UNDER OSCILLATING VAPOR PRESSURE DESORPTION CONDITIONS AT 25°C.

In figure 2 the moisture content—relative vapor pressure isotherms for Sitka spruce are plotted for 10°F. temperature intervals from room temperature to the boiling point of water. The changes in the fiber-saturation points (saturation moisture content) with temperature are given in figure 3. The fiber-saturation points change linearly with the temperature, increasing approximately 0.1 per cent for a decrease in temperature of 1°C.

In figure 4 are plotted the differential heats of swelling calculated with the aid of equation 2 from the data of figure 2 together with differential

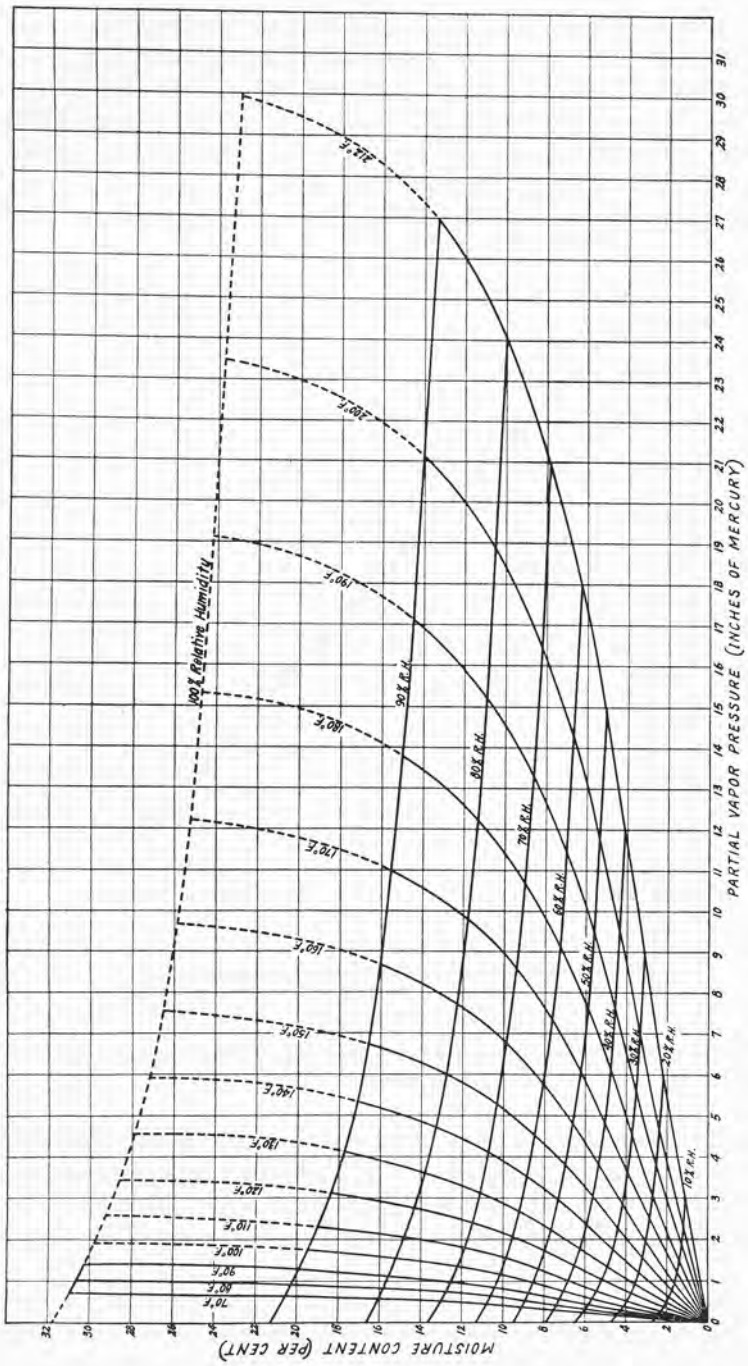

FIG. 2. THE MOISTURE CONTENT OF SITKA SPRUCE AT EQUILIBRIUM WITH VARIOUS TEMPERATURES, PARTIAL VAPOR PRESSURES, AND RELATIVE HUMIDITIES UNDER OSCILLATING VAPOR PRESSURE CONDITIONS

