THE
ADSORPTION OF WATER
BY WOOD

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A Thesis
Presented to the Faculty of Graduate Studies and Research
of
McGill University,

by
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In Partial Fulfilment of the Requirements for the Degree of
Doctor of Philosophy.

Montreal, Canada,
April, 1929.

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GENERAL INTRODUCTION.

The chemical and physical nature of wood and cellulose lead to their classification as colloidal substances. Among the most important properties of colloids is the phenomenon of adsorption. In the case of wood, water is the most common adsorbate and is the one which plays the largest part in affecting its physical properties. Water occurs in wood in two forms, Free water, and adsorbed water. The former has no physical significance, while the latter plays a definite role in the swelling, shrinking, and variation of mechanical strength,

In spite of the importance of these phenomena there have been no careful investigations of the adsorption of water by wood throughout an extended range of vapor pressure and temperature. Many determinations of the final saturation value have been made, but they are very conflicting and have largely been obtained by methods which are incapable of any degree of accuracy.

Two fundamental errors have vitiated the results of many previous researches: first, no provision has been to prevent the condensation of free water on the sample at vapor pressures near the saturation point; and second, the samples which were examined were of such large size that the rate of adsorption was confused with the rate of diffusion into the interior of the sample, also the time required for the final establishment of equilibrium was so great that it became impossible to maintain constant conditions of pressure and temperature.

In the present research a method is detailed whereby these scources of error have been eliminated. The adsorption of water by wood samples weighing no more than .10 g. has been measured throughout a complete range of vapor pressures and between the temperatures of 12° and 42° C. The complete adsorption isothermals for several species of the coniferous woods have been determined for the first time. The values for cotton cellulose have been re-determined by the new method and, due to the elimination of all possible condensation, these values have proved to be considerably lower than those previously accepted.

The second part of this research comprises an examination of the rate at which water vapor diffuses through the internal structure of wood. The importance of a knowledge of the manner by which hygroscopic moisture moves through wood has been frequently emphasized, yet no picture of the actual mechanism is available. The experimental procedure developed in this research offers a method whereby the rate of penetration of a vapor through wood may be comparatively measured.

By this means the rate of penetration of water vapor has been measured in various directions through the wood such as loggitudinal, radial, and tangential, and particularly on the longitudinal direction, for samples of varying thickness.

Wood has been experimentally and theoretically treated as a colloidal substance, it has been classified as an elastic gel, and by an application of the modern theory of gel structure the experimental results have received theoretical explanation.

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HISTORICAL INTRODUCTION.

It has long been known that water was taken up or lost by wood under varying conditions of humidity. This variation in water content was indicated by the phenomenon of swelling. It is recorded that the ancient Egyptians (Ref.1) were aware of this property and employed it to split rocks. Dry wooden wedges were driven into holes bored in the rock and moistened with water, the great swelling pressure which was so produced being sufficient to split the stone. In certain parts of Germany the inhabitants are said to ascertain the relative humidity by the drooping of the branches of certain dead trees due to uneven swelling (Ref.2). Actual measurements of the water taken up by wood have been made only in quite recent times.

M.E. Dunlap determined the percent of moisture in several species by exposing the dried samples to an atmosphere maintained at some known relative humidity, and weighing from time to time until a constant value was obtained. (Ref.3)

Tiemann (Ref.4) determined the fibre saturation points of a number of woods by a method ~~the~~ based on the observation that as soon as the moisture content falls below the fibre saturation point, the wood begins to shrink and increase in strength. This method depends on the fact that free water in the wood has no effect on physical properties, while, on the other hand, variation in the amount of adsorbed water directly effects size, strength, and other physical properties.

There is a great lack of agreement between the values for the fibre saturation point as obtained by different investigators. Thus Tiemann's values run from 20 to 30 per cent, while Browne (Ref.5) found that only 12.2 percent of water was taken up when dry wood was exposed to a saturated atmosphere after the elapse of 25 days at a temperature of 20°C. McKenzie, (Ref. 6) on the other hand, found that blocks of spruce wood 1 inch x 1 inch x 6 inches held at 12°C. in air saturated with water vapor, took up 43.2 per cent water in 79 days and adsorption was still taking place though slowly. In this latter case adsorption is undoubtedly confused with liquid condensatinn, which would account for the abnormally high adsorption value.

As a result of the many commercial applications of wood in the form of planks and beams, there has been a tendency on the part of investigators to employ samples of large size in which the rate of adsorption becomes confused with the rate of diffusion into the interior of the wood, and adsorption curves cannot be readily interpreted. Thus Tiemann found that two years were required for the centre of a beam 12 inches square and 16 feet long to fall to the fibre saturation point. (Ref. 7)

Zeller (Ref. 8) investigating the effect of resin-content on hygroscopicity, noticed little effect until the humidity approached 100 per eent, in the vicinity of which hygroscopicity is reduced by a high resin content. He also found that there was little difference between the adsorption values of heartwood and sapwood.

Fenchel and Cornelly (Ref. 9) working with paper and paper pulps noticed that water was adsorbed more rapidly than it was lost, though they stated that adsorption was not complete after 14 days at 18°. Cotton was found to adsorb 16.5 percent and spruce mechanical pulp 22.35 percent, when exposed to a saturated vapor.

The movement of water through wood, both as free and imbibed water, has been investigated to some extent, but no picture of the mechanism is available. Schorger (Ref. 10) suggests that it may pass in the vapor stage from one cell wall to the other, where it condenses to the liquid phase and the process is repeated.

Stillwell (Ref. 11) has measured the rate of diffusion of water vapor through a sample the opposite ends of which were held in equilibrium at different relative humidities, and has roughly plotted the resulting moisture gradients.

Stamm (Ref. 12) has studied the motion of free water through wood under the influence of an electric potential. The values obtained for the capillary cross-section are in good agreement with those obtained by direct microscopic measurement.

In a recent paper Stamm (Ref. 13) has measured the adsorp- of various gases on wood in an interesting manner. The density of wood meal was determined by displacement of Helium gas, which, it has been shown is not adsorbed by wood. The difference between the density by this method and that obtained from measurements with other gases and liquids is taken as a measure of the adsorption of these substances.

While the state of knowledge in the case of wood is very incomplete, cotton cellulose, on the other hand, has been investigated fairly thoroughly.. Due to the importance of the moisture relations ~~of~~in the textile industry, much attention has been given to the adsorption of water both by raw cotton and by pure cotton cellulose.

Schloesing (Ref. 14) examined the so-called moisture "regain" of cotton by passing a stream of air over the dried sample " until equilibrium had been obtained". The moisture content of the air was ascertained by absorbing the water in a weighed drying train, and that of the cotton found by heating above 100° and noting the loss of weight. A second method was employed in which the sample was exposed in a dessicator to a sulphuric acid solution of known concentration and hence of known vapor pressure. The sample was weighed from time to time until equilibrium was established. Schloesing's first method has received criticism on the ground that the time allowed for the attainment of equilibrium was quite arbitrary, and also that the cotton was dried at high temperature after the experiment, so that the exact initial condition was unknown. His second method, while open to serious objection, has formed the basis for many subsequent investigations. The adsorption isotherms given in this publication, are,however, of the same general form as those of all recent researches,, being of a pronounced sigmoid character.

Beadle and later Beadle and Dahl (Refs. 15 & 16) pointed out the great hygroscopicity of cotton and also that a considerable amount of heat is liberated when water was adsorbed by the dry substance.

Masson and Richards,(Ref. 17) following these observations, measured these effects by immersing two thermometers in a saturated water vapor, one surrounded by dry cotton wool and the other uncovered. They were thus able to measure roughly the heat of adsorption, and, by weighing the thermometers, they found the amount of water taken up. Masson and Richards indicated a hysteresis effect for cotton similar to that of a silicic acid gel discovered by Van Bemmeln (Ref. 18). They obtained two different values of the moisture regain of a sample of cotton in an atmosphere of given relative humidity according as to whether the cotton was wet or dry when introduced into the atmosphere. A few of their results are reproduced below:-

Relative V.P.		0.100	0.294	0.500	0.710	0.956	0.972
% H_2O taken up by .094 g. dry cotton.	Dry	.0175	0.0356	0.0509	0.076	0.1378	0.1563
	Wet	.0198	0.0406	0.0593	0.079	0.1606	0.1792

These differences were attributed to incomplete establishment of equilibrium, not to a permanent hysteresis effect. The true adsorption value was consequently taken as the mean of the two.

Trouton (Ref. 19) studied the adsorption of water by flannel by placing the sample in an evacuated space into which a measured amount of water vapor could be introduced. The corresponding pressures were indicated on a mercury manometer. Twelve hours was allowed to elapse between each addition of water vapor to ensure the restoration of equilibrium. Trouton pointed out two general facts: 1. the amount of adsorption is in general independent of the temperature and is a function of the relative humidity only, 2. an abnormally large adsorption takes place near the saturation temperature, It was found that cotton containing a definite a mount of water behaves like an aqueous solution in that at different temperatures it exhibits a vapor pressure that is ever a constant fraction of that of pure water. Troutons adsorption isotherms were convex to the pressure axis and were a approximately parabolic.

This investigation was repeated by Travers (Ref.20) who found that, for a considerable range of vapor pressure, the adsorption isothermal was concave to the pressure axis. Trouton's work has been further discounted by later investigations and it has been generally recognized that his theoretical considerations apply only to his own work.

Hatshorne, (Ref. 21) working with cotton, observed the hysteresis effect and again assumed the mean value to be the true amount of adsorption. He devised a rather ingenious method to obtain this result. Two skeins of yarn of identical dry weight were prepared, one was dried, the other wetted, and both were suspended from the arm of a small balance in a chamber in which the relative humidity was regulated with sulfuric acid solutions.

Half the resulting equilibrium weight was the accepted as the true equilibrium weight of the skein. A complete set of values for the moisture regain of cotton on this basis was drawn up by the use of an interpolation formula.

