

**THE BONDING FORCE OF CELLULOSIC MATERIALS  
FOR WATER (FROM SPECIFIC VOLUME  
AND THERMAL DATA)**

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(THE BONDING FORCE OF CELLULOSIC MATERIALS FOR WATER  
(FROM SPECIFIC VOLUME AND THERMAL DATA)<sup>1</sup>)

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An attempt was made in a previously reported research (14) to determine the volumetric contraction occurring in the water adsorbed by cellulosic materials. Apparent density measurements of wood and cellulose containing various amounts of adsorbed water were made in benzene. Benzene causes no swelling of cellulosic materials, indicating that its affinity for cellulosic materials is small. This, together with the fact that the internal surface of contact is relatively small, would make the adsorption compression of benzene negligible. It is questionable, however, that benzene penetrates the void structure of the dry cell walls completely. For this reason the benzene can be relied upon as a displacing medium only when the moisture content of the cellulosic material is sufficiently high for water to have opened up or itself filled all of the void structure. It was shown that the volumetric contraction occurring in the adsorbed water could be calculated down to a moisture content of about 6 percent from the measurements in benzene. Below this point accurate data for the true density of the cellulosic materials are required to make the calculations.

Howard and Hulett (6) have determined the density of carbon in helium and have shown that at room temperatures the helium is practically nonadsorbed. Davidson (3) similarly concluded that helium is nonadsorbed on cellulose. Because of its low molecular weight it should further penetrate the void structure completely. Hence, measurements of the density of the same cellulosic materials used in the previous investigation were made in helium.

The essential features of the apparatus used for making the density measurements are shown in figure 1. A and B are two Pyrex glass bulbs of about 200-cc. capacity, separated by a stopcock  $S_1$ . The sample bulb A can be removed at the ground-glass joint J and filled with the cellulosic material by removing the stopcock.  $S_1$ ,  $S_2$ , and J are provided with mercury seals to prevent leaks. M is a mercury manometer, which was read with a cathetometer to 0.005 cm. L is a 200-cc. bulb used to keep the mercury level in the right-hand arm of M at the same point for all the

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measurements by adjusting the pressure over L with stopcocks S<sub>3</sub> and S<sub>4</sub>. This made unnecessary any volume corrections. The whole apparatus was immersed in a thermostatically controlled water bath at 30° C.  $\pm$  0.01°.

The volume of A was determined by calibration with water. With A empty the apparatus was completely evacuated, helium was admitted to B, the pressure determined, and then the pressure was again determined after expansion into A. The volume of B plus the connecting tubes could then be calculated from the volume of A and the two pressures, using the perfect gas law. The same procedure was followed in determining the void space in A when filled with a sample of wood or cellulose. The material was oven-dried at 105° C. prior to filling the bulb and then vacuum-dried at 105° C. for about 24 hours after assembly of the apparatus by surrounding the bulb with a heating coil jacket. A final vacuum of about  $10^{-4}$  mm. of mercury was attained. The system was then brought to 30° C. and held for about half a day before making the measurements, to insure thermal equilibrium. Weighings of the sample bulb were made at atmospheric pressure just after the vacuum drying and again after a series of expansions.

Density measurements were also made in water and benzene in 200-cc. plate-top pycnometers. The air was removed from the submerged materials in the half-filled pycnometers by carefully applying a vacuum and releasing until no sign of air bubbles was obtained up to a vacuum which caused boiling of the liquid when the pycnometers were immersed in an ice bath.

The densities of the following materials determined in helium, water, and benzene, are given in table 1: benzene-alcohol extracted white spruce sawdust of 40 to 60 mesh; the same in the expanded aerogel form (8); standard cotton linters alpha-cellulose; a normal spruce sulfite pulp and the same after beating for 20 hours; and spruce and maple lignin prepared by the modified sulfuric acid method of the Forest Products Laboratory (11). The expanded aerogel was prepared according to the method of Kistler (8), using methanol and acetone as intermediate replacing agents. Measurements on control blocks showed that a large proportion of the normal shrinkage occurred in the final expansion step, regardless of the technic used. Because of this shrinkage the density value for the expanded wood determined in benzene, although greater than the corresponding density value for the unexpanded wood, was not so great as the density value determined in helium. In all cases the density values determined in helium are intermediate between those determined in water and those determined in benzene, as has been previously reported (3, 12). The difference between the helium and benzene values for the cotton is practically the same as that found by Davidson (3).

