

# **DENSITY OF WOOD SUBSTANCE, ADSORPTION BY WOOD, AND PERMEABILITY OF WOOD**

BY ALFRED J. STAMM

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## DENSITY OF WOOD SUBSTANCE, ADSORPTION BY WOOD, AND PERMEABILITY OF WOOD

BY ALFRED J. STAMM<sup>1</sup>

A knowledge of the true density of wood substance and of its apparent densities in different liquids and gases is of considerable importance. Such information should help in giving some idea of the nature of the colloidal and the molecular dispersion of the materials making up the cell wall. It should give the relative permeability of the cell wall to different liquids, the extent to which compressive adsorption of the liquids takes place on the internal wood surfaces, and the adsorption of gases by wood. Values for the apparent densities of wood substances in various aqueous solutions together with adsorption measurements should give additional information as to the nature of the adsorption. The value for its true density is useful also in the calculation of the total void volume of wood or the average void cross section of thin sections of wood. All of these properties are important in the study of the flow of liquids through wood.<sup>2</sup>

### Previous Density Determinations

Unfortunately most of the previous known determinations of the density of wood substance are based upon experimental methods that, with the advance in science, have become somewhat questionable. Though they give the correct order of magnitude and indicate that the variations in the values among the different species are slight, they fail to furnish all of the information that such experimental work should disclose.

Sachs<sup>3</sup> determined the density of wood substance, applying Archimedes' principle, by weighing thin wood sections both in air and in a liquid of known density, using in turn water and alcohol. He also found the densities of calcium nitrate and of zinc nitrate solutions in which thin wood sections were in approximate equilibrium, that is, sank very slowly. The first method gave 1.5 for pine with distilled water as the immersion liquid and 1.523 with alcohol, whereas the second one gave 1.54. Hartig,<sup>4</sup> using the second method, obtained 1.555 for the average of the densities of five different species. Dunlap,<sup>5</sup> also using the method of equilibrium in salt solutions, obtained values ranging from 1.4990 to 1.5639 for the seven species that he investigated.

Though the equilibrium method is simple in experimental manipulation and may give reproducible results, theoretically it is not entirely sound. It depends upon the erroneous assumption that the concentration of the salt

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<sup>2</sup>Stamm: J. Ggr. Research 38, No. 2 (1929). "The Capillary Structure of Softwoods. I.— As indicated by Electroendosmotic Flow Studies."

<sup>3</sup>Arb. Bot. Inst., Würzburg, 2, 291 (1897).

<sup>4</sup>Untersuch. Forestbott. Inst., München, 2, 112(1882)

<sup>5</sup>J. Agr. Research, 2, 423 (1914).

solution will be the same in the fine inner structure of the wood as in bulk. Adsorption, either positive or negative, or an osmotic or Donnan equilibrium effect resulting in a non-uniform distribution of the salt and solvent, or a change in the extent of penetration will affect the density. This fact is illustrated by some of the data presented in the present paper.

Richter<sup>6</sup> determined the density of wood substance using the pycnometric method with alcohol as the displacement liquid. Black spruce gave 1.512 for the heartwood and 1.516 for the sapwood, while white spruce gave the corresponding values 1.517 and 1.528. Previous extraction with ether and alcohol increased the values somewhat, the black spruce sapwood then giving 1.569. As will be seen later, the results using 95 per cent alcohol for the displacement liquid agree quite well with those in which water is similarly used.

The previous determinations of the density of cellulose alone have, in general, been more satisfactory than those for wood substance. De Mosen-thal<sup>7</sup> determined the density of various celluloses by means of the pycnometric method using water for the displacement liquid. He obtained 1.607 for cotton cellulose, 1.575 for wood cellulose, 1.570 for ramie cellulose, and 1.548 for flax. Alcohol gave practically the same values, and benzene somewhat less. Richter<sup>6</sup> also determined the density of cellulose by the same method. He obtained 1.584 for cotton cellulose and 1.583 for filter paper, in alcohol. Lewis<sup>8</sup> made similar determinations on cotton cellulose using both water and toluene; the first medium gave 1.593 to 1.607 and the second 1.560 to 1.582. He also determined the effect of temperature on the density of the cellulose, from 20° to 50°C. In water the density decreased over this range from 1.612 to 1.590 in approximately a linear fashion. The effect of temperature upon the density in toluene was quite erratic, the general trend being towards an increase in density with an increase of temperature. This trend is diametrically opposed to the results of the following reference and the results of the investigation now reported.

After completing the experimental work of this investigation a recent publication by Davidson<sup>9</sup> came to the author's attention. This investigator determined the density of cotton cellulose pycnometrically, using water and several different organic liquids for displacement. He also determined the displacement by helium gas in a manner similar to that of the author's work. Davidson's measurements with the pycnometer at 20°C., using a soda-boiled cotton, gave 1.612 with water and 1.550 to 1.558 with six different non-polar organic liquids. Helium gas displacement gave 1.567. Cotton from different sources, soda-boiled and mercerized, viscose, cuprammonium, and nitro artificial silks, all gave practically the same density for each particular determination medium. Davidson further determined the effect of temperature from 0° to 80°C. for water and for toluene displacement. Both of these gave

<sup>6</sup>Wochenbl. Papierfabr., **46**, 1529 (1915).