According to Scheurer (Ref. 22) dry bleached cotton willtake up 19.0 to 20.2 percent of water from a saturated atmosphere. The amount of water adsorbed by cotton is greatly affected by certain non-cellulose constituents. Thus Lester (Ref. 23) found that the water-soluble constituents adsorbed 28.7 per cent of water in comparison with 8 per cent for cotton under the same conditions.

Williams (Ref. 24) examined the hygroscopicity of cotton and developed a number of adsorption isostere equations which have not, however, received much attention from later investigators.

Wilson and Fuwa (Ref. 25) determined the humidity equilibria of a number of substances by evacuating through a weighed drying train. Wood was found to have a higher adsorption value than most other common substances. The highest values were found in the case of mechanical pulp which has the lignin still present. Wood, cotton, clay, etc., all possesed the same general curve as that found previously by Masson and Richards.

Wilson (Ref. 26) examined the humidity relationships of a number of sugars by exposing them to saturated air and weighing repeatedly. It was again noticed that under such conditions, great time was necessary for the complete establishment of equilibrium. A hysteresis effect similar to that of cotton was noticed for the sugars. Based on these observations Wilson pointed out the errors which must arise in any measurement of relative humidity by a method depending on the change in weight of a hygroscopic substance.

Kujirai (Ref. 27) discussing the moisture relations of a number of fibrous insulating materials, indicated the presence of a hysteretic lag and also stated that the relation between moisture content and relative humidity was represented by a formula derived from that of Langmuir for the adsorption of a gas on a solid:

$$Q = \frac{1}{a/H\ b - Hc}$$

Q amount adsorbed.
H relative humidity.
a,b,c constants.

An elaborate examination of the moisture relations of soda-boiled cotton have been conducted by Urquhart and Williams, who have published their results in a number of communications. (Ref. 28)

Their first experiments were made using sulphuric acid solutions in dessicators after the method of Schloesing. Weighing bottles containing the samples placed in dessicators until constant weight was obtained, the time required varied from 3 days to 3 months, the longer times being required at higher humidities. A difference was noted in the case of raw cotton, between the dry weight of a sample dried by heating to 110°C. and that of a sample dried at 15°C. in vacao over P_2O_5. This difference practically disappeared with pure cellulose indicating the loss of some volatile, non-cellulose constituent in the first case. They also noticed that the removal of impurities increased the amount of hysteresis (which was found in every case. This has not been borne out in the present investigation.

This method was not applicable to very low relative humidities or to values near the saturation point, hence, in their second paper, the authors revived the method of Trouton. Water was added to an evacuated space containing the sample from a burette readable to 1/200 cc. and the corresponding pressure noted. With this apparatus they investigated the extremities of the adsorption isotherm. It was found that the hystereisi ceased below a relative humidity of 1.8, while at the upper end the curves did not necessarily close. In this connection it must be pointed that this apparatus would be expected to yield erroneous results near the saturation point, as the actual amount of water adsorbed on the cotton is not directly measured, but is obtained only as a difference. Consequently near the saturation point, liquid water might be condensing on tha walls of the apparatus but the calculation would attribute this to the cellulose. Urquhart and Williams calculated the size of the pores by means of Kelvin's formula for the reduction of vapor pressure with radius of curvature and found them to be approximately 1.5 times the accepted molecular dimensions.

In a third paper the effect of temperature was investigated utilizing the same experimental procedure. Cotton saturated with moisture was heated to various temperatures and the corresponding pressures noted. Adsorption values were plotted and adsorption isosteres obtained. According to their nomenclature an adsorption isostere represents the variation of pressure with temperature for some constant adsorption.

Fisher (Ref. 29) studied the rate of drying of a number of colloidal substances such as wool, cotton, clay, etc. It was observed that the velocity of drying diminished greatly in the final stages and this was attributed to shrinkage which would reduce the available surface for evaporation. In a later paper by the same author this explanation was discounted on the grounds that other substances which shrink on drying did not show the abnormal curvature in drying curves. It was then assumed that the observed rate of drying was due to the combined effect of imbibed and interstitial water, the latter having a constant vapor pressure while the former exhibited a vapor pressure which diminished with the amount of water present.

It will be seen from the foregoing that, in the case of wood, there has been no systematic measurement of the amount of adsorption over a range of temperature and relative humidity. A considerable number of determinations of the fibre saturation point have been made but the values differ widely. In most cases the samples employed have been of such size that great time was require for establishment of equilibrium, times so great that the maintainence of carefully regulated conditions was impossible. Practically no measurements have been made showing the rate of penetration of vapors in different woods and different directions in the wood. The state of knowledge is indicated by Hawley and Wise (Ref. 30) " From these few data. therefore, it seem that water is adsorbed by wood with lowering of the vapor pressure and giving off of heat up to a limit or saturation point. As in the case of other adsorptions of volatile liquids by solids, the actual mechanism is unknown. It may be condensation in fine capillaries, or surface adsorption on a peculiar fine structure existing in the wood, or the watter may form a solid solution with the wood entering into the crystalline structure of the cell wall, or perhaps there may not be any essential difference between these three mechanisms."

In the case of cotton cellulose the field has been covered more thoroughly. The moisture equilibria of cotton and cotton cellulose is known fairly accurately at all humidities and at temperatures from 12° to 110° C. Two objectiond may be raised to all the previous work. Firstly, no provision is made to prevent condensation from taking place on the walls of the apparatus and even on the sample itself, and secondly, the great time required for equilibrium is not in keeping with the general ideas of the rate of adsorption of a gas on a solid, which is generally a rapid process.

PURPOSE AND METHOD OF ATTACK OF PRESENT RESEARCH.

Since wood is a substance of complicated structure, the adsorption of a vapor will consist of two factors; first, the penetration of the adsorbate through the wood structure, and second, the actual adsorption of the vapor on the walls of the internal structure. In much of the previous work on the subject the existance of two factors has been persistently overlooked. In the present investigation an attempt has been made to separate them. A brief description of the structure of wood will illustrate the principle of the method which has been followed.

In the coniferous woods (to which attention has been confined) there are no continuous longitudinal passages through the tree as are common in the hardwoods, so the passage of liquids and vapors must take place through the fibres themselves.

Fig. 1 is a diagramatic interpretation of a section of spruce wood.

The vertical direction represents the vertical direction in the tree from which the sample was cut, and is called the longitudinal direction. The actual length of the sample would be about 6 mm. The top of the block represents transverse sections of the wood. The rectangular units which make up this surface are sections through vertical

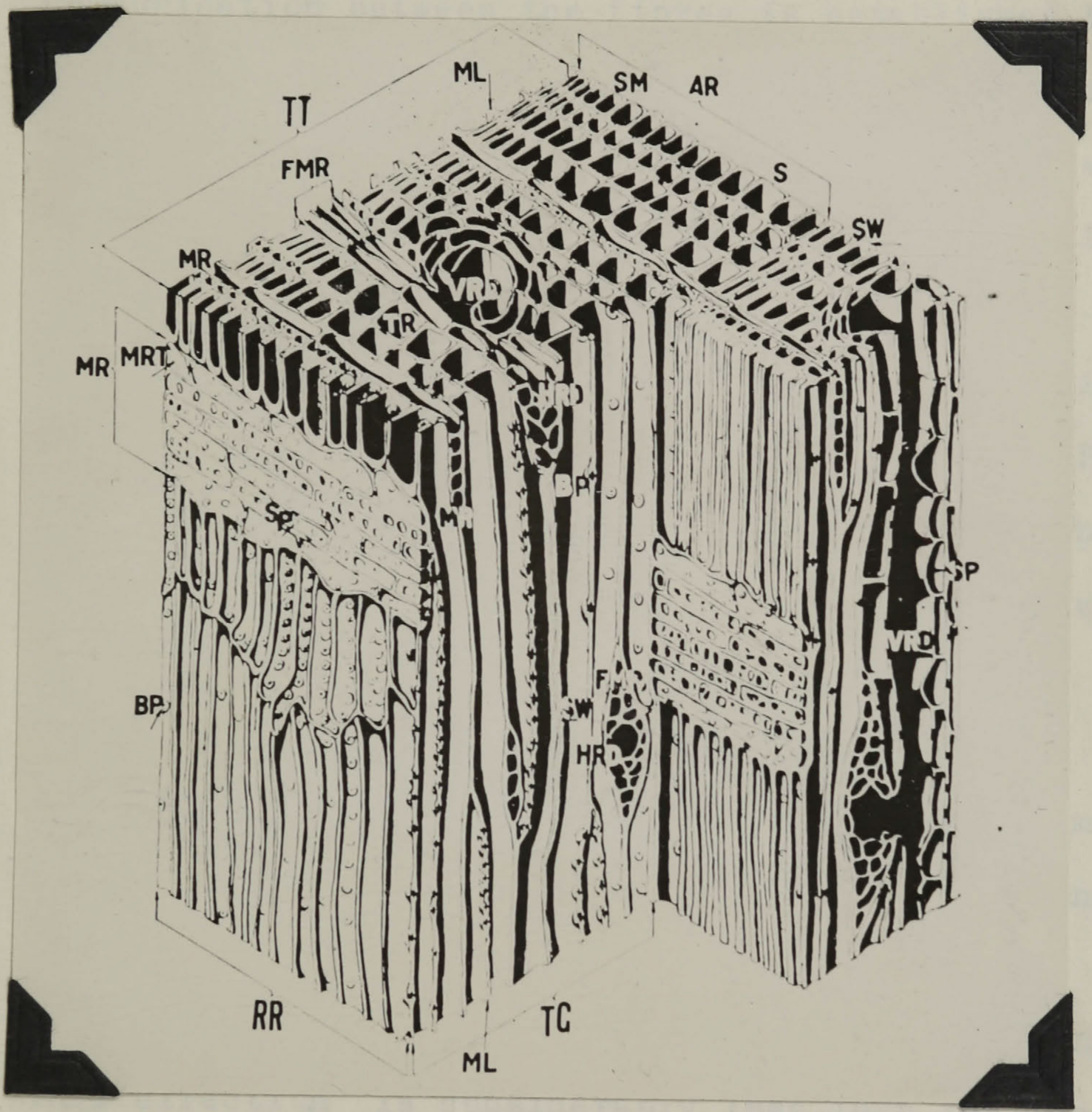

Fig. 1.