Table 1.--Densities of wood, cellulose, and lignin substance at 30° C.

Substance	Helium displacement			Water displacement			Benzene displacement		
	Den-	Aver-	Num-	Den-	Aver-	Num-	Den-	Aver-	Num-
	sity	age	ber of	sity	age	ber of	sity	age	ber of
	:	error:	deter-	:	error:	deter-	:	error:	deter-
	:	:	mina-	:	:	mina-	:	:	mina-
	:	:	tions	:	:	tions	:	:	tions
Extracted white spruce.....	1.4603	0.0005	10	1.5332	0.0002	2	1.444	0.007	2
Expanded aerogel from extracted white spruce.....	1.4604	.0004	4	1.530		1	1.450	.005	2
Standard cotton linters.....	1.585	.0012	7	1.6028	.0003	2	1.571	.0005	2
Spruce sulfite pulp:									
Unbeaten.....	1.570	.0024	6	1.590	.0005	2	1.555		1
Beaten.....	1.593	.0022	6	1.616	.0008	2	1.578		1
Spruce lignin (modified sulfur-ic acid method)...	1.377	.0008	10	1.399	.0010	2	1.366		1
Maple lignin (modified sulfur-ic acid method)...	1.406	.0011	6	1.422	.0007	2	1.388		1

The volume contraction occurring in the cellulosic material-adsorbed water system was calculated from the previously determined data in benzene (14), using the newly found density values in helium as the true densities of the cellulosic materials. The external pressure  $P$  in kilobars that would be required to cause this volume change  $\Delta v$  per gram of water, on the basis of the volume change occurring entirely in the water phase, was then calculated from the following compressibility relationship for water given by Gibson (5):

$$\Delta v = 0.307 \log \frac{2.923 + P}{2.923} \quad (1)$$

The values for white spruce, cotton, and sulfite pulp are plotted in figure 2. The values for the beaten and the unbeaten pulp were so nearly identical that only the average value is plotted.

Campbell and Russell (2) have doubted whether helium completely penetrates the void structure of cellulose, because they obtained density values for swollen cellulose in benzene by replacement of water with alcohol and of alcohol with the benzene that were slightly greater than the helium values. This difference, it seems, can be better explained by assuming that a small amount of water was not replaced in their measurements, rather than by assuming that the helium fails to penetrate the cellulose completely. In order to meet these investigator's objections, however, it seemed advisable to attempt determining the compression effect by an entirely different method.

Katz (7) has shown that a qualitative proportionality exists between the initial heat of solution or the heat of swelling of binary aqueous systems and the accompanying volume change. He gives values for the ratio  $\bar{C}_0/\bar{H}_0$  ranging from 1 to  $3 \times 10^{-3}$  for a series of solutions and swelling systems in which  $\bar{C}_0$  is the volume change in cubic centimeters and  $\bar{H}_0$  is the heat of solution or swelling in gram-calories resulting when 1 g. of water is added to an infinite amount of dry solute or swelling material. It is apparent that this relationship cannot be general, as there should be a greater change in volume per unit thermal change for a more compressible liquid than for a less compressible liquid. It thus seemed logical to substitute the change in internal pressure  $\bar{P}_e$ , which causes the change in volume, for the change in volume and thus compare values of the differential ratio  $\bar{P}_e/\bar{H}$ . Partial differential values are used, as compression may occur in both constituents of the liquid-liquid systems considered.

Gibson (5) gives the relationship between the specific compression of water, the internal or intrinsic pressure change, and the externally applied pressure which can be expressed in the following partial differential form:

$$-\frac{\Delta P_V}{x_1} = 0.307 \log \frac{2.923 + \bar{P}_e + P}{2.923 + \bar{P}_e} \quad (2)$$

where  $\frac{\Delta P_V}{x_1}$  represents the partial compression of the water per gram of water resulting from the partial internal pressure change of the water  $\bar{P}_e$  in kilobars caused by the presence of the solute and the external pressure change  $P$  in kilobars. The partial specific compression can be obtained by plotting the compression per gram of solution against the weight fraction of the water and drawing tangents to the curve. The intercept of the water axis gives the partial specific compression for water in a solution the composition of which is represented by the point of tangency (9).