The solid lines in the curves are based on experimental data; the dotted parts of the lines are calculated

heat of swelling obtained from the integral heat of swelling data of Volbehr (9). The 87.8°C. curve was calculated from the 200° and 180°F. isotherms, the 71.1°C. curve from the 200° and 120°F. isotherms, and the 54.4°C. curve from the 140° and 120°F. isotherms. The 0°C. curve is the experimental curve of Volbehr. Below 6 per cent moisture content the curves are all identical within experimental error. Above this moisture content the values of ΔH increase with a decrease in temperature. Vol-

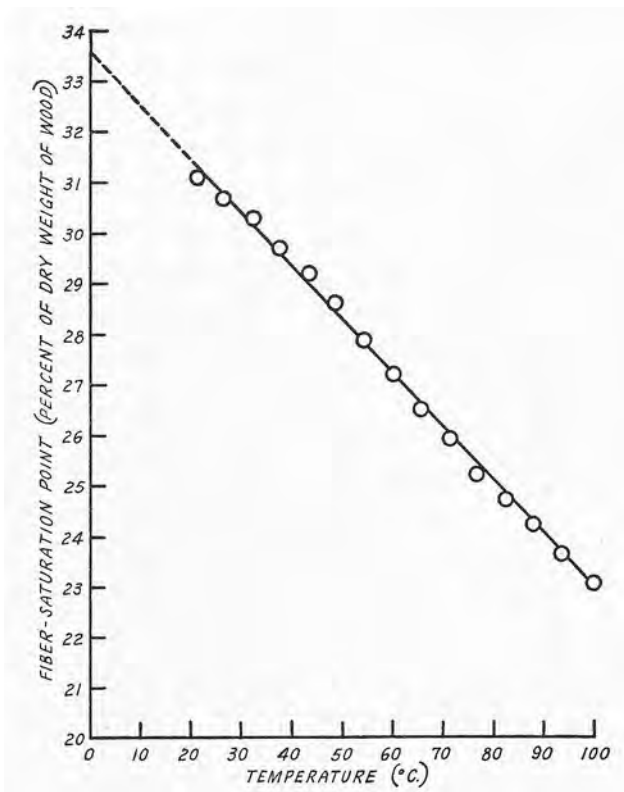

FIG. 3. CHANGE IN FIBER-SATURATION POINT WITH TEMPERATURE FOR SITKA SPRUCE

behr's experimental values for pine are in complete accord with the calculated values given for Sitka spruce. The agreement between species is not surprising, as practically all softwoods have almost identical fiber-saturation points (7) and would be expected to have similar adsorptive powers.

In figure 5 are plotted the isosteres, logarithm of vapor pressure against the reciprocal of the absolute temperature, for a number of different moisture content values from the data of figure 2. The linear isosteres at the