Diagramatic Section of a Typical Coniferous Wood.

cells, mostly the tracheids or water carriers, T R, the walls of which form the bulk of the wood substance. The tracheids vary in length from .5 mm. to 10 mm. having in spruce, an average value of 3.53 mm. (Sutermeister) Communication between the fibres is established by means of the bordered pits, B P, which are apertures containing a valve-like flap known as the torus. In the heartwood is assumed that this flap is glued to one side with resin thus accounting for the impenetrability of this part of the tree. The bordered pits also communicate between the tracheids and the medullary rays M R, which supply a passage for radial flow in the tree. The cross-section of the medullary ray is seen on the tangential face, T G. There are other special intercellular spaces known as the resin ducts, V R D, which serve to store and conduct resin. The summerwood fibres are smaller than the springwood which forms the differentiation known as the annual ring.

It will be seen that in a sample where the longitudinal direction is considerably less than the length of the fibres, all the walls of the wood structure are immediately accessible to an entering vapor. That is, if a vapor suddenly surrounds such a sample, the apparent rate of adsorption will correspond to the true rate for the gas-solid interface in question. The wood structure has no influence on the rate of adsorption. Actually, as will be seen later, the rate of adsorption for a sample of 1.5 mm. longitudinal direction is the same as for finely ground wood meal in which the wood structure has been largely destroyed.

If a larger sample is taken, one in which the longitudinal direction is greater than the length of the fibre, it will be seen, that to reach the inner fibres, the entering vapors must pass through such passages as exist in the wood structure. Thus by comparing the time to saturation of such a sample with that of the standard where the wood structure plays no part, a comparative measure of the rate of penetration of the vapor through the wood is obtained. By employing thicker samples of one, two, three, etc., fibre lengths it will be possible to isolate the effect of a single fibre on the penetration by a vapor. This will form a valuble method to compare various woods and various parts of the same wood.

Since wood is an anisotropic substance the rate of penetration in the three directions, longitudinal, radial, and tangential, will not be the same. These rates may be examined by masking the required faces thus restrict- the flow to the desired directions.

DESCRIPTION OF APPARATUS.

Requirements which must be fulfilled.

There are certain conditions to which the apparatus must conform. It must be capable of giving an accurate measure of weight at any time, and combined with this, it must be of such form that at all times the sample is enclosed, and all gases other than the vapor in question are removed from the system. Some provision must made to prevent condensation of the liquid on the sample at vapor pressures near the saturation point.

Apparatus .

The apparatus which has been employed is essentially a spring balance suspended from the top of a tube. This tube is connected to a drying tube, pumping system, manometer, and scource of water vapor.

A diagramatic representation of the apparatus is indicated in Figure 2.

The spirals were mounted in triplicate in three special chambers (C,D,E,) furnished with ground glass joints. The spirals were suspended from glass hooks sealed just above the ground joint. Connecting these tubes to the pumping system was a P_2O_5 tube (G) closed by a stopcock. To supply water vapor to the apparatus a tube was placed

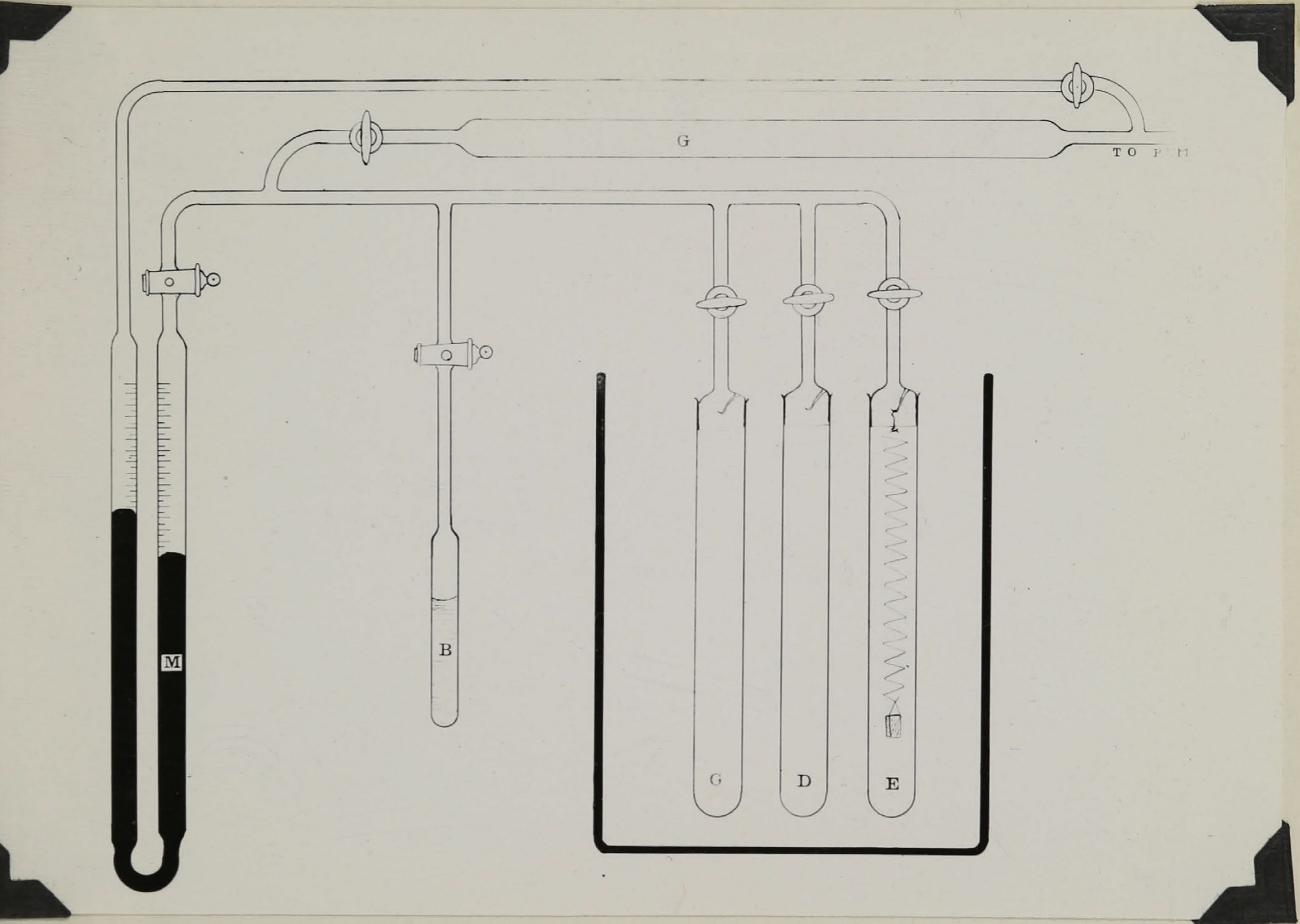

Fig. 2.

Apparatus.

at (B). The liquid, water in most cases, was carefully freed from dissolved gases by freezing and evacuating several times. The stopcocks connecting the water tube, drying tube, and the samples, were of special type containing a large bore to reduce any lag in the establishment of a constant pressure throughout the apparatus. The tubes containing the spirals were immersed in a glass-sided thermostat fitted with a thermoregulator giving control to 0.018 C. By means of a cooling coil of lead piping a working range of from 10° to 42° C. was obtainable with the room temperature averaging 24° C. When an experiment was performed the required vapor pressure was maintained in the apparatus by controlling the temperature of the tube (B).

Deflections of the spiral were measured with a cathetometer accurate to 0.05 mm. Before each reading of the deflected end of the spiral, the position of the fixed end was taken as a reference point, the difference between the the two giving the length of the spiral when deflected by the given weight. By this means it was possible to obviate any error due to accidantal displacement of the cathetometer or apparatus .

Apparatus (in detail).

Spirals.

In choosing the material for the spring balance it is essential that the substance posses a very high elasticity so that the spiral will show no lag in returning to the zero position after deflection. This requirement is best filled by quartz as it forms an exceedingly sensitive balance, and,due to its cystalline nature and high melting point, no permanent elongation occurs even after continued stress.

Construction.

A piece of quartz tube or rod of convenient size is heated in the oxygen flame. When a small lump is obtained in the molten condition, the ends of the rod are rapidly drawn out to arms length. The quartz fibre so-formed will have a thickness which depends on the size of the original lump and the length to which the fibre has been drawn. The desired thickness depends on the weights to be supported and the sensitivity required. A thick fibre must wound to a larger helix and be longer than a thin fibre to produce equal sensitivity. The correct thickness must be found by trial. The fibre is then wound into a helix on a carbon rod by playing a small flame on the appropriate point to allow the fibre to bend about the rod. The most convenient flame for this purpose proved to be a small gas jet without internal air supply. This flame is sufficiently hot to bend the fibre without danger of fusing it off, a frequent eventuallity if any type of blast is employed. The ends of the spiral are shaped into hooks for the suspension of spiral and load.

The balance was calibrated throughout the working range by means of known weights. A calibration curve of deflection plotted against corresponding weight was in all cases a straight line and in most cases it passed through the origin. (Fig. [illegible])

Calibration of Spiral A.