<sup>7</sup>J. Soc. Chem. Ind., **26**, 443 (1907).

<sup>8</sup>Cross and Dorée: "Researches on Cellulose," Vol. 4, p. 27 (1910-21).

<sup>9</sup>J. Textile Inst., **18**, T175 (1927).

a linear decrease in density with an increase in temperature. With water as the displacement liquid the density decreased from 1.615 to 1.575, and with toluene from 1.552 to 1.535.

#### Pycnometer Method for the Determination of the Apparent Densities of Wood Substance

Determinations of the apparent density of wood substance were made at 25°C., in 50 cc. Gay-Lussac pycnometers, on samples of wood meal. The measurements were made using distilled water, various organic liquids, and a series of aqueous solutions for the displacement media. The data necessary for the calculation of the density are the oven-dry weight of the wood (which has been dried to constant weight at 105°C.),  $m$ ; the density of the displacement liquid,  $d_{42}^{25}$ ; the weight of the pycnometer filled with the displacement liquid alone,  $p + w_0$ ; and the weight of the pycnometer filled with the wood and the displacement liquid,  $p + m + w_1$ . The density  $D$  can then be determined from the equation,

$$D = \frac{m}{\frac{w_0 - w_1}{d}} = \frac{md}{m - [(p + m + w_1) - (p + w_0)]}$$

All weighings were made with a similar pycnometer serving as a weighing tare.  $2.000 \pm 0.001$  grams of wood were used in each of the determinations.

In the preliminary experiments, in which distilled water and benzene were used in turn as the displacement liquids, two different procedures were tried to insure complete replacement of air by the liquid. (a) The dry wood meal in the pycnometers was first exposed to the vapors of the displacement liquid for several hours in order to obtain saturation of the fine structure. The moistened meal was then completely covered with the liquid and was gradually subjected to vapor treatment a second time by boiling the liquid nearly to dryness. The meal was again completely covered with the liquid and boiled for an hour. After standing for two days, being brought to the boiling point several times during this period, the final weighings were made to constant weight at 25°C. (b) The dry wood meal was immediately covered with the displacement liquid, was warmed slightly on the water bath, and was then subjected intermittently to a reduced pressure of a few centimeters of mercury in a vacuum desiccator. The application of suction was continued intermittently for from two days to two weeks. As the following data will show, these two procedures gave the same results, within the limits of experimental error; after learning this fact, procedure (b) was adopted for all subsequent measurements, since it is less limited in its experimental application than (a). In the measurements involving aqueous solutions, the weight was determined just before and just after heating and subjecting to the vacuum treatment, so that an appropriate correction could be made for the slight change in concentration caused by evaporation of the solvent.

### Gas-Displacement Method for the Determination of the Density of Wood Substance

The essential parts of the gas-displacement apparatus used in this investigation are shown in Figure 1.<sup>10</sup> *A* is the displacement bulb of 135 cc. capacity in which the wood meal is placed; *B* is a 100 cc. gas burette with mercury leveling tube *L*; *M* is a mercury manometer of capillary bore; *J*, *J*<sub>1</sub>, and *J*<sub>2</sub> are water jackets through which water is rapidly circulated from a water thermostat; tube *D* is connected to the purification train and source of gas used for displacement; tube *C* is connected to a phosphorus pentoxide drying tube, a mercury-vapor vacuum pump, a McLeod vacuum gauge, and a Cenco oil-immersed vacuum pump. All volume readings were made at 760 mm. of mercury pressure, a small temperature correction for the slight volume of the apparatus not held at constant temperature being taken into account.

In making the determinations, the gas burette *B* and connections were first flushed free from air by filling *B* several times with the displacement gas and discharging it through stop cock *S*<sub>1</sub>. With the empty bulb *A* in place and *S*<sub>1</sub> closed, the bulb was evacuated with the oil-immersed pump and then with the mercury-vapor pump to from  $10^{-4}$  to  $10^{-5}$  mm of mercury. To insure the removal of all water vapor, *A* was immersed in a beaker of boiling water during the latter stages of the evacuation. *B* was filled with gas from *D* and the 2-way stop cock *S* was then opened to the manometer *M*; at the same time *S* was closed to *D*. The volume of the gas in *B* was read after adjusting *L* so that the pressure reading was 760 mm of mercury plus for the correction. *S*<sub>2</sub> was closed and *S*<sub>1</sub> was gradually opened enough to allow

about 60 cc. of gas to pass into *A*, after which *S*<sub>1</sub> was again closed and the volume taken from *B* was determined. The burette *B* was then refilled from *D* and the pressure and volume readings for it were taken as before. After again opening *S*<sub>1</sub>, this time letting it stand open, the equilibrium volume of *A* and *B* was read with the pressure adjusted to 760 mm of mercury plus the correction. This same procedure was followed when the bulb *A* was filled with wood meal except that a greater length of time was allowed after filling the bulb with gas