The external pressure  $P$  that would cause the same volume change in the solvent as occurs in the process of solution can be calculated from equation 1 expressed in a partial form:

$$v_1 - \bar{v}_1 = 0.307 \log \frac{2.923 + \bar{P}}{2.923} \quad (3)$$

in which  $v_1$  is the specific volume of the water and  $\bar{v}_1$  is the partial specific volume of the water in the system, obtainable in a similar way to the partial specific compression.

Gibson (5) gives data for both the specific volume and the compressibility of a sulfuric acid-water system. From these data the external pressure required to give the partial specific volume change of the water can be calculated, using equation 3, and the change in the internal pressure that causes the change in compressibility can be calculated, using equation 2. These values are given in table 2. The data show that the internal pressure change of water in the solutions is equal to the external pressure required to cause an equal change in volume in the water alone. It is thus valid to consider the pressure changes in figure 2 equivalent to internal pressure changes.

Table 2.--Change in partial internal pressure of water in aqueous sulfuric acid solutions calculated from the specific volumes and from the specific compressions

Solute	: Weight fraction of H <sub>2</sub> O : ( $x_1$ )	: Specific volume of H <sub>2</sub> O : ( $v_1 - \bar{v}_1$ )	: External pressure on H <sub>2</sub> O to give volume change : (P)	: Partial specific compression of H <sub>2</sub> O per kilobar : ( $-\frac{\Delta p v}{x_1}$ )	: Change in partial internal pressure of H <sub>2</sub> O : ( $\bar{P}_e$ )
			Kilobars		Kilobars
H <sub>2</sub> SO <sub>4</sub>	0.0	0.308	26.8	0.0048	26.0
	.0723	.283	21.3	.0055	21.0
	.1365	.193	9.3	.0110	8.7
	.2167	.093	3.0	.0225	2.5
	.4048	.038	.95	.0312	.85
	.6699	.012	.28	.0367	.25
	.7333	.008	.17	.0380	.13
	.8734	.004	.08	.0390	.04

Table 3 gives the ratios of the partial internal pressure change to the partial heat of solution of water in aqueous solutions of organic compounds, inorganic acids, bases, and salts, and salts of organic acids all of which dissolve with the evolution of heat. The partial internal pressure changes were calculated from specific volume data only (International Critical Tables), as specific compression data were available only for the sulfuric acid solutions. The heat of solution data with the exception of that for sulfuric acid (10) were also obtained from the International Critical Tables. Because of the difficulty of obtaining accurate graphical values for  $\bar{v}_1$  and for  $\bar{H}$  at high concentrations of

water, the values for the ratio  $\bar{P}_e/\bar{H}$  could not be determined at concentrations higher than those given in table 3 with any degree of accuracy. In all cases where miscibility is complete, the ratios of  $\bar{P}_e/\bar{H}$  for zero concentration of water are about equal, the average deviation from the average value 12.5 being 4 percent. The same constancy exists for all the data at high concentrations of water. In some cases the agreement is good over the whole concentration range, whereas in other cases, such as that of sulfuric acid, the ratio decreases at intermediate concentrations. In the case of the salts and bases the agreement is good up to concentrations approaching saturation.

This relationship fails to hold for exothermic solutions. The expansion accompanying the absorption of heat is invariably too small, and in some cases there is a slight contraction accompanying the absorption of heat. The relationship also fails in cases where the constituent other than water is more compressible than water. As neither of these cases applies to cellulose-water systems, it seemed justifiable to apply the ratio  $\bar{P}_e/\bar{H} = 12.5$  kilobars per kilojoule in the calculation of  $\bar{P}_e$  from thermal data. Values of  $\bar{P}_e$  for the wood and cotton calculated from the heat of swelling data (13) that were obtained from vapor pressure data (13, 15) and from direct heat of swelling data (1) are plotted in figure 2, together with the values of  $P$  obtained from adsorption compression. The agreement is good. It tends to substantiate the contention that true density values for cellulosic materials can be obtained in helium and strengthens the validity of the calculated internal pressure values.