Weight. g.	Deflection mms.	Wt. per 1 mm. def. g.
.0486	20.55	.00236
.0650	27.80	.00234
.0890	37.95	.00235
.1065	45.05	.00236
.1234	52.30	.00236

With the cathetometer reading to 1/20 mm. a weight of .0001 g. could be detected with this spiral. That is the total weight of a sample weighing .0.1 g. could be determined to an accuracy of .15%. Since the maximum differences noted in the investigation were about 20% of the weight, or .0200 g. in the case above, the theoretical accuracy

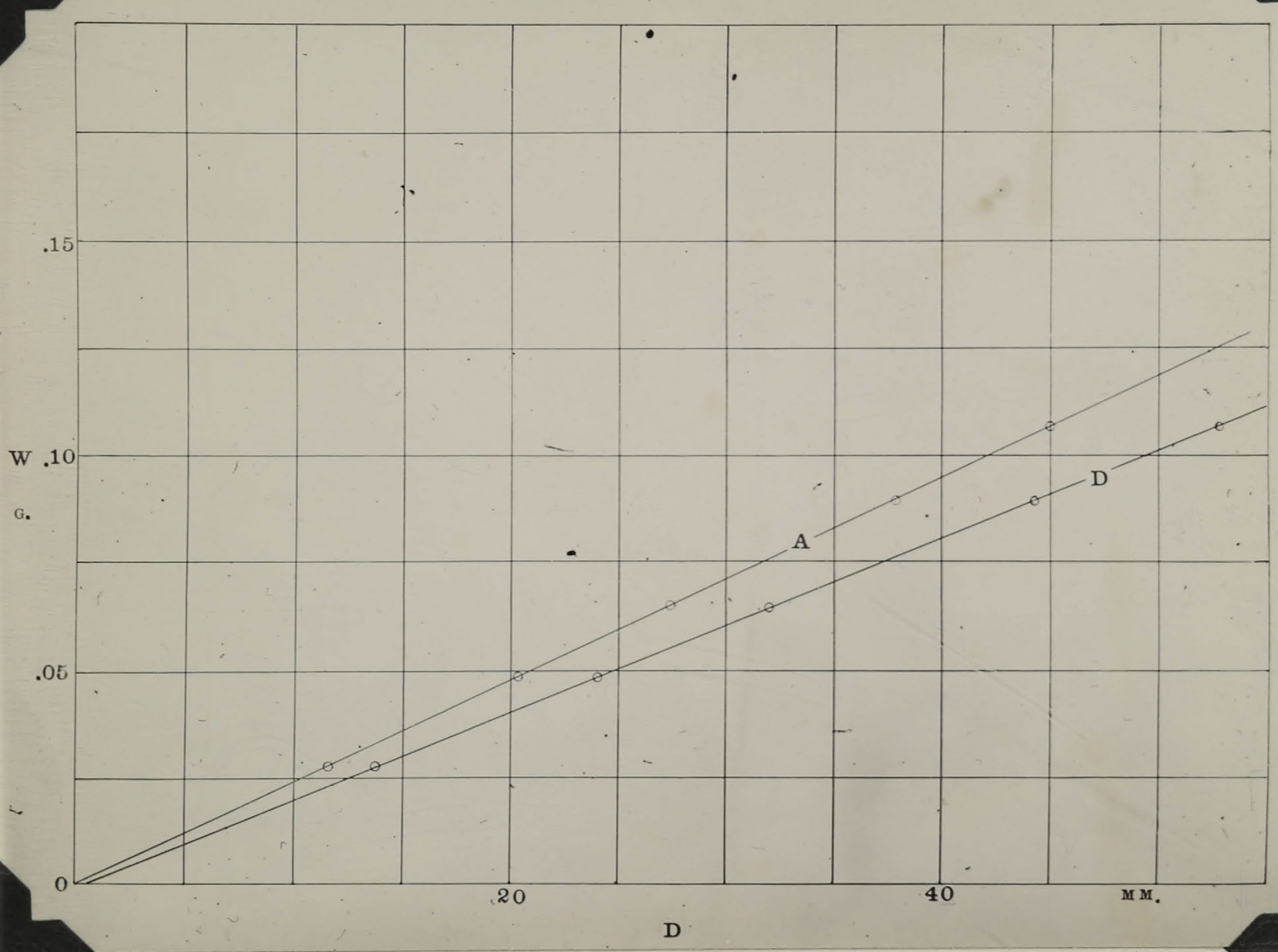

Fig. 4.

Calibration curve of Quartz Spirals.

was within 0.5% of the differences measured.

In making a reading with the cathetometer it was found convenient to focus the cross-hairs of the instrument on the extreme end of the spiral, which, if illuminated from behind, is extremely visible, even through the medium of the thermostat.

Manometer.

In preliminary experiments a mercury manometer was employed, but it proved unsatisfactory for low pressures. It was replaced with a manometer of a heavy non-volatile oil. Dissolved air and volatile gases were removed by heating and long evacuation. The specific gravity of the oil, determined at the average room temperature, gave a conversion factor to convert the readings to mm. of Hg. This manometer gave a reading about fourteen times that of a similar mercury manometer.

Pumping System.

The first system consisted of a Töpler pump fitted with a Maass automatic control. With this pump pressures down to .0003 mm. Hg could be obtained by long continued pumping. The Töpler pump was later superseded by a Langmuir Mercury Condensation pump and retained as a fore-pump for the latter. With the Langmuir Pump much lower pressures were obtainable and with much greater

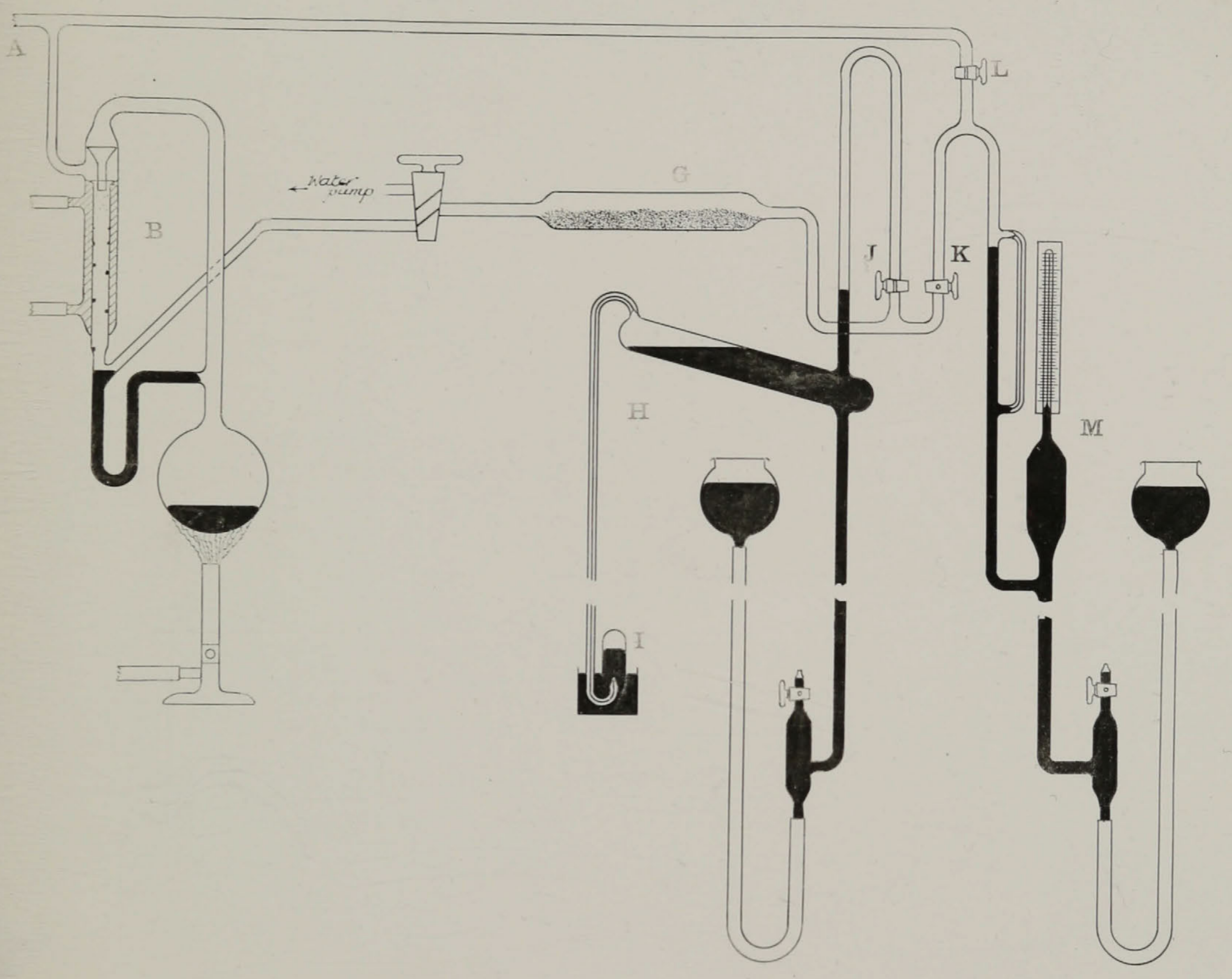

Fig. 3.

Pumping System.

rapidity. No difference in the adsorption results were noticed between runs made with the Töpler and those with the Langmuir, the great advantage of the condensation pump being its great rapidity.

The pressures were read on a McLeod gauge of the ordinary type.

Samples.

Only the coniferous woods have been examined and in particular

Spruce -- - Picea Canadensis
Jack Pine - Pinus Banksiana

Standard cotton cellulose (Ref.31) was carefully examined, and several other substances such as filter paper and lignin wre investigated for comparative purposes. The wood samples included :-

Spruce A.	Spruce wood freshly cut and dipped in paraffin to preserve the original condition.
Spruce B.	Spruce wood dried in the open on a wood pile (Pulp mill).
Jack Pine.	Fresh wood (as Spruce A.)

Samples were cut across these logs with a fine circular saw. The thickness varied from 1.5 mm to 20 mm. From these sections the actual samples were cut either from heartwood or sapwood as desired. The average sample weighed from .1 to .2 g.

Two methods were employed to support the samples from the hook of the quartz spiral:

a) In the case of the thin samples a slit was cut near one and the spiral inserted.

b) For thicker samples a stirrup of fine silver wire was provided. For these samples certain desired faces such as radial, transverse, etc were blocked off with paraffin . The weight of stirrup and paraffin was found before the experiment and subtracted from the weight as calculated by the deflection of the spiral. A blank run showed that paraffin does not adsorb enough to interfere with gravimetric measurements, a fact which has hbeen previously noted (Ref. 32).

EXPERIMENTAL PROCEDURE.

Two general methods were followed:

I. Vapor pressure fixed by maintaining a known constant temperature in a body of water in communication with the samples.