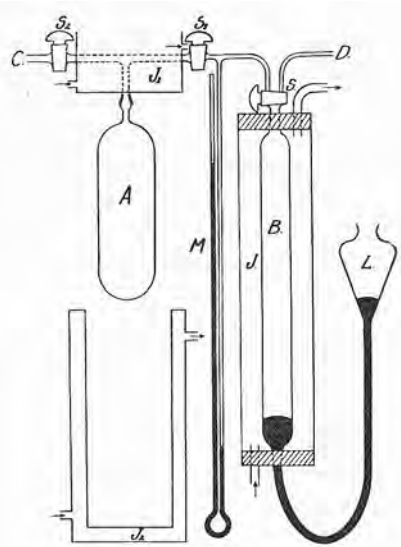


FIG. I  
Apparatus for the gas replacement method  
for the determination of the density of  
wood substance

<sup>10</sup> The author is indebted to Dr. T. G. Finzel of the Chemistry Department of the University of Wisconsin for the use of his adsorption apparatus, which suited admirably the requirements of this research.

before taking the final reading; equilibrium was in all cases obtained in less than an hour. The volume of the wood in *A* is then the difference in the volume of the bulb when empty and when filled with wood.

#### Materials for the Experimental Work

The heartwood of seven different softwoods and of two hardwoods was studied. All of the samples were ground to pass a mesh of either 0, 40, or 80 to the inch. Extractives were removed from the wood, only in the cases specified, by successive extractions with hot water, alcohol, and ether. The cotton cellulose used was sterile absorbent cotton manufactured by Bauer and Black. The wood cellulose was obtained from catalpa heartwood by chlorination and extraction of the lignin with sodium sulfite (the method of Cross and Bevan); it was then digested with boiling water for several hours to remove the readily hydrolyzable carbohydrates. The lignin was obtained by removing the cellulose and other carbohydrates from the heartwood of western yellow pine with 72 per cent sulfuric acid.

The organic liquids and salts used were of high commercial purity, so that no further purification was resorted to in any case. The helium gas used, which was obtained from the Bureau of Mines, contained a small amount of nitrogen, the removal of which was unnecessary, as the following results indicate. All of the gases used were dried by passing them through concentrated sulfuric acid and over solid potassium hydroxide, and traces of oxygen were removed from the other gases by passing them over hot metallic copper.

TABLE I  
Apparent Densities of Wood Substances obtained by the Water Displacement Method, at 25°C.

Species of wood; heartwood only	Apparent density of wood substance	Size of particles in meshes to the inch	Treatment to secure complete penetration of the liquid*
Alaska cedar	1.545	20	(a)
Do.	1.549	20	(a)
Do.	1.551	20	(a)
Do.	1.547	20	(b)
Do.	1.546	20	(b)
Do.	1.547	20	Repetition of (b) on previous sample after evaporation to dryness
Sitka spruce	1.529	40	
Do.	1.527	40	
Do.	1.525	80	
Do.	1.530	80	
Do.	1.529	80	

\* (a) Vapor treatment followed by liquid treatment and boiling.

(b) Liquid treatment followed by warming and intermittent subjection to reduced pressure.

## Experimental Work

*Water displacement.*

The effect of the method of treatment and of the size of the wood meal upon the apparent densities of wood substances as obtained by the pycnometric method with water as the displacement liquid are presented in Table I. The size of the wood meal showed no effect upon the densities obtained, indicating that the equilibrium penetration and the total surface are independent of the particle size. Check experiments in all cases showed a maximum observed deviation of 0.4 per cent from the mean density value.

*Organic liquid displacement.*

Table II shows the effect of the displacement liquid upon the apparent density of the wood substance. The liquids that were used are placed in the table approximately in the order of their increasing polarity. The apparent density appears to be dependent upon the polarity of the displacement liquid, an increase in polarity giving an increase in apparent density. The densities, viscosities, and compressibilities of the displacement liquids apparently have no effect. With very viscous liquids like "Stanolax," a heavy hydrocarbon oil, and glycerine a longer and more vigorous treatment is required to remove all of the air from the wood capillaries, but the equilibrium values, nevertheless, seem to be independent of the viscosity. The non-polar liquids seem also to show a smaller adhesion tension towards wood than the polar liquids and in consequence either less penetration of the wood, a lower degree of surface compression, or orientation of the adsorbed surface layers.

TABLE II

Apparent Densities of Alaska Cedar Wood Substance ground to pass 20 Meshes to the Inch, obtained by Displacement with Different Liquids at 25°C.