The values of  $\bar{P}_e$  represent the increase in the internal pressure of water, so that the normal internal pressure of water, which is about 12.5 kilobars, should be added to these values to obtain the total internal pressure. The data thus show that the initial bonding force of cellulosic materials for water is about twice that of water for itself. This seems much more reasonable than the value of sevenfold to eightfold greater calculated from the data of Filby and Maass (4), especially in the light of the fact that the initial attractive force of sulfuric acid for water is only three times that of water for water (see table 3). It is of interest to note that the surface-bound water corresponding to the inflection point of the moisture content-relative vapor pressure curves, 5 to 6 percent for wood and about 3 percent for cotton, exhibits the same internal pressure of about 22.5 kilobars for both wood and cotton. The average force with which all the water is held below the fiber-saturation point varies for the different cellulosic materials; 15.5 kilobars for the wood, 14.7 for the cotton, and 13.5 for the pulp, or 24, 17, and 8 percent greater than the force with which water holds water.

Table 3.--Relationship between the change in the partial internal pressure of water and the partial heat of solution of water in the formation of various aqueous solutions

Solute	Weight fraction of H <sub>2</sub> O (x <sub>1</sub> )	Specific volume minus partial specific volume of H <sub>2</sub> O (v <sub>1</sub> - v̄ <sub>1</sub> )	Changes in partial internal pressure of H <sub>2</sub> O (P̄)	Partial heat of solution of H <sub>2</sub> O (H̄)	Ratio ( $\frac{\bar{P}}{\bar{H}}$ )
			Kilobars	Kilojoules	
Glycerol	0.0	0.040	1.00	0.081	12.3
	.1	.028	.69	.056	12.3
	.2	.023	.55	.043	12.8
	.3	.019	.45	.037	12.2
	.4	.012	.28	.027	10.4
	.5	.010	.22	.021	10.5
	.6	.0075	.16	.014	11.4
	.7	.004	.09	.008	11.2
Glycol..	.0	.053	1.40	.100	14.0
	.1	.044	1.15	.0865	13.3
	.2	.035	.88	.065	13.5
	.3	.026	.63	.049	12.9
	.4	.019	.45	.0375	12.0
	.5	.014	.325	.029	11.2
	.6	.009	.20	.022	9.1
	.7	.005	.11	.0125	8.8
HNO <sub>3</sub> ....	.8	.002	.045	.0035	12.8
	.0	.198	10.2	.90	11.3
	.1	.190	9.3	.80	11.6
	.2	.163	7.0	.59	11.8
	.3	.136	5.0	.39	12.8
	.4	.086	2.7	.22	12.0
	.5	.058	1.6	.13	12.3
	.6	.036	.9	.08	11.2
	.7	.011	.25	.02	12.5

(continued on next page)



Table 3.-- Continued.

Solute	Weight frac- tion of H <sub>2</sub> O (x <sub>1</sub> )	Specific volume minus partial specific volume of H <sub>2</sub> O (v <sub>1</sub> - v <sub>1</sub> )	Changes in par- tial internal pressure of H <sub>2</sub> O (P̄)	Partial heat of solution of H <sub>2</sub> O (H̄)	Ratio ( $\frac{\bar{P}}{\bar{H}}$ )
			Kilobars	Kilojoules	
H <sub>3</sub> PO <sub>4</sub> ...	(.0	0.129	4.80	0.43	11.2
	(.1	.093	3.00	.37	8.1
	(.2	.068	1.95	.25	7.8
	(.3	.038	1.00	.14	7.1
	(.4	.028	.70	.08	8.7
	(.5	.021	.50	.05	10.0
	(.6	.010	.23	.02	11.5
	(.7	.006	.13	.015	11.5
	(.0	.306	26.5	1.92	13.8
	(.05	.292	23.0	1.75	13.1
	(.10	.260	17.5	1.50	11.7
	(.15	.182	8.5	1.12	7.6
	(.20	.106	3.6	.78	4.6
H <sub>2</sub> SO <sub>4</sub> ...	(.30	.052	1.4	.43	3.3
	(.40	.0355	.92	.26	3.5
	(.50	.0265	.64	.14	4.6
	(.60	.0170	.40	.08	5.0
	(.70	.0095	.22	.04	5.5
	(.80	.0045	.10	.015	6.7
	(.90	.0025	.05	.004	12.5
	(.425	.115	4.00	.420	9.5
KOH.....	(.5	.083	2.57	.255	10.1
	(.6	.045	1.20	.110	10.9
	(.7	.014	.33	.027	12.2
	(.8	.0075	.17	.014	12.1
	(.6	.104	3.50	.295	11.9
NaOH....	(.7	.068	1.95	.140	13.9
	(.8	.023	.55	.040	13.7