The samples were suspended from the spirals and the ground joints lubricated and set in place. The pumping system was then actuated and pumping was continued for 12 hours. At the end of this time the pressure in the apparatus had fallen to .00005 mm. Hg. and the sample was considered dry (see below). The deflection of the samples was then noted and from it the dry weight was calculated. The tube (B) was then immersed in a Dewar flask maintained at any stated temperature, the corresponding vapor pressure of which could be obtained from tables. Temperatures from -40° to 0° C. were obtained by manually dropping pieces of solid CO_2 into a stirred ether mixture. From 0° up to the saturation temperature the required point was manitained by adding ice water in the required amounts. When the bulb (B) had reached a constant temperature the stopcock was opened placing it in contact with the samples. The tap to the drying tube having been previously closed, the vapor of water filled the apparatus. Readings were now taken of the deflections of the spirals, and the time noted. When only the final equilibrium point was required about two hours was allowed to elapse before taking the reading. After the reading was completed the temperature of the tube was altered, either up, to measure adsorption at a higher vapor pressure, or down, to measure the equilibrium when water is lost, the so-called "desorption" value.

By this method pressures corresponding to all temperatures below that of the room could be employed. The apparatus as designed does not allow this point to be exceeded as water would condense in the colder parts of the apparatus. If, however, the temperature of the thermostat be maintained just below that of the room, all pressures up to the saturation pressure may be employed. Also it will be seen that as long as the temperature of the water tube (B) is slightly below that of the rest of the apparatus, there will be no possibility of liquid condensation taking place on the sample, hence the saturation value may be approached without error due to this cause.

Method II Measurement of vapor pressure directly.

In this method only one sample may be examined at a time. The sample is pumped out as before and when completly dried the stopcock leading to the P_2O_5 tube is closed. The dry weight is noted after which the tap to the water tube (B) is momentarily opened thus permiting a certain amount of water vapor to enter the apparatus. The pressure will be indicated on the oil manometer and will fall from its initial value as the water is adsorbed by the wood. When equilibrium is attained the weight of the sample is noted and the corresponding vapor pressure is read directly on the manometer. Much longer time is required for equilibrium by this method, as the vapor pressure falls off as ~~the~~ adsorption increases, while in the first method the pressure is maintained from the water tube which acts as an inexhaustible reservoir.

The process may be repeated and an additional amount of water vapor added and the amount of adsorption for a higher vapor pressure determined. When the saturation point is reached the vapor pressure remain constant and the apparent adsorption increases enormously due to the condensation of liquid water on the sample. The process may be conveniently reversed to examine the desorption equilibrium values. Starting with the saturated sample, various amounts of water vapor are withdrawn by opening, at intervals, the tap leading to the drying tube . The weight of the sample is found each time after equilibrium has set in. This method, it will be seen, is particularly applicable to the examination of hysteresis effects, but cannot be advantageously employed for the measurement of rates of adsorption.

Method I has been used more generally as it is convenient for the measurement of rate of adsorption, and while it requires more careful attention, three samples may be examined concurrently. This possesses an added value in that three samples may be compared under absolutely identical conditions of temperature and pressure.

CALCULATION OF RESULTS.

To indicate the significance of the various columns given in the tables of results, a specimen run is herewith submitted.

Sample 1. Spruce sapwood(A)

Dry weight of sample .... .0707 g.

Transverse thickness .... 2.0 mm.

Spiral A.

Length with zero weight .... 9.275 cm.

1 mm. corresponds to .... .002 g.

Temperature of thermostat .... 33oC.

T. °C.	V.P. mm. Hg.	R.H. %	L. cm.	D. mm.	W. g.	H_2O g.	S. %
-40	.03	.07	12.920	35.45	.0709	.0002	0.27
-30	.29	.77	12.955	35.60	.0712	.0005	o.71

------------------ etc. -------------------

In column T. is placed the temperature of the water tube, the corresponding vapor pressure of which is listed in the column under V.P.

If p_t is the vapor pressure at a temperature t and p_{33^o} the vapor pressure at the temperature of the thermostat, that is the saturation temperature, the relative humidity is given by $p_t/p_{33^o} \times 100$. The value so-obtained is placed under R.H. in the third column.

A reading is taken of the top and bottom of the spiral

The difference (column D) gives the deflection of the spiral, from which is subtracted the unsprung ~~weight~~ length of the spiral as listed at the head of each table. The value so-obtained (D) represents the deflection from the zero position of the weight in question. The latter value follows immediately by multiplying the deflection by the factor for the balance. This value is placed in the column (W)

The amount of water adsorbed (H_2O) will be the difference between this weight and the dry weight of the sample.

In the last column the amount of adsorption is expressed as a per cent of the dry weight.

Method II (Specimen).

R_1. cm.	R_2. cm.	D. cm.	N.D. mm.	H_2O. g.	S. %	P_{Hg} mm.	P_{oil} cm.
22.245	5.625	16.620	4.10	.0097	5.88	16.73	25.25
22.245	5.675	16.570	3.60	.0085	5.15	12.32	18.60

------- etc. -------------

In tables XIX to XXII which contain the results of the second method of precedure, a slightly simpler method of calculation was followed. Since the method was employed only to examine the hysteresis effect the actual weights were not calculated. The dry weight is found and listed at the head of the table.

R_1 and R_2 are the readings of the top and bottom of the spiral, and D, as before, is the difference. By subtracting from D the deflection for the dry weight of the sample a column N.D. is obtained which represents the deflection caused by the adsorbed water only. The product of this value and the factor for the spiral is at once the weight of the adsorbed water. This value is expressed as a percentage of the dry weight as before. The vapor pressure as read on the oil manometer and the corresponding pressure in mm. of Hg are given in the last two columns.

DRY POINT.

According to the procedure adopted, the adsorption value is considered to be the difference between the weight of the sample when immersed in a given vapor pressure of water and its weight when evacuated in the presence of P_2O_5. It is probable that this latter value is not the true dry weight. It has been pointed out in the literature that cellulose is probably the most hygroscopic substance known (Ref.33) . That is, even in the presence of P_2O_5 the samples will still contain some water. These effects, however, are not large. Jahn and Wise (Ref. 34) found that at 23°C. cellulose increased in weight .4% when evacuated in the presence of P_2O_5, while under the same conditions at 76°C. it was perfectly dry. It will be seen that such differences are less than the experimental errors attendant with the method.

So the equilibrium condition which wood or cellulose assumes when evacuated inthe presence of P_2O_5 has throughout been considered as the true dry weight.

A simple calculation will also indicate that the error consequent of weighing the sample in a vacuum and later in an atmosphere of water vapor is quite outside the experimental accuracy. The first signifigant figure due to buoyancy is in the fifth decimal place of a gram.

Nomenclature.

Throughout the tables of experimental results the term "transverse length" is intended to indicate the length between two transverse planes. That is the thickness of a transverse sample.

EXPERIMENTAL RESULTS.

Table of contents.

ADSORPTION OF WATER BY WOOD.

A Final equilibrium values at various temperatures.

B. Rate of establishment of equilibrium. Rate of penetration,

TABLE I.

Sample 1.

Spruce sapwood (A)

Dry weight of sample .. . . .0707 g.

Transverse thickness . . . . 2.0 mm.

Temperature of thermostat .. 33°C.

Spiral A. (early calibtration)

Length with zero weight . 9.375 cms

1 mm. corresponds to .002 g.

T. °C.	V.P. mm. Hg.	R.H. %	L. cms.	D. mm.	W. g.	H_2O. g.	S %
-50	.03	.07	12.920	35.45	.0709	.0002	0.27
-40	.09	.27	12.925	35.50	.0710	.0003	0.42
-30	.29	.77	12.935	35.60	.0712	.0005	0.71
-20	.77	2.87	12.945	35.70	.0714	.0007	0.99
-10	1.95	5.22	12.970	35.95	.0719	.0012	1.69
0	4.58	12.35	13.020	36.45	.0729	.0024	3.5
12	10.51	27.90	13.090	37.15	.0743	.0036	5.07
24.5	23.34	61.2	13.265	38.90	.0778	.0071	10.01

TABLE II.

Sample 2.

Spruce sapwood (A)

Transverse thickness	1.5 mm.
Dry weight of sample	.0808 g.
Temperature of thermostat	33°C.
Spiral A.	
Length with zero weight	9.220 cms.
1 mm. corresponds to	.00236 g.

T. °C.	V.P. mm. Hg.	R.H. %	L. cms.	D. mm.	W. g.	H_2O. g.	S. %
-50	.03	.07	12.640	34.35	.0810	.0007	.87
-40	.09	.27	12.645	34.40	.0811	.0008	.99
-30	.29	.77	12.655	34.50	.0814	.0011	1.37
-20	.77	2.87	12.660	34.55	.0816	.0012	1.45
-10	1.95	5.22	12.695	34.80	.0823	.0020	2.49
-5	3.01	6.07	12.710	35.05	.0827	.0024	2.98
0	4.58	12.35	12.770	35.65	.0841	.0028	3.45
5	6.54	17.51	12.780	35.75	.0843	.0040	4.95
10	9.21	24.9	12.785	35.80	.0845	.0042	5.23
21.1	18.71	4916	12.905	37.00	.0873	.0070	8.81

TABLE III.

Sample 3.

Spruce heartwood (A).

Transverse thickness .... 1.5 mm.

Dry weight of sample .... .0933 g.

Temperature of thermostat .... 33° C.

Spiral D.

Length with zero weight .... 7.120 cms

1 mm. deflection corresponds to .... .0022 g.

T. oC.	V.P. mm. Hg.	R.H. %	L. cms.	D. mm.	W. g.	H_2O. g.	S. %
-50	.03	.07	11.380	42.60	.0937	.0004	0.43
-40	.09	.27	11.385	42.65	0938	.0005	0.53
-30	.29	.77	11.400	42.80	.0941	.0008	0.85
-20	.776	2.87	11.415	42.95	.0945	.0012	1.28
-10	1.95	5.22	11.470	43.50	.0957	0024	2.55
-5	3.01	8.07	11.490	43.70	.0961	0028	3.00
0	4.58	12.35	11.540	44.20	.0972	.0037	4.10
5	6.54	17.51	11.565	44.45	.0978	.0045	4.83
10	9.21	24.9	11.600	44.80	.0985	0052	5.35
21.1	18.71	49.6	11.715	45.95	.1011	.0078	8.35
25.5	24.65	65.30	11.890	47.70	1049	.0114	12.32

TABLE IV.