Displacement liquid	Density of liquid $d_{25}^{25}$	Number of determinations	Apparent density of wood substance; heartwood only
"Stanolax"	0.8694	1	1.460
Carbon disulfide	1.2562	2	1.474
Carbon tetrachloride	1.5840	3	1.474
Benzene	0.8727	7	1.476
Dimethyl aniline	0.9529	I	1.477
Nitrobenzene	1.2020	I	1.478
Chloroform	1.4716	2	1.478
n Butyl alcohol	0.8134	I	1.482
n Propyl alcohol	0.8023	2	1.481
Glycerine	1.2523	I	1.484
Ethyl alcohol (absolute)	0.7856	3	1.537
Ethyl alcohol (95 per cent)	0.8056	I	1.547
Water	0.9970	6	1.548

Whether the differences in apparent density are due to differences in penetration, in adsorption compression, or in both is a difficult question to answer. The same problem has arisen in the studies of the apparent densities of charcoal. Cude and Hulett<sup>11</sup> attribute such differences to differences in penetration, whereas Williams<sup>12</sup> and Harkins and Ewing<sup>13</sup> have evidence in favor of the adsorption-compression view. The latter investigators calculate from their data adsorption-compression pressures of 10,000 atmospheres and greater. Lowry<sup>14</sup> on the other hand shows no partiality to either of these views, believing that with the proper technique very similar values can be obtained with quite different displacement liquids.

It is desirable to call attention here to the fact that the degree of swelling of wood in itself has no effect upon the values obtained for the true density. Swelling, which affects the dispersion of the material in the cell wall, will of course make the internal structure more accessible to the displacement liquid and will thus increase the calculated value of the density. This effect, however, is identical with that caused by the differences in penetration of various liquids and thus need not be considered separately. Swelling cannot affect the true density of wood substance, because the true density is the value for the ultimate material that is impermeable to both liquids and gases.

#### *Helium gas displacement*

Because an accepted explanation of the deviations in their apparent densities in different liquids was lacking for other materials as well as for wood, measurements using helium gas for displacement were undertaken by the author in the hope of clarifying the situation. Howard and Hulett<sup>15</sup> had found that the adsorption of helium by charcoal was negligible at room temperatures. Since the adsorption of other gases by wood is much less than that by charcoal, the author assumed in carrying out his work that the adsorption of helium by wood is also negligible. Davidson<sup>9</sup> has assumed in a similar manner that the adsorption of helium gas by cotton is negligible; he further strengthened his assumption by showing that the densities obtained by making his measurements at different pressures of helium gas were the same.

Table III records the apparent densities of wood substance calculated from the displacement of gases on the basis of no adsorption of the gas, and also the adsorption of each gas (the increase in the observed volume of the wood caused by immersion in the gas) determined on the assumption that immersion in helium gave the true volume of the wood. The adsorption values for spruce are approximately one one-thousandth of the corresponding ones for charcoal.<sup>16</sup>

<sup>11</sup> J. Am. Chem. Soc., 42, 391 (1920).

<sup>12</sup> Proc. Roy Soc., 98, 223 (1920).

<sup>13</sup> J. Am. Chem. Soc., 43, 1787 (1921).

<sup>14</sup> J. Am. Chem. Soc., 46, 824 (1924).

<sup>15</sup> J. Phys. Chem., 28, 1082 (1924).

<sup>16</sup> Hempel and Vater: Z. Elektrochemie, 18, 724 (1912).



TABLE III

Apparent Densities of Sitka Spruce Wood Substance, obtained by Displacement with Different Gases at 25°C., and the Volume of Gas adsorbed, assuming that Helium Gas gives the True Density

Displacement gas	Number of determinations	Apparent density of wood substance; heartwood only	CC. of gas adsorbed per gram of wood, at 760 mm. pressure
Helium	5	1.522	0.000
Hydrogen	2	1.553	0.013
Nitrogen	3	1.570	0.020
Oxygen	2	1.626	0.042

The density measurements using helium gas, a volumetric method, could not be checked with quite the accuracy of the pycnometric measurements, which were obtained by weighing, the maximum observed deviation from the mean being 0.7 per cent. As in the case of the pycnometric measurements, the density value obtained is not affected by the size of the wood particles.

*Comparison of densities in different media.*

Table IV compares the densities obtained with helium gas, water, and benzene as the displacement media for several different species of wood. The values obtained with helium gas are intermediate to those for water and for benzene displacement.

TABLE IV

Summary of the Apparent Densities of Wood Substance at 25°C. for Different Species, determined with the Three Types of Displacement Media

Species of wood; heartwood only	Density with helium gas		Apparent density with water		Difference between water and helium values		Apparent density with benzene	
	Number of determinations	Value	Number of determinations	Value			Number of determinations	Value
Alaska cedar	2	1.536	6	1.548	+0.012		7	1.476
Sitka spruce	5	1.522	5	1.528	+0.006	""%		1.471
Western yellow pine	2	1.520	2	1.529	+0.009	—	—	—
Yellow poplar	2	1.508	2	1.516	+0.008	—	—	—
Red fir	2	1.518	4	1.533	+0.015	—	—	—
Western red cedar	3	1.503	2	1.521	+0.018	—	—	—
Redwood (extracted)	3	1.495	2	1.511	+0.016	—	—	—
Redwood (not extracted)	4	1.484	2	1.506	+0.022	—	—	—
Loblolly pine	—	—	3	1.531	—	%		1.466
White oak	—	—	5	1.540	—	% ""%		1.473

Assuming that the helium gas displacement gives the true density of wood substance, which would be the case if penetration were complete and there were no adsorption, the results indicate that the difference between the

values obtained by water and by benzene displacement is due to both an adsorption compression effect with water and to lack of complete penetration by benzene.