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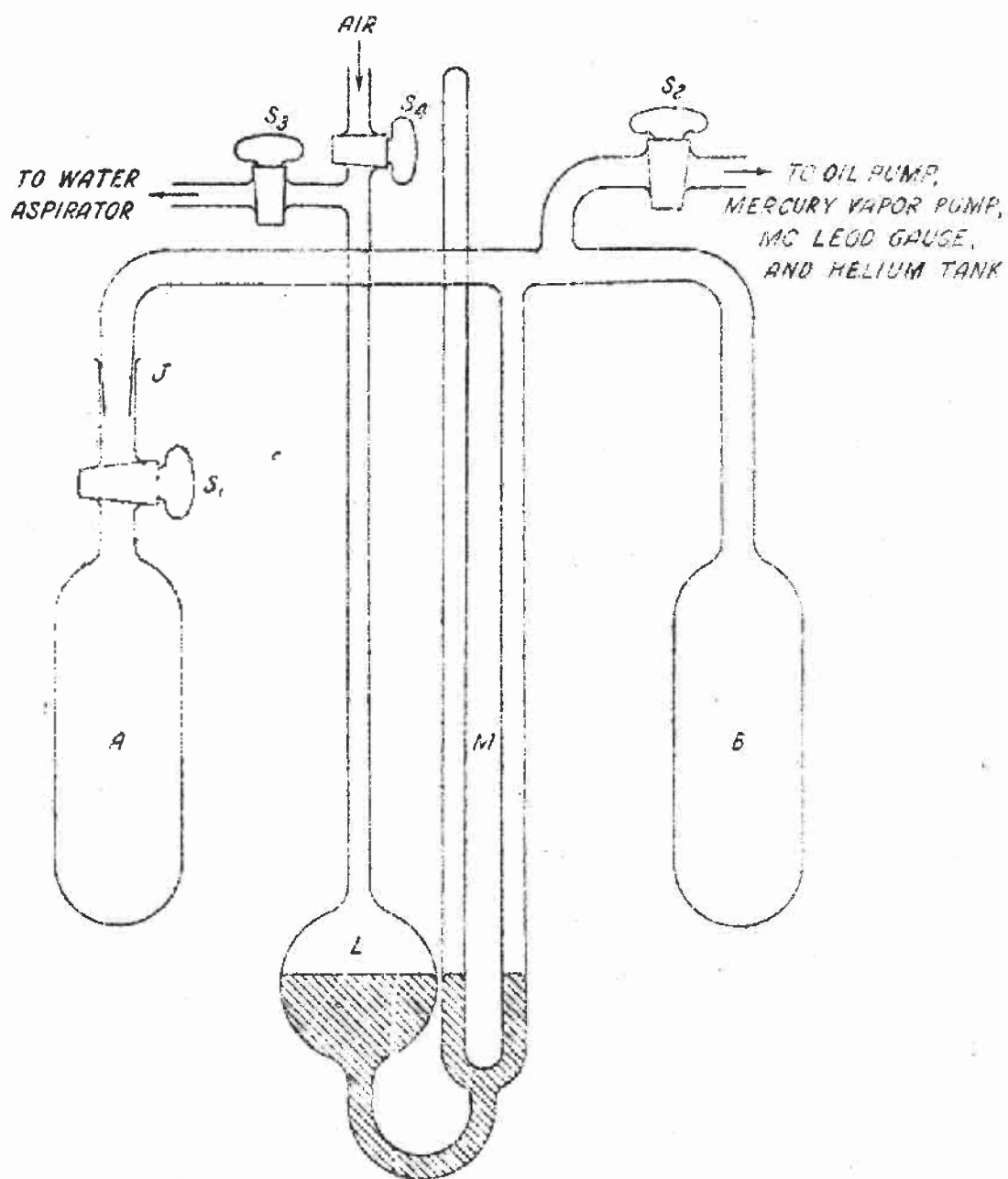
Table 3.-- Continued.