Sample 4.

Spruce sapwood.

Transverse thickness .... 1.5 mm.

Dry weight of sample .... .0671 g.

Temperature of thermostat.................... 33°C.

Spiral A.

Length unsprung .... 9.205 cm.

1 mm. deflection corresponds to .... .00236 g.

T. °C.	V.P. mm. Hg.	R.H. %	L. cms.	D. mm.	W. g.	H_2O g.	S. %
-30	.289	.77	12.065	28.60	.0675	.0004	.29
-20	.776	2.87	12.090	28.85	.0681	.0010	1.45
-10	1.950	5.22	12.100	28.95	.0683	.0012	1.79
-5	3.013	8.07	12.120	29.15	.0687	.0016	3.01
0	4.579	12.25	12.145	29.40	.0694	.0023	3.43
5	6.543	17.51	12.175	29.70	.0702	.0031	4.62
10	9.209	24.70	12.240	30.35	.0716	.0045	6.71
23.8	22..32	63.75	12.345	31.40	.0741	.0070	10.41

TABLE V.

Sample 5.

Spruce heartwood (A)

Transverse thickness	1.5 mm.
Dry weight of sample	.0784 g.
Temperature of thermostat .	33° C.
Spiral D.	
Length unsprung	7.120 cms.
1 mm. deflection corresponds to	0022 g.

T. °C.	V.P. mm. Hg.	R.H. %	L. cms.	D. mm.	W. g.	H_2O. g.	S. %
-30	.289	.77	10.715	35.95	.0791	.0007	.8
-20	.776	2.87	10.730	36.10	.0794	.0010	1.27
-10	1.950	5.22	10.760	36.40	.0801	.0017	2.17
-5	3.013	8.07	10.770	36.50	0803	.0019	2.43
0	4.579	12.25	10.805	36.85	.0811	.0027	3.44
5	6.543	17.51	10.840	37.20	.0818	.0034	4.35
10	9.209	24.70	10.980	38.60	.0849	.0065	8.3
23.8	22.132	63.75	11050	39.30	.0864	.0080	10.21

TABLE VI.

Sample 6.

Spruce sapwood (A).

Transverse thickness . . . . 1.5 mm.

Dry weight of sample . . . . .1055 g.

Temperature of thermostat . . . . 33° C.

Spiral A.

Length unsprung . . . . 9.205 cms.

1 mm. deflection corresponds to . . . . .00236 g.

T. °C.	V.P. mm. Hg.	R.H %	L. cms.	D. mm.	W g.	H_2O. g.	S. %
-30	.29	.77	13.685	44.80	.1057	.0007	.67
-20	.77	2.87	13.700	44.95	.1061	.0011	1.04
-10.2	2.01	5.48	13.745	45.40	.1071	.0021	2.00
-5.4	3.0	18.10	13.770	45.65	.1075	.0025	2.48
0	4.58	12.25	13.805	46.00	.1085	.0035	3.34
5	6.54	17.51	13.845	46.40	.1095	.0045	4.28
10	9.21	24.70	13.870	46.65	.1100	.0050	4.77
15	12.78	34.28	13.930	47.25	.1114	.0064	6.10
22.2	20.13	54.01	14.095	48.90	.1154	.0104	9.89

TABLE VII.

Sample 6.

Spruce sapwood (A).

Transverse thickness	1.5 mm.
Dry weight of sample	.1055 g.
Temperature of thermostat	12° C.
Spiral A.	
Length unsprung	9 205 cms.
1 mm corresponds to	.00236 g.

T. °C.	V P. mm. Hg	R.H. %	L. cms.	D. mm.	W. g.	H_2O. g.	S. %
$\frac{3}{4}$#)							
-30	.29	2.76	13 790	45.85	.1082	.0027	2.56
-20	.77	7.52	13.850	46.45	.1096	.0041	3.90
-10	1.95	18.51	13 895	46.90	.1107	.0052	4 93
0	4.58	43.60	14 030	48.25	.1138	.0083	7 87
15	6.54	62.25	14.195	49 90	.1177	.0122	11 56
10	9.20	87.61	14.440	52 35	.1235	.0180	17.05

TABLE VIII

Sample 6.

Spruce sapwood (A)

Transverse thickness .... 1.5 mm

Dry weight of sample .... .1050g.

Temperature of thermostat .... 18°C.

Spiral A.

Length with zero weight .... 9.205 cms.

1 mm deflection corresponds to .... .00236 g.

T. °C.	V.P. mm. Hg.	R.H. %	L. cms.	D. mm.	W. g.	H_2O. g.	S. %
-30	.29	1.87	13.740	45.55	.1070	.0021	2.00
-20	.77	5.04	13.770	45.65	.1077	.0028	2.56
-10	1.95	12.59	13.845	46.40	.1085	.0035	3.33
-5	3.01	19.45	13.865	46.60	.1099	.0049	4.66
0	4.58	29.68	13.940	47.35	.1117	.0067	6.37
5	6.54	42.30	14.025	48.20	.1137	.0087	8.29
10	9.21	59.57	14.095	48.90	.1154	.0104	9.9
15	12.78	82.48	14.330	51.25	.1209	.0159	15.14

TABLE IX.

Sample 6.

Spruce sapwood (A)

Transverse thickness	1.5 mm.
Dry weight of sample	.1043 g.
Spiral A.	
Length with zero weight	9.205 cms.
1 mm. deflection corresponds to	00236 g
Temperature of thermostat	23°C.

T. °C.	V.P. mm.Hg.	R.H. %	L. cms.	D. mm.	W g.	H_2O. g.	S. %
-29.7	30	1.42	13.690	44.85	1058	.0015	1.44
-20	.77	3.67	13.720	45.15	.1065	0022	2.12
-10	1.95	9.26	13.760	45.55	1075	.0032	3.07
-5	3.01	14.27	13.795	45.90	1083	.0040	3.83
0	4.58	21.72	13.845	46.40	1096	.0053	5.07
5.	6.54	31.00	13.920	47.15	.1102	0059	5.66
10	9.21	43.75	14.060	48.55	1145	.0102	9.77
15	12.78	60.68	14.105	49.00	.1156	0113	10.83

TABLE X.

Sample 6

Spruce sapwood (A)

Transverse thickness . . . . . . 1.5 mm.

Dry weight of sample . . . . .1049 g.

Spiral A.

Length with zero weight . .. 9.205 cms.

1 mm. deflection corresponds to . .00236 g.

Temperature of thermostat . . . . 29oC.

T. oC.	V.P. mm. Hg.	R.H. %	L. cms.	D. mm.	W. g.	H_2O. g.	S. %
-30	.29	.96	13.690	44.85	1058	.0009	.86
-20	.77	2.56	13.710	45.05	.1063	.0014	1.33
-10	1.95	6.48	13.755	45.50	1074	0025	2.38
-5	3.01	10.05	13.775	45.70	.1079	0030	2.86
0	4.58	15.22	13.820	46.15	1088	0039	3.72
10	9.21	30.69	13.985	47.80	.1128	0079	7.52
15	12.78	43.60	14.050	48.45	.1133	0084	8.01
19.8	17.30	57.69	14.085	48.80	1142	.0093	8.86

TABLE XI.

Sample 6.

Spruce sapwood (A)

Dry weight of sample . . . . .1050 g.
Transverse thickness . . . . 1.5 mm.

Spiral A.

Length with zero weight . . . . 9.205 cms

1 mm. deflection corresponds to . . . . .00236 g.

Temperature of thermostat . . . . 42° C.

T. °C.	V.P. mm. Hg.	R.H. %	L. cms.	D. mm.	W. g.	H_2O. g.	S. %
-30	.29	.44	13.675	44.70	.1055	.0005	.47
-20	.77	1.31	13.690	44.85	.1058	.0008	.72
-10	1.95	3.00	13.720	45.15	.1065	.0015	1.43
0	4.58	7.06	13.755	45.50	.1073	.0023	2.18
5	6.54	10.05	13.770	45.65	.1077	.0027	2.57
10	9.21	14.15	13.810	46.05	.1086	.0036	3.43
24.2	22.5	34.60	13.935	47.30	.1116	.0066	6.28

TABLE. XII

Sample 7.

Spruce heartwood (A)

Dry weight of sample . . . . .1155 g.

Transverse thickness . . . . 1.5 mm.

Spiral D.

Length with zero weight 7 120 cms.

1 mm. deflection corresponds to .0022 g.

Temperature of thermostat 12°C.

T. °C.	V P mm. Hg	R.H. %	L. cms.	D. mm.	W. g.	H_2O. g.	S. %
-30	.29	2.76	12 500	53 80	.1183	.0028	2.42
-20	77	7 32	12.565	54.45	.1198	.0043	3.72
-10	1 95	18.51	12 620	55 00	.1210	.0055	4.76
0	4.58	43.60	12.765	56.45	.1241	.0086	7 44
5	6.54	62.25	12.975	58.55	1288	.0133	11 50
10	9.20	67.61	13.225	61.05	1343	.0188	16.25

TABLE XIII.

Sample 7.

Spruce heartwood (A).

Dry weight of sample . . . . 1151 g.

Transverse thickness . . . . 1.5 mm.

Spiral D.

Length with zero weight . . . . 7.120 cm.

1 mm. deflection corresponds to . . . . .0022 g

Temperature of thermostat . . . . 18°C.