The mean compression in the adsorbed water film can be calculated approximately by assuming that the difference between the specific volumes of wood substance in water and in helium gas are due to a compression that takes place entirely within the volume of water that is adsorbed by the wood in securing equilibrium with 100 per cent relative humidity. For Alaska cedar this volume is about 0.285 cc. per gram of wood. The resulting compression amounts to 0.0195 cc. per gram of wood. Dividing this figure by the compressibility of water per atmosphere of applied pressure a mean adsorption compression pressure of 433 atmospheres is obtained. The force of adhesion between wood and water must be equal to or greater than the cohesion of water itself because of the fact that wood can be completely wetted by water. The cohesion of water has been determined by Edser<sup>17</sup> to be about 12,450 atmospheres. If, for purposes of calculation, it is assumed that the adhesion between wood and water is just equal to the cohesion of water, and that the attractive force varies as the fifth power of the distance from the surface, as was found to be the case by Edser,<sup>17</sup> then the film that shows a mean compression of 433 atmospheres will have an effective thickness of 30 molecular diameters or 9.2 m $\mu$ . This value for the mean thickness of the adsorbed water film on wood is of the same order of magnitude as values obtained by other investigators for other materials. McHaffie and Lenher<sup>18</sup> found the thickness of the adsorbed film of water on glass, quartz, and platinum plates in equilibrium with saturated vapor to exceed 100 molecular diameters. Calculations from the data given by Edser<sup>17</sup> indicate that an adsorbed film 600 molecules thick can be held against gravity. It is natural that the value obtained for the mean thickness of the adsorbed film of water on wood should be less than these two values since the thickness of a large part of the adsorbed water is limited by the fine closed capillary structure.

Another interesting approximate calculation can be made. Dividing the volume of the adsorbed water by the mean thickness of the adsorbed film gives 310,000 sq. cm. total adsorbing surface per gram of wood substance. The total surface of the microscopically visible structure can be estimated from some previous results of the author's.<sup>19</sup> A square centimeter of a transverse section of Alaska cedar contains about 135,000 cell cavities of 0.002 cm. average diameter. Since the internal surface of all the cell cavities in a cubic centimeter of such wood is substantially equal to that of 135,000 tubes of the same diameter and of uniform bore and 1 cm. long, the total internal area of a cubic centimeter is 850 sq. cm. Per gram of wood the surface will

<sup>17</sup> "Fourth Report on Colloids," British Association for Advancement of Science, pp. 40-114 (1922).

<sup>18</sup> J. Chem. Soc., **127**, 1559 (1925), **128**, 1785 (1926).

<sup>19</sup> J. Agr. Research 38, No. 2 (1929). "The Capillary Structure of Softwoods. II.—As indicated by Hydrostatic Flow Studies."

be above the value divided by the bulk density of the wood, or 1930 sq. cm. Thus, only about 0.6 per cent of the total adsorbing surface is visible under the microscope.

Though the adsorption compression effect with water accounts for part of the difference between density values of the same wood substance as determined with water and with non-polar organic liquids, the effect of incomplete penetration of the organic liquids presumably is responsible for the major part of each difference.

The figures of Tables II and IV indicate that if accurate values for the absolute density of wood substance are required, the determinations should be made with helium gas. For ordinary purposes, however, the apparent densities determined by water displacement should suffice.

#### *Temperature coefficient.*

The effect of temperature upon the densities of wood substance as obtained with the three different displacement media is given in Table V. The temperature coefficients for each of the media are the same, each showing a linear decrease in density, at the same rate, with an increase in temperature. Davidson<sup>1</sup> found practically the same temperature coefficient for the density of cotton cellulose in water. His temperature coefficient for toluene displacement, however, was somewhat smaller. The fact that the three different media give the same coefficient is a strong indication that neither the equilibrium penetration for benzene nor the adsorption compression film for water is appreciably affected by temperature, over the range investigated. The thermal coefficient of cubical expansion of Sitka spruce wood substance calculated from these data is  $3.7 \times 10^{-4}$  per degree centigrade. The measured external cubical expansion of a block of wood caused by heat will be less than the value calculated by means of this coefficient, because part of the expansion of each cell wall will be relieved inward, in the internal capillary structure, in the same way that swelling caused by a liquid is partially relieved. Measurements on blocks of Sitka spruce with radial and tangential dimensions of 5 by 5 centimeters and a length of 0.7 centimeter gave a coefficient of

TABLE V  
Effect of Temperature on the Density of Sitka Spruce Wood Substance;  
Heartwood only

Temperature °C.	Density with helium gas		Apparent Density with water		Apparent Density with benzene	
	Number of determi- nations	Value	Number of determi- nations	Value	Number of determi- nations	Value
10.0	2	1.533	2	1.536	1	1.479
25.0	5	1.522	5	1.528	1	1.471
40.0	2	1.514	2	1.514	1	1.462