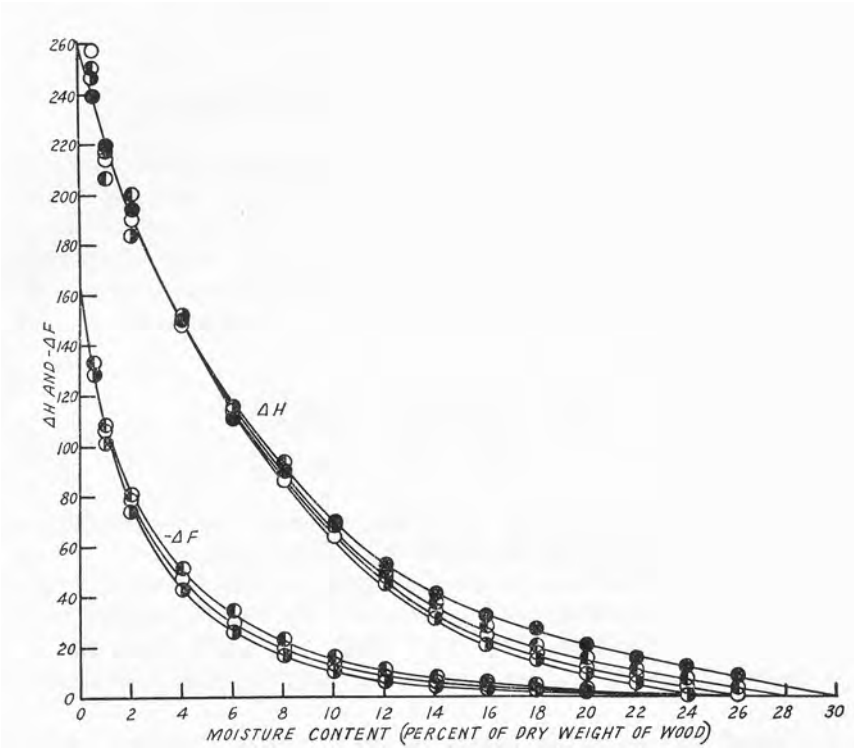

FIG. 4. DIFFERENTIAL HEAT OF SWELLING AND FREE ENERGY CHANGE WITH MOISTURE CONTENT FOR SITKA SPRUCE

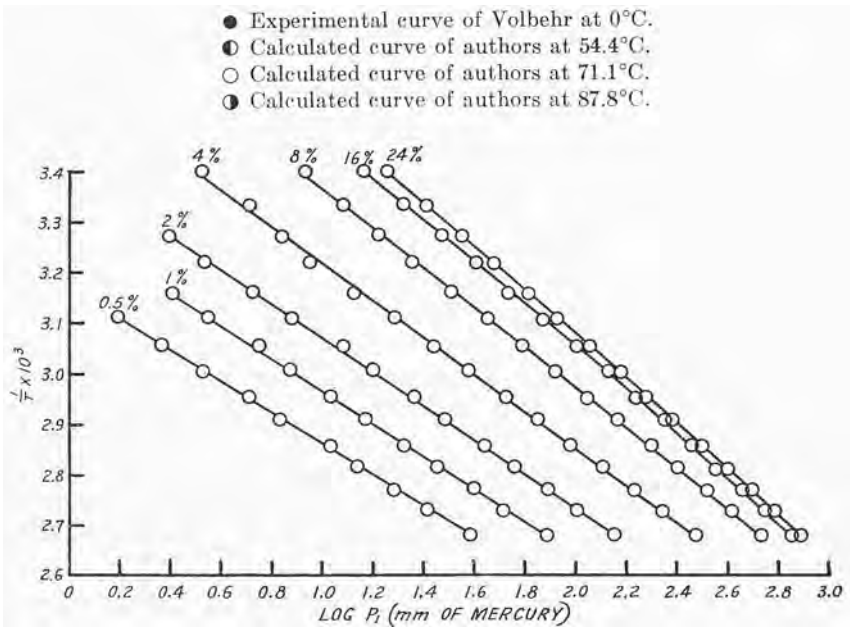

FIG. 5. LOGARITHM OF VAPOR PRESSURE—RECIPROCAL OF THE ABSOLUTE TEMPERATURE ISOSTERES FOR SITKA SPRUCE AT THE INDICATED MOISTURE-CONTENT VALUES

lower moisture content values indicate that the temperature coefficient of the heats of swelling is zero. The slight convex curvature of the isosteres at higher moisture contents indicates that the ΔH values increase slightly with a decrease in temperature. This agrees with ΔH curves in figure 4. The heat of swelling can also be calculated from these isosteres by taking the difference between the slope of any isostere and the saturation isostere thus:

$$\Delta H = -\frac{R}{M}\left(\frac{\mathrm{d}\ln P_1}{\mathrm{d}\frac{1}{T}} - \frac{\mathrm{d}\ln P_0}{\mathrm{d}\frac{1}{T}}\right) \tag{4}$$

The isosteres for the lowest moisture content values approach parallelism. This would be strictly true only if Henry's law were obeyed.