T. °C.	V.P. mm.Hg.	R.H. %	L. cm.	D. mm.	W. g.	H_2O. g.	S. %
-30	29	1.87	12.455	53.35	.1173	.0022	1.91
-20	77	5.04	12.495	53.75	.1182	.0031	2.69
-10	1.95	12.59	12.575	54.55	.1200	0049	4.26
-5	3.01	19.45	12.610	54.90	.1207	.0056	4.86
0	4.58	29.68	12.700	55.80	.1227	.0076	6.78
5	6.54	42.30	12.800	56.80	.1249	.0098	8.50
10	9.21	59.57	13.000	58.80	.1293	0142	12.32
15.	12.78	82.48	13.150	60.30	.1326	0175	15.20

TABLE XIV.

Sample 7.

Spruce heartwood (A).

Dry eweight of sample . . . . .1149 g

Transverse thickness ... .. 1.5 mm.

Spiral D.

Length with zero weight . .. .. 7.120 cm.

1 mm. corresponds to . .0022 g.

Temperature of thermostat . . . 23°C.

T. °C.	V.P mm. Hg.	R.H. %	L. cm.	D. mm.	W. g.	H_2O. g.	S. %
-29.7	.30	1.42	12.415	53.95	.1165	.0016	1.39
-20	.77	3.67	12.455	53.35	.1173	.0024	2.09
-10	1.95	9.26	12.515	53.95	.1187	.0038	3.13
-5	3.01	14.27	12.535	54.15	.1191	.0042	3.63
0	4.58	21.72	12.605	54.85	.1206	.0057	4.97
5	6.54	31.00	12.710	55.90	.1230	.0081	7.06
10	9.21	43.75	12,835	57.15	.1257	.0108	9.50
15	12.78	60.68	12.900	57.80	.1271	.0122	11.69

TABLE XV.

Sample 7.

Spruce heartwood (A).

Dry weight of sample .... .1153

Transverse thickness .... 1.5 mm.

Spiral D.

Length with zero weight .... 7.120 cm.

1 mm. corresponds to .... .0024 g.

Temperature of thermostat .... 29° C.

T. °C.	V.P. mm. Hg.	R.H. %	L. cm.	D. mm.	W. g.	H_2O. g.	S. %
-30	.29	.96	12.400	52.80	.1161	.0008	.69
-20	177	2.56	12.425	53105	.1167	.0014	1.21
-10	1.95	6.48	12.485	53.65	.1179	.0026	2.24
-5	3.01	10.05	12.505	53.85	.1185	.0032	2.77
0	4.58	15.22	12.565	54.45	.1198	.0045	3.91
10	9.21	30169	12760	56.40	.1241	.0088	7.55
15	12.78	43.60	12.830	57.10	.1256	.0103	8.92
19.8	17.30	57.69	12.865	57.45	.1264	.0111	9.62

TABLE XVI.

Sample 7.

Spruce heartwood (A).

Dry weight of sample . . .. .1153 g.

Transverse thickness .... .. 1.5 mm.

Spiral D.

Length with zero weight .. . 7.120 cm.

1 mm.c deflection corresponds to .. .. 0022 g.

Temperature of thermostat ..... . 33°C,

T. °C.	V.P mm. Hg	R.H. %	L. cm.	D. mm.	W. g.	H_2O. g.	S. %
-30	.29	.77	12.410	52.90	.1164	.0011	1.04
-20	.77	2.87	12.445	53.25	.1171	.0018	1.56
-10.2	2.01	5.48	12.480	53.60	.1179	.0026	2.25
-5.4	3.0	~~1~~8.10	12.515	53.95	.1187	.0034	2.95
0	4.58	12.25	12.530	54.10	.1190	.0037	3.22
5	6.54	17.51	12.565	54.65	.1202	.0049	4.25
10	9.21	24.70	12.630	55.10	1212	.0059	5.12
15	12.78	32.28	12.690	55.70	1225	0072	6.10
22.2	20.13	54.01	12.905	57.85	.1273	.0120	10.40

TABLE XVII.

Sample 7.

Spruce heartwood (A).

Spiral D.

Length with zero weight	7.120 cm.
1 mm. corresponds to	.0022 g.
Dry weight of sample	.1155 g.
Transverse thickness	1.5 mm.
Temperature of thermostat	42° C.

T. °C.	V.P. mm. Hg.	R.H. %	L. cm.	D. mm.	W. g.	H_2O. g.	S. %
-30	.29	.44	12.385	52.65	.1158	.0003	.26
-20	.77	1.31	12.395	52.75	.1160	.0005	.43
-10	1.95	3.00	12.425	53.05	.1167	.0012	1.03
0	4.58	7.06	12.485	53.65	.1180	.0025	2.16
5	9.21	10.05	12.495	53.75	.1183	.0028	2.42
10	9.21	14.15	12.540	54.20	.1192	.0037	3.21
24.2	22.51	34.60	12.795	56.75	.1248	.0093	8.04

TABLE XVIII.

Spruce sapwood. Wodd meal passed through #60 mesh screen.

Investigation of hysteretic lag and values near saturation point.

Weight of sample and container .... .1818 g.

Net dry weight of sample .... .1083.g.

Weight of container .... .0735 g.

Spiral D. Length .... 7.110 cm.

1 mm. deflection corresponds to .... .0022 g.

Temperature of thermostat .... 23° C.

ADSORPTION.

T. °C.	V.P. mm. Hg.	R.H. %	L. cm.	D. mm.	W. g.	H_2O. g.	S. %
-30	.29	1.40	15.420	83.10	.1828	.0010	.92
-20	.77	3.67	15.450	83.40	.1835	.0017	1.57
-10	1.95	9.26	15.510	84.00	.1848	.0030	2177
0	4.58	21.72	15.605	84.95	.1869	.0051	4.72
10	9.21	43.75	15.735	86.25	.1897	.0079	7.30
15	12.78	60.68	15.845	87.35	.1921	.0103	9.52
18	15.51	73.82	15.950	88.40	.1945	.0127	11.73
20	17.45	83.22	16.035	89.25	.1963	.0143	13.2
21.4	19.10	91.18	16.090	89.80	.1975	.0157	14.51
21.5	19.20	91.41	16.130	90.20	.1984	.0166	15,32
22	19.81	94.38	16.220	91.10	.2004	.0186	17.15
22.7	20.6598.	98.37	16.370	92.60	.2037	.0219	20.20

TABLE XVIII (Continued

DESORPTION

T. oC.	V.P. mm. Hg.	R.H. %	L. cm.	D. mm.	W. g.	H_2O. g.	S. %
20	17.45	83.22	16.070	89.60	.1971	,0153	14.15
18	15.51	73.82	16.060	89.50	.1969	.0151	13.85
15	12.78	60.68	15.980	88.70	.1951	.0133	12.30
12	10.5	50.31	15.875	87.65	.1928	.0110	10.15
10	9.21	43.75	15.845	87.35	.1921	.0103	9.50
0	4.58	21.72	15.630	85.20	.1874	.0056	5.17

TABLE XIX.

Sample 31.

Spruce sapwood (A).

Investigation of hysterisis effect. P measured with oil manomete

Density of oil at 25° C. .... .9011

Conversion factor to mm Hg. .... .06627

Spiral A Length .... 9.220 cm.

1 mm. deflection corresponds to .... .00236 g.

Temperature of thermostat .... 42°C.

Dry weight of sample .... .1649 g.

Deflection of dried sample .... 16.210 cm

R_1	R_2	D.	N.D.	H_2O.	S.	P_{Hg}	P_{oil}
6m666666m.		cm.	mm.	g.	%	mm.	cm.
DESORPTION.							
22.245	5.625	16.620	4.10	.0097	5.88	16.73	25.25
22.245	5.675	16.570	3.60	.0085	5.15	12.32	18.60
22.245	5.710	16.535	3.25	.0077	4.73	9.89	14.94
22.245	5.795	16.450	2.40	.0056	3.40	5.57	8.43
22.245	5.865	16.380	1.70	.0040	2.43	3.23	4.87
22.245	5.910	16.335	1.25	.0029	1.76	1.62	2.45
ABSORPTION.							
22.040	5.745	16.295	.85	.0018	1.09	1.32	2.00
22.040	5.610	16.430	2.20	.0052	3.16	7.42	11.20
22.040	5.590	16.450	2.40	.0056	3.40	9.13	13.87
22.040	5.515	16.525	3.15	.0074	4.49	12.95	19.54
22.040	5.460	16.580	3.70	.0088	5.33	19.51	29 52.

TABLE XX.

Sample 31.

Investigation of Hysterisis effect cont. (see table XIX)

Temperature of thermostat .... 33° C.

Spiral A.

Deflection of dry sample .... 16.225 cm.

Dry weight of sample .... .1653 g.

R_1 cm.	R_2 cm.	D. cm.	N.D. mm.	H_2O g.	S. %	P_{Hg} mm.	P_{oil} cm.
Desorption							
22.180	5.170	17.010	7.85	.0185	11.18	18.90	28.56
22.185	5.365	16.820	5.95	.0140	8.46	12.83	19.38
22.185	5.540	16.645	4.20	.0099	5.98	7.34	11.08
22.185	5.675	16.590	2.85	.0067	4.06	3.92	5.93
22.185	5.740	16.445	2.20	.0052	3.17	2.10	3.3
22.185	51790	16.395	1.70	.0040	2.42	1.62	1.73
Adsorption.							
22.200	5.770	16.430	2.05	.0049	2.96	3.43	5.18
22.200	5.730	16.470	2.45	10058	3.51	4.92	7.43
22.200	5.560	16.640	4.15	10098	5.93	10.61	15.70
22.200	5.440	16.760	5.35	.0126	7.58	14.76	22.33
22.200	5.375	16.825	6.00	.0141	8.53	17.58	26.58
22.200	5.365	16.835	6.10	.0144	8.71	18.43	27.88

TABLE XXI.

Sample 31.

Hysterisis effect continued (see table XIX)

Temperature of thermostat .... 23° C.

Deflection of dry sample .... 16.260 cm.

Dry weight of sample .... .1661 g.