Density at  $t^{\circ}\text{C.} = \text{Density at } 0^{\circ}\text{C.} (1 - 0.00037 t).$

<sup>21</sup> Z. Botan., 52, 227 (1894).

the extractives is less than that of the wood substance, for removing the extractives increases the density. Richter<sup>6</sup> made this same observation with black and with white spruce. Assuming 60 per cent of the wood to be made up of cellulose (density 1.594) and the remaining 40 per cent to be made up of lignin (density 1.451), together with materials of similar density, the calculated density of wood substance would be 1.538. This agrees satisfactorily with the values for the density of different wood substances listed in Table IV. Even if the densities of all of the isolated constituents could be accounted for, exact agreement between observed and built-up total values could hardly

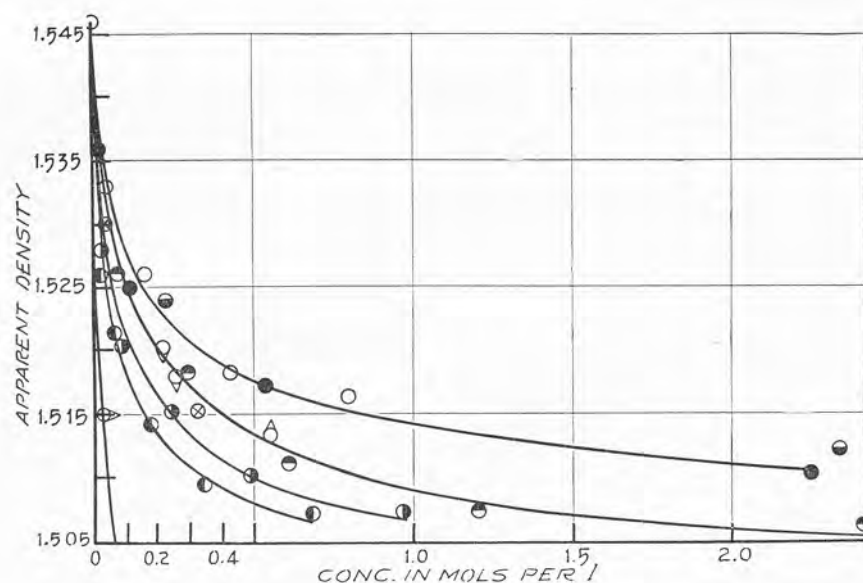


FIG. 2

Effect of solutes upon the apparent density of wood substance:

- |               |                                  |
|---------------|----------------------------------|
| ○ Glucose     | ○ KOH                            |
| ● Glycerine   | ● BaCl <sub>2</sub>              |
| ⊙ Acetic Acid | ⊙ H <sub>2</sub> SO <sub>4</sub> |
| ● NaCl        | ● K <sub>3</sub> PO <sub>4</sub> |
| △ HCl         | △ H <sub>3</sub> PO <sub>4</sub> |

be expected, since lignin undoubtedly is changed in the process of isolation. The deviations in the densities of wood substance for the different species can also be accounted for in a general way by the slight variations in composition. For example, a sample of western yellow pine containing 57 per cent of cellulose and 27 per cent of lignin has a higher density than a sample of redwood that is made up of only 48 per cent cellulose and 34 per cent lignin.

#### *Displacement of various aqueous solutions.*

Table VII gives the apparent density of Alaska cedar wood substance as determined in different aqueous solutions at various concentrations. In Figure 2 the apparent densities are plotted against the concentration in mols. per liter. In all cases there is a decided drop in apparent density with an in-

crease in concentration. All of the curves are definitely parabolic. The non-electrolytes, glucose and glycerine, depress the apparent density to the same extent with an increase in molal concentration. The weak electrolyte, acetic acid, shows a similar depression. The strong electrolyte, sodium chloride, on the other hand gives the same depression of apparent density with about half as great a molal concentration. Barium chloride does it for one-third the concentration and potassium phosphate for one-fourth. These facts make the drop appear like a vapor-pressure depression or an osmotic-pressure phenomenon, that is, the depression in apparent density seems to be proportional to the total number of ions plus undissociated molecules making up the solution. Though the dissociation of these salts is by no means complete, it is approximately so within the accuracy of these determinations. Sulfuric acid is not so greatly dissociated as the tri-ion salt, barium chloride; thus a greater concentration of the acid is required to give the same depression in apparent density. The same is true of phosphoric acid but to a considerably greater extent; a concentration of the acid twice that of the corresponding salt is required to give the same depression in apparent density. The degree of dissociation of the salt is likewise about twice that of the acid.

TABLE VII  
Effect of Aqueous Solutions upon the Apparent Density of Alaska Cedar  
Wood Substance at 25°C.