The changes in the free energy of swelling calculated with the aid of equation 1 are plotted in figure 4 together with the heat of swelling curves. These were calculated from the 190°, 160°, and 130°F. isotherms, respectively. The —ΔF values increase very slightly with a decrease in temperature.

In figure 6 are plotted the entropy change curves calculated with the aid of equation 3. They show that a definite entropy change accompanies swelling up to the fiber-saturation point. The entropy changes for the moisture content values below 6 per cent are unaffected by the temperature. At higher moisture content values there is a definite increase in the entropy change with a decrease in the temperature.

The ΔH, —ΔF, and ΔS curves are all smooth curves which show no sign of a sharp transition between the bound or surface adsorbed water and the capillary condensed water or water held by van der Waals forces, although the AS curves show a slight inflection at low moisture content values. This is in keeping with the moisture content—relative vapor pressure curves which also lack a sharp discontinuity. The points of adsorption must thus vary in activity as in the case of a metal catalyst. The attractive force at the weakest of these adsorption points must be of the same order of magnitude as the van der Waals force exerted by the most active adsorption point at a distance of at least one molecular diameter from the surface. Such a gradual transition, with perhaps a slight overlapping, from surface-bound water to water held by the van der Waals forces has been recently illustrated in a diagrammatic manner by Sheppard and Newsome (6). It is also very similar to the two-phase adsorption theory of Pierce (4) who, however, believes that a dynamic equilibrium is set up over the whole sorption range between the surface-bound water and water held by van der Waals forces such that the fraction of the total water taken up that goes into the bound phase is proportional to the ratio of unoccupied true adsorption positions to the total

number of adsorption positions. According to these conceptions the inflection point in the moisture content—relative vapor pressure curves corresponds approximately to the transition point between the surface-bound water and the water held by van der Waals forces. It is interesting to note from figure 2 that this inflection point occurs at a relative vapor pressure of about 0.30 for all of the temperatures. This relative vapor pressure

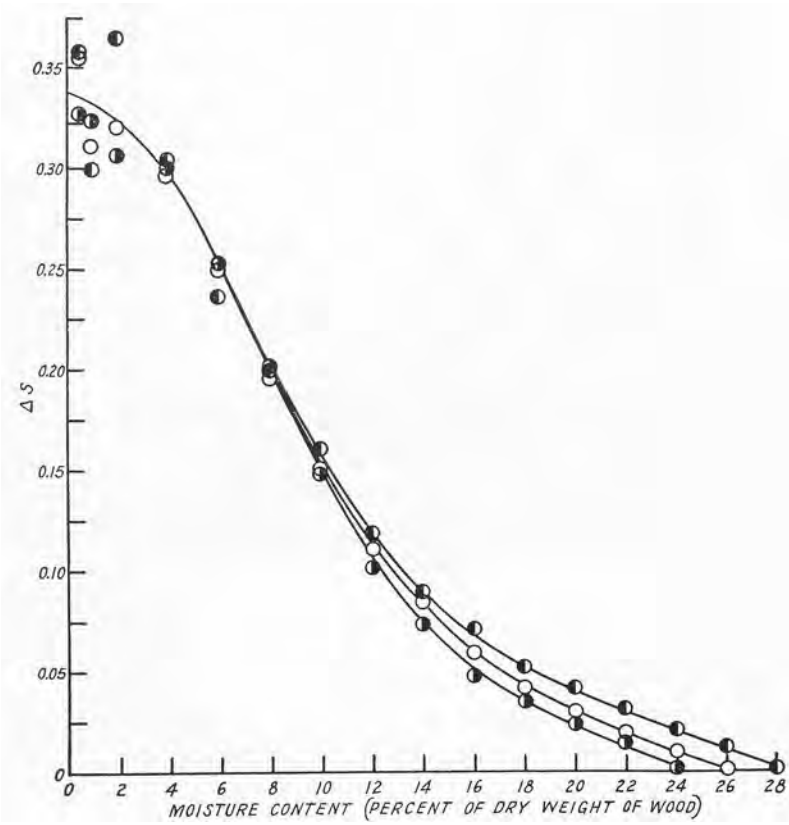

FIG. 6. CHANGES IN ENTROPY WITH CHANGES IN MOISTURE CONTENT OF SITRA SPRUCE

◐ 54.4°C. ○ 71.1°C. ◑ 87.8°C.