Solute	Weight frac- tion of H <sub>2</sub> O (x <sub>1</sub> )	Specific volume minus partial specific volume of H <sub>2</sub> O (v <sub>1</sub> - v̄ <sub>1</sub> )	Changes in par- tial internal pressure of H <sub>2</sub> O (P̄)	Partial heat of solution of H <sub>2</sub> O (H̄)	Ratio ( $\frac{\bar{P}}{\bar{H}}$ )
			Kilobars	Kilojoules	
K <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	(.4	0.038	0.97	0.075	12.9
	(.5	.027	.66	.053	12.4
	(.6	.018	.43	.035	12.3
	(.7	.008	.175	.013	13.5
	(.8	.0015	.032	.0022	14.5
	(.9	.0005	.013	.001	13.0
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	(.7	.006	.13	.010	13.0
	(.8	.002	.045	.0035	12.8
	(.9	.0005	.013	.001	13.0
CaCl <sub>2</sub> ...	(.6	.044	1.15	.096	12.0
	(.7	.020	.48	.038	12.6
	(.8	.009	.20	.015	13.3
MgCl <sub>2</sub> ...	(.7	.032	.80	.070	11.4
	(.8	.012	.28	.025	11.2
ZnCl <sub>2</sub> ...	(.4	.052	1.4	.130	10.8
	(.5	.039	1.0	.087	11.5
	(.6	.024	.58	.048	12.1
	(.7	.017	.40	.033	12.1
	(.8	.009	.20	.018	11.1
	(.9	.004	.09	.008	11.2
LiCl....	(.7	.014	.33	.095	3.6
	(.8	.009	.20	.018	12.0
	(.9	.004	.09	.007	12.8
CuCl <sub>2</sub> ...	(.6	.032	.80	.055	14.5
	(.7	.022	.52	.036	14.4
	(.8	.009	.20	.016	12.5

(Table 3 concluded)

# REFERENCES

- (1) Argue, G. H., and Maass, O.: Can. J. Research 12, 564 (1935).
- (2) Campbell, W. G., and Russell, J. K.: Quart. Rev. Forest Products Lab. (Canada), Jan.-Mar., p. 24 (1935).
- (3) Davidson, G. F.: J. Textile Inst. 18, T175 (1927).
- (4) Filby, E. A., and Maass, O.: Can. J. Research 7, 162 (1932).
- (5) Gibson, R. E.: J. Am. Chem. Soc. 56, 4 (1934); 57, 284, 1551 (1935).
- (6) Howard, H. C., and Hulett, G. A.: J. Phys. Chem. 28, 1082 (1924).
- (7) Katz, J. R.: Koninkl. Akad. Wetenschappen Amsterdam, Proc. Sec. Sci. 13, 975 (1910) (in English); Trans. Faraday Soc. 29, 279 (1933).
- (8) Kistler, S. S.: J. Phys. Chem. 36, 52 (1932).
- (9) Lewis, G. N., and Randall, M.: Thermodynamics, p. 38. The McGraw-Hill Book Co., New York (1932).
- (10) Marschall, A. L.: in H. S. Taylor's Treatise on Physical Chemistry, 1st edition, Vol. I, p. 217, D. Van Nostrand Co., New York (1924).
- (11) Sherrard, E. C., and Harris, E. E.: Ind. Eng. Chem. 24, 103 (1932).
- (12) Stamm, A. J.: J. Phys. Chem. 33, 398 (1929).
- (13) Stamm, A. J., and Loughborough, W. K.: J. Phys. Chem. 39, 121 (1935).
- (14) Stamm, A. J., and Seborg, R. M.: J. Phys. Chem. 39, 133 (1935).
- (15) Urquart, A. R., and Williams, A. M.: J. Textile Inst. 15, T559 (1924).



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Figure 1.--Apparatus for determining the void volume of cellulosic materials by gas displacement.