Solute	Concentration mols. per liter	pH	Apparent density of wood substance; heartwood only
Glycerine	0.0223		1.536
Do.	0.1115		1.524
Do.	0.535		1.517
Do.	2.230		1.510
Glucose	0.0406		1.533
Do.	0.164		1.526
Do.	0.420		1.518
Do.	0.793		1.516
Acetic acid	0.233	2.5	1.524
Do.	2.33	1.7	1.512
NaCl	0.075		1.526
Do.	0.300		1.518
Do.	0.600		1.511
Do.	1.200		1.507
Do.	2.400		1.506
HCl	0.035	1.5	1.528
Do.	0.223	0.7	1.520
Do.	0.270	0.6	1.518

TABLE VII (Continued)

BaCl <sub>2</sub>	0.0240		1.527
Do.	0.0961		1.520
Do.	0.2402		1.515
Do.	0.4805		1.509
Do.	0.9610		1.508
H <sub>2</sub> SO <sub>4</sub>	0.0077	2.5	1.530
Do.	0.270	0.5	1.515
K <sub>3</sub> PO <sub>4</sub>	0.0171		1.526
Do.	0.0683		1.521
Do.	0.1708		1.514
Do.	0.3415		1.508
Do.	0.6830		1.507
H <sub>3</sub> PO <sub>4</sub>	0.550	1.0	1.513
Water	—	5.6	1.548
KOH	—	7.1	1.541
Do.	0.00001	9.2	1.523
Do.	0.101	13.0	1.498 (1)
Do.	1.013	13.9	1.484 (2)
Water	—	5.6	1.541 (3)*
Do.	—	5.6	1.533 (4)*

\* (3) is the water-displacement value of the apparent density for the wood sample of (1), after the sample had been washed free from alkali. (4) is the similar value for (2).

One marked exception to the preceding generalization, that the relative depression of the apparent density is proportional to the combined ionic and molecular concentration of the solution used for displacement, was found, namely, strong alkali. Potassium hydroxide depressed the apparent density to a far greater extent than would be expected from the other results.

#### Adsorption

The decrease in the apparent density of wood substance with increase in concentration of the solution employed can be more readily explained after studying the adsorption of solutes by wood. Table VIII gives the results of a series of adsorption experiments. To respective samples of  $2.000 \pm 0.001$  grams of oven-dry Alaska cedar meal 25 or 50 cc. of each of the aqueous solutions was added. The concentrations given are with respect to the ion indicated. The determinations of the cations and anions were not made on the same solution, hence the difference in their concentrations. The samples before the analysis was made in order to insure the attainment of equilibrium. Blank determinations were made in each case and any slight necessary correction was applied.

TABLE VIII  
Adsorption of Salts by Alaska Cedar Heartwood at 25° c.

Salt	Ion determined	Mols. per liter concentration		Volume of solution Cc.	Mols. adsorption per gm. of wood
		Originally	After adsorption		
KOH	OH <sup>-</sup>	1.0130	0.9180	50	+0.002375
KOH	OH <sup>-</sup>	0.1013	0.05670	50	+0.00112
HCl	H <sup>+</sup>	1.1130	1.11323	50	-0.000006
NaCl	Cl <sup>-</sup>	0.21002	0.21125	25	-0.000015
BaCl <sub>2</sub>	Cl <sup>-</sup>	0.22215	0.22310	25	-0.000012
BaCl <sub>2</sub>	Ba <sup>++</sup>	0.19948	0.19902	50	+0.000012
AlCl <sub>3</sub>	Cl <sup>-</sup>	0.30703	0.30760	25	-0.000007
AlCl <sub>3</sub>	Al <sup>+++</sup>	0.2914	0.2906	50	+0.000020

Potassium hydroxide alone showed a considerable positive adsorption as determined by the change in alkalinity. Hydrochloric acid on the other hand showed a slight negative adsorption from the change in acidity. The mono-, di-, and trivalent cation salts all gave a slight negative adsorption with respect to the chloride ion and a slight positive adsorption with respect to the cation. This indicates that the adsorption of salts is hydrolytic in character. Barium and aluminum hydroxides presumably are selectively adsorbed as a result of a surface hydrolysis of the salts, thus leaving the solution acid. The potassium hydroxide is adsorbed as such. In this case the extent of adsorption is not limited by the increasing counter tendency of the acid formed during the hydrolysis to cause a reversal of the reaction. The existence of such hydrolytic adsorption has been recently confirmed by Miller,<sup>22</sup> through the use of ash-free charcoal. Though the wood used in the wood-density experiments had an ash content of 0.1 per cent, this content was almost entirely insoluble and siliceous in character. Hence the chances of the adsorption being an exchange adsorption are not great.

Vignon<sup>23</sup> obtained a positive adsorption of sodium hydroxide and barium hydroxide on cotton cellulose, of the same order of magnitude as that of potassium hydroxide on wood. He further found a negligible adsorption of sulfuric acid.

The selective and hydrolytic adsorption of OH<sup>-</sup> ions and hydroxides obtained in the investigation reported here further agrees with the author's<sup>24</sup> findings on the effect of electrolytes upon the contact potential of wood with respect to water.

Not only is the adsorption of wood of electrolytes other than hydroxides very small, but that nonelectrolytes is also. Some unpublished experiments by Salzberg of the Forest Products laboratory indicated through optical

<sup>22</sup> "Colloid Symposium Monograph," 5, 55 (1927).