further gives a capillary radius when applying Kelvin's equation for the relationship between meniscus curvature and vapor pressure that is only 2.3 times the molecular diameter. This is very near the limiting distance expected for primary molecular attraction, and should represent the limiting size of capillary in which capillary condensation can take place.

In figure 7 are plotted the ΔH, $-\Delta F$, and ΔS versus moisture content curves for soda-boiled cotton calculated from the adsorption data of Ur-

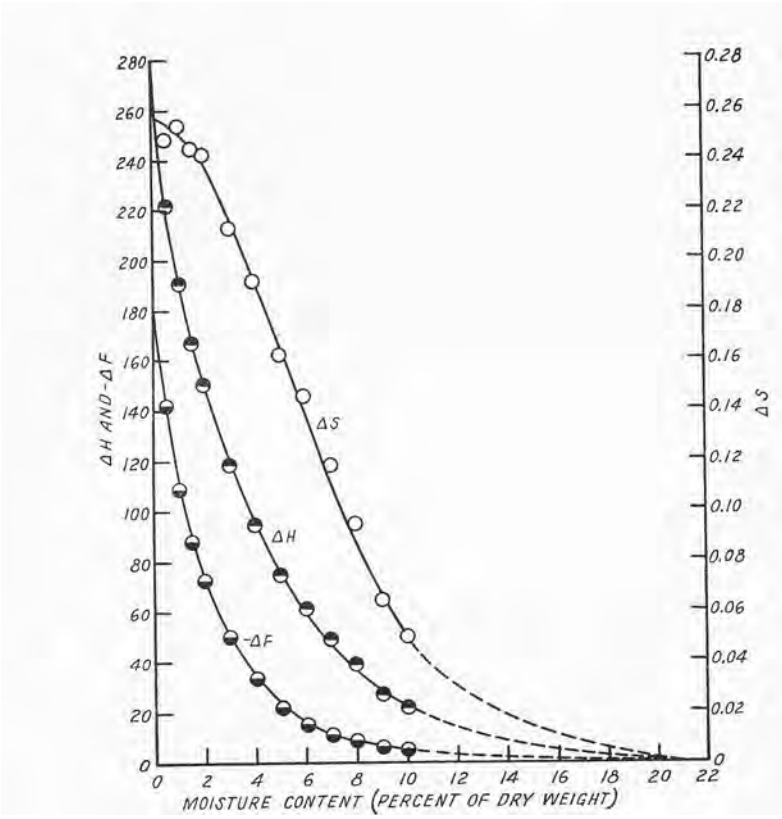

FIG. 7. DIFFERENTIAL HEAT OF SWELLING AND FREE ENERGY AND ENTROPY CHANGES WITH MOISTURE CONTENT AT 50°C. FOR SODA-BOILED COTTON CALCULATED FROM THE DATA OF URQUHART AND WILLIAMS