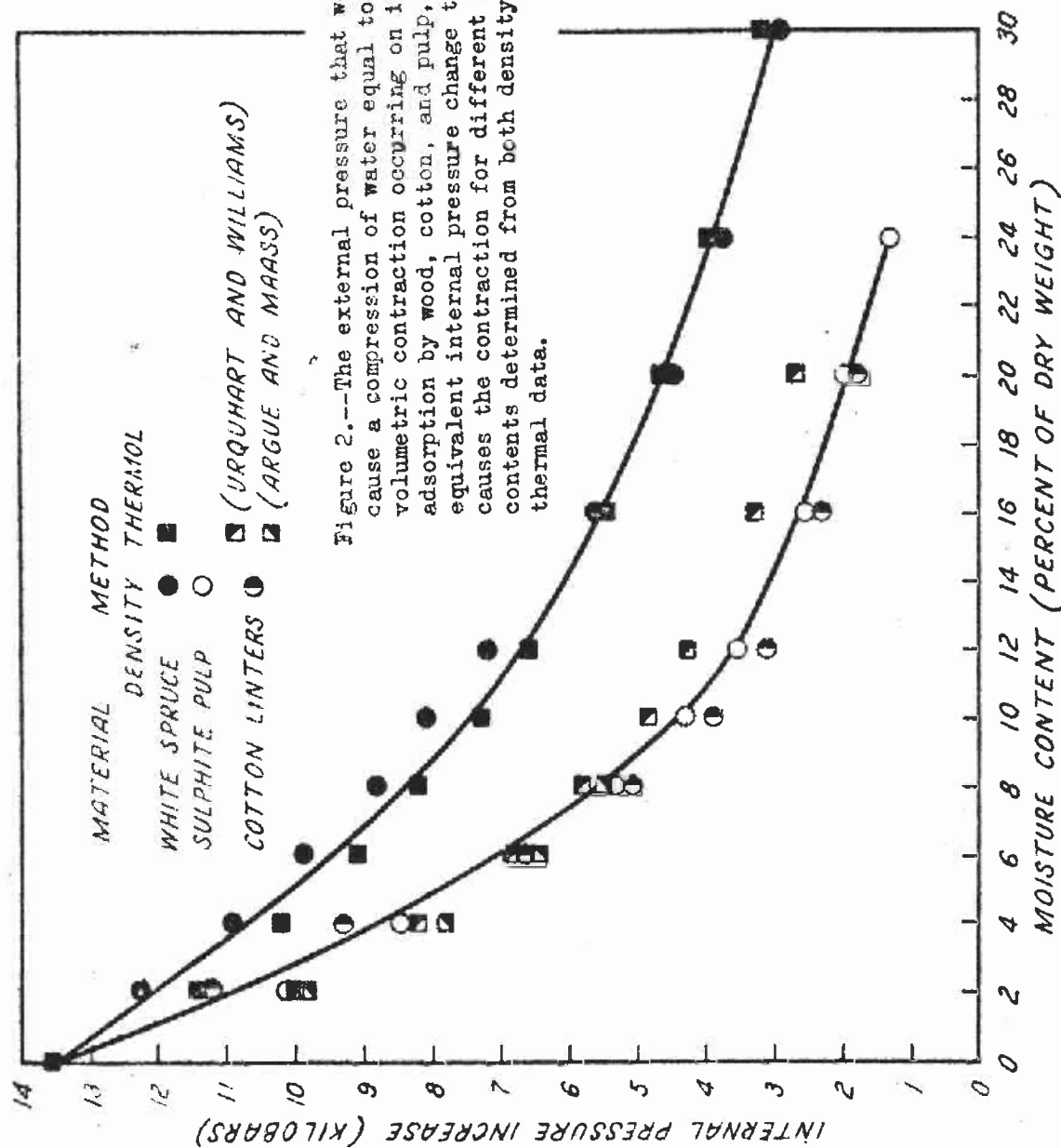


Figure 2.--The external pressure that would cause a compression of water equal to the volumetric contraction occurring on its adsorption by wood, cotton, and pulp, or the equivalent internal pressure change that causes the contraction for different moisture contents determined from both density and thermal data.