<sup>23</sup> Compt. rend., 143, 550 (1906).

<sup>24</sup> "Colloid Symposium Monograph," 5, 361 (1927).



rotation measurements that glucose shows a slight negative adsorption on wood. Moreover, wood appears to show a selective adsorption of water from non-electrolyte solutions, and a selective adsorption of  $\text{OH}^-$  ions from electrolyte solutions.

#### Discussion of Results

The absence of any appreciable positive adsorption for all of the solutes listed in Tables VII and VIII, with the exception of potassium hydroxide, eliminates the possibility of the depression in apparent density of wood substance with increase in molal concentration being due to a positive adsorption, that is, to the solute being removed from solution with an increase in volume of the entire system. The increase in the volume of the system caused by the salt leaving the solution, however, may show a slight effect upon the apparent density of wood substance in the case of potassium hydroxide solutions.

The decrease in the apparent density of wood substance with an increase in concentration of the solute presumably must then be due to a decrease in the surface adsorption compression of the negatively adsorbed water, a decrease in the penetration of the solution, or both. The first possibility cannot entirely account for the phenomenon since the decrease in density is greater than that which would result if the adsorption compression were reduced to zero. There must then be a decrease in penetration of solution into the fine wood structure with a resulting increase in concentration. A sort of osmotic equilibrium may be set up with the wood substance acting as a kind of semi-permeable membrane, the fine structure being permeable to water but not to the solute. Such a condition would tend to prevent water from entering part of the internal structure, and the extent of this effect would be dependent upon the total ionic and molecular concentrations of the solute.

To determine whether the abnormal effect of the potassium hydroxide was not due to a chemical action on the wood, the densities of wood substance determined in water after removing the alkali by washing are given at the end of Table VII. These show that the action of potassium hydroxide of appreciable concentration causes a permanent reduction in the density of wood substance, which increases with an increase in the concentration of the alkali used to treat the wood. Other investigators have found mercerization of cellulose to decrease its density permanently<sup>25</sup> as well as to change its X-ray crystal lattice diagram. This permanent effect of alkalies seems to manifest itself appreciably only in higher concentrations. It is well illustrated by the effect of alkalies on electroendosmose through wood membranes.<sup>24</sup> The so-called hydration of pure cellulose and of wood by alkali appears then to cause a distention of the crystal lattice of the wood. Such a distention would have to more than compensate for any presumed increase in surface, which would cause an increase in the extent of the surface compression film, in order to account for the decrease in apparent density of wood substance that was observed.

<sup>25</sup> Herzog: *Pulp and Paper Magazine of Canada*, 24, No. 24, June 17 (1926); *Naturwissenschaften*, 12, 955 (1924).

A similar distention of the crystal lattice of the material making up the cell wall of wood may also result from the addition of other electrolytes, but to a degree less marked than with alkalies. Since the alkalies alone are strongly positively adsorbed and alone show a definite effect upon the crystal lattice, however, such distention of the crystal lattice for the other solutes is not probable.

#### Summary

The apparent density of wood substance in water, in organic liquids, and in various aqueous solutions has been determined, as well as its actual density in helium gas. The size of the wood particles has no effect upon the density.

The densities obtained by means of helium gas displacement are slightly less than the apparent densities obtained by displacement with water, and are larger than the values obtained by displacement with non-polar organic liquids. The adsorption compression for water calculated from the various data is about 433 atmospheres, which corresponds to an average thickness of the adsorbed film of 30 molecular diameters and a total adsorption surface per gram of wood of 310,000 sq. cm. The microscopically visible surface is about 0.6 per cent of this value.

The effect of variations in temperature upon the density of wood substance was determined and the coefficient of cubical thermal expansion of wood substance was found to be  $3.7 \times 10^{-4}$  per degree centigrade. This is about three times the expansion transmitted to the external dimensions of a block of wood.

The density of wood substance varies slightly among species as a result of variation in the chemical composition of the substance. The density of isolated wood cellulose is similar to that of cotton cellulose and is somewhat greater than that of wood substance in entirety. The density of isolated lignin is correspondingly less than that of wood substance.

The presence of a solute in the aqueous displacing media causes a decrease in the apparent density of wood substance, in a parabolic fashion, with an increase in concentration. The depression seems to be a function of the total number of ions and undissociated molecules in the displacing solution. Alkalies bring about abnormally great depression of the apparent density, and cause a slight permanent depression of it even after removal of the alkali; this is shown by subsequent water displacement.

Of the materials studied, gases are but very slightly adsorbed by wood. Aqueous non-electrolyte solutions are negatively adsorbed, while aqueous electrolyte solutions show a selective and hydrolytic adsorption. Alkalies show a considerable positive adsorption and acids a negative one. The hydroxides are hydrolytically adsorbed to a slight extent from their salt solutions.

The values for the apparent density of wood substance, obtained by using different liquids for displacement, indicate that the finer structure of wood is not permeable to non-polar organic liquids. The permeability of this structure increased with an increase in polarity of the displacement liquid.