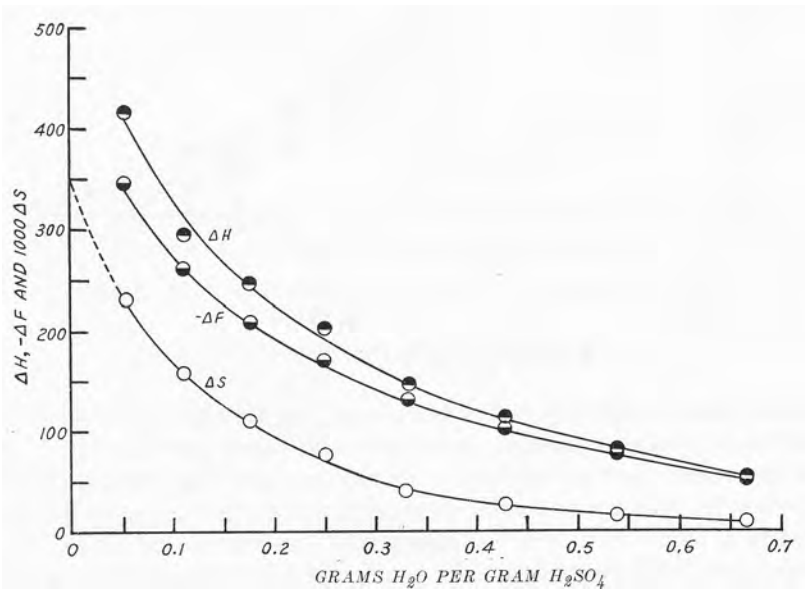

FIG. 8. HEAT OF SOLUTION AND FREE ENERGY AND ENTROPY CHANGES FOR SULFURIC ACID-WATER MIXTURES AT 50°C., CALCULATED FROM DATA TAKEN FROM THE INTERNATIONAL CRITICAL TABLES

quhart and Williams (8). The ΔH values were calculated from the 60° and 40°C. moisture content—relative vapor pressure isotherms and the $-\Delta F$ values from the 50°C. isotherm. It was not possible to correct for the effect of hysteresis; hence the values should be considered only approximations. All three curves are very similar, however, to those for wood. Urquhart and Williams (8) also give isosteres similar to those of figure 5. All of them, however, show a very slight convex upward curvature.

In figure 8 are plotted the ΔH, $-\Delta F$, and ΔS versus moisture content curves for sulfuric acid—water mixtures calculated from data obtained from the International Critical Tables. As Katz (2) has pointed out,

TABLE 1

Thermodynamic constants for the swelling and solution of various materials in water expressed in gram-calories per gram of water added to an infinite amount of the material at the moisture content indicated in the subscripts

MATERIAL	SOURCE OF DATA	ΔH_0	ΔS_0	$\Delta H_{4.0}$	$-\Delta F_{4.0}$	$\Delta S_{4.0}$
Wood:						
Sitka spruce	Stamm and Loughborough	270	0.34	150	46	0.30
Pine	Volbehr (9)	260		150		
Cotton	U. and W. (8)	280	0.26	95	33	0.19*
Cotton	Katz (2)	390				
Starch	Katz (2)	320				
Nuclein (from yeast)	Katz (2)	200				
Casein	F. and L. (1)			166	70	0.35
Casein	Katz (2)	200				
Agar-agar	F. and L. (1)			222	125	0.35
Keratin	F. and L. (1)			150	90	0.22
Sulfuric acid	International Critical Tables			440	365	0.23
Sulfuric acid	Katz (2)	550				

* No correction made for hysteresis effect.

there is a close analogy between solution and swelling. Unfortunately, the data do not extend to moisture content values sufficiently low to determine if the ΔS curve has an inflection point.

Table 1 gives the initial heat of swelling or solution, the initial entropy change, and also the differential heat of swelling and free energy and entropy changes at 4 per cent moisture of a number of materials in water. Although the variation in ΔH and $-\Delta F$ values among the different materials is as great as five to ten times, the variation in ΔS values is less,than twofold, showing that the non-reversible work of sorption is fairly constant for a wide variation of materials.

SUMMARY

1. Relative vapor pressure—moisture content desorption isotherms from room temperature to the boiling point of water have been determined for the system wood—water under conditions which minimize the hysteresis effect.

2. The fiber-saturation points decrease with an increase in temperature in a linear manner, the fiber-saturation point being reduced 0.1 per cent for each rise in temperature of 1°C.

3. Differential heats of swelling and free energy and entropy changes were calculated over the entire sorption range. All give smooth curves with zero values at the fiber-saturation point.

4. The nature of the curves with respect to the mechanism of sorption is discussed.

5. Comparisons are made between heats of swelling and free energy and entropy changes for the swelling and solution of various materials in water.

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