R_1 cm.	R_2 cm.	D. cm.	N.D. mm.	H_2O g.	S. %	PHg mm.	P_{oil} cm.
Desorption							
22.175	4.030	18.145	18.85	.0445	26.67	20.70	31.22
22.190	4.205	17.985	17.25	.0407	24.50	19.50	29.45
22.190	4.465	17.725	14 65	.0346	20.70	17.31	26.17
22.190	4.670	17.520	12.60	.0297	17.70	16.30	24.65
22.190	5.235	16.955	6.95	.0164	9.85	8.57	12.95
22.190	5.450	16.740	4.80	.0113	6.80	5.40	8.15
22.200	5.695	16.505	2.45	.0057	3.32	1.90	2.93
22.200	5.805	16.395	1.35	.0032	1.93	0.66	0.94
22.200	5.830	16.370	1.100	.0026	1.56	0.38	0.57
22.200	5.874	16.325	0.65	.0015	.90	0.18	0.28
22.200	5.920	16.280	0.20	.0005	.280	0.05	0.08
Adsorption							
22.190	5.845	16.345	0.85	.0020	1.21	0.38	0.58
22.190	5.745	16.445	1.85	.0044	2.62	1.18	1.78
22.190	5.685	16.505	2.45	.0058	3.50	2.46	3.72
22.190	5.500	16.690	4.30	.0102	6.12	6.05	9.12
22.190	5.130	17.060	8.00	.0189	11.38	12.71	19.2
22.190	4.975	17.215	9.55	.0227	12.66	14.98	22.60
22.190	4.830	17.360	11.00	.0259	15.60	16.37	24.70

TABLE XXII.

Spruce Heartwood. (B).

Transverse thickness ....111111.................. 1.5 mm.

Spiral B. Length without load . ... 11.465 cm.

1 mm. corresponds to .... .00338 g.

Temperature of thermostat .... 23° C.

T. °C	V.P. mm. Hg	R.H. %	D. cm.	N.D. mm.	H_2O. g.	S. %
Dry sample			17.350	weight	.1989 g.	
0	4.58	21.72	17.600	2.45	.0085	4.32
6	7.01	33.43	17.700	3.50	.0119	5.98
10	9.21	43.75	17.755	4.05	.0137	6.89
15	12.78	60.68	17.900	5.50	.0186	9.35
22	19.81	94.38	18.325	9.75	.0339	17.05

Spruce sapwood (B)

Spiral A. Length .. 9.220 cm. 1 mm. . ... .00236 g.

Dry sample deflection .. 16.770 weight .. .1781

0	4.58	21.72	17.155	3.85	.0090	5.07
6	7.01	33.43	17.295	5.25	.0124	6.95
10	9.21	43.75	17.385	6.15	.0145	8.15
15	12.78	60.68	17.565	7.95	.0187	10.50
22	19.81	94.38	18.165	13.95	.0329	18.49

TABLE XXIII.

Sample 1j.

Jack-pine heartwood.

Transverse thickness . ... 1.5 mm

Spiral B.

Length with zero weight .... 13.210 cm.

1 mm. corresponds to .. .. .00338 g

Temperature of thermostat .... 23°C.

T. °C.	V.P. mm. Hg	R.H. %	L. cm.	D. mm.	W. g.	H_2O. g.	S %
-30	.29	1.40	17.670	44.60	.1507	.0015	1.02
-20	.77	3.67	17.720	45.10	.1524	.0032	2.14
-10	1.95	9.26	17.770	45.60	.1541	.0049	3.28
0	4.58	21.72	17.900	46.90	.1585	.0093	6.23
6	7.01	33.43	17.955	47.45	.1603	.0111	7.43
12	10.51	50.31	18.040	48.30	.1632	.0140	9.38
21.3	18.97	90.35	18.450	52.40	.1771	.0279	18.70
22.5	20.40	97.20	18.710	55.00	.1859	.0367	24.60

TABLE XXIV.

Jack-pine sapwood.

Samples 2j and 3j .

Temperature of thermostat .... 23° C.

Spiral A. Sample 2j.

T. °C.	V.P. mm. Hg	R.H. %	L. cm.	D. mm.	W. g.	H_2O. g.	S. %
Dry weight			14.900	56.80	.1342	-	-
-30	.29	1.40	14.970	57.50	.1357	.0013	0.98
-20	.77	3.67	15.020	58.00	.1369	.0027	2.05
-10	1.95	9.26	15.065	58.45	.1380	.0038	2.83
0	4.58	21.72	15.205	59185	11412	.0070	5.21
6	7.01	33.43	15.340	61.20	.1444	.0102	7.60
12	10.51	50.31	15.430	62.10	.1465	.0123	9.16
21.3	18.97	90.35	15.910	66.90	.1542	.0200	14.19
22.5	20.40	97.20	16.335	71.15	.1679	.0337	25.11

Spiral D. Sample 3j

T. °C.	V.P. mm. Hg	R.H. %	L. cm.	D. mm.	W. g.	H_2O. g.	S. %
Dry weight			13.965	68.55	.1508	-	-
-30	.29	1.40	14.035	69.25	.1523	.0015	0.99
-20	.77	n 3.67	14.090	69.80	.1535	.0027	1.79
-10	1.95	9.26	14.155	70.45	.1550	.0042	2.78
0	4.58	21.72	14.345	72.35	.1591	.0083	5.56
6	7.01	33.43	14.475	73.67	.1620	.0112	7.42
12	10.51	50.31	14.585	74.75	.1644	.0136	9.01
21	18.65	88.72	15.360	82.50	.1815	.0307	20.35
22.5	20.40	97.20	15.650	85140	.1879	.0371	24.60

TABLE XXI.

Standard cotton cellulose.

Spiral C: L ... 5.695 cm. 1 mm. corresponds to .. .0047 g.

Temperature of thermostat .... 33° C.

T. °C.	V.P. mm. Hg.	R.H. %	L. cm.	D. mm.	W. g.	H_2O. g.	S. %
-30	.29	.77	9.640	39.45	.1863	.0013	0.70
-20	.77	2.87	9.655	39.60	.1869	.0019	1.02
-10.2	2.01	5.48	9.665	29.70	.1875	.0025	1.35
-5.4	3.00	8.10	9.685	39.90	.1883	.0033	1.78
0	4.58	12.25	9.695	40.00	.1887	.0037	2.00
5	6.54	17.51	9.710	40.15	.1895	.0045	2.43
10	9.21	24.70	9.735	40.40	.1909	.0059	3.19
15	12.78	34.28	9.755	40.65	.1918	.0068	3.68
22.2	20.13	54.01	9.815	41.20	.1948	.0098	5.3
Dry weight			9.620	39.25	.1850	-	-

Temperature of thermostat .... 29° C.

T. °C.	V.P. mm. Hg.	R.H. %	L. cm.	D. mm.	W. g.	H_2O. g.	S. %
-30	.29	.96	9.620	39.25	.1860	.0010	0.50
-20	.77	2.56	9.655	39.60	.1868	.0018	0.97
-10	1.95	6.48	9.675	39.80	.1879	.0029	1.57
-5	3.01	10.05	9.685	39.90	.1883	.0033	1.78
0	4.85	12.78	9.710	40.15	.1893	.0043	2.32
10	9.21	39.69	9.760	40.65	.1925	.0075	4.06
15	12.78	43.60	9.795	41.00	.1937	.0087	4.70
19.8	17.30	57.69	9.820	41.25	.1950	.0100	5.40

TABLE XXVI.

Cotton Cellulose.

Thermostat temperature .... 18°C.

Spiral B. Length ... 12.375 cm. 1 mm. ..... .00338 g.

T. °C.	V.P. mm. Hg	R.H. %	L. cm.	D. mm.	W. g.	H_2O. g.	S. %
Dry weight			17.845	54.70	.1849	-	-
-10	1.95	12.59	18.020	56.45	.1908	.0058	3.13
-5	3.01	19.45	18.045	56.70	.1916	.0066	3.57
0	4.58	29.69	18.055	56.80	.1920	.0070	3.78
5	6.54	42.30	18.100	57.25	.1935	.0085	4.59
10	9.21	59.57	18.190	58.15	.1965	.0115	6.22
15	12.78	82.48	18.300	59.25	.2002	.0152	8.23
Temperature of thermostat .... 12° C.							
Dry weight			18.630	62.55	.2114	-	-
-30	.29	2.76	18.740	63.65	.2151	.0037	1.75
-20	.77	7.32	18.760	63.85	.2158	.0044	2.08
-10	1.95	18.51	18.785	64.10	.2166	.0052	2.46
0	4.58	43.60	18.890	65.15	.2202	.0088	4.13
5	6.54	62.25	19.015	66.40	.2244	.0130	6.14
10	9.20	87.61	19.170	67.95	.2297	.0183	8.66
Temperature of thermostat .... 42° C.							
Dry weight			18.470	60.95	.2059	------	
-30	.29	.44	18.490	61.15	.2066	.0006	0.29
-20	.77	1.31	18.500	61.25	.2070	.0010	0.48
-10	1.95	3.00	18.525	61.50	.2078	.0018	0.87
0	4.58	7.06	18.550	61.75	.2087	.0027	1.31
10	9.21	14.15	18.600	62.25	.2104	.0044	2.13
24.2	22.5	34.60	18.695	63.20	.2135	.0075	3.64

TABLE XXVII.

Investigation of hysteresis effect and also the magnitude of equilibrium values near the saturation temperature in the case of cotton cellulose (S_c) and extracted wood cellulose (S_w).

Thermostat ... 23° C.

T. θ °C.	V.P. mm. Hg	R.H. %	S_c. %	S_w. %
ADSORPTION.				
-30	.29	1.40	0.57	1.51
-20	.77	3.67	0.88	1.91
-10	1.95	9.26	1.78	3.49
0	4.58	21.72	2.75	5.40
10	9.21	43.75	3.6	8.10
15	12.78	60.68	5.57	11.17
18	15.51	73.82	6.70	13.17
20	17.45	83.22	7.52	14.55
21.4	19.10	91.18	8.00	17.06
21.5	19.20	91.41	8.27	18.00
22	19.81	94.38	9.05	18.90
22.7	20.65	98.37	9.94	23.00
DESORPTION.				
20	17.45	83.22	7.82	16.15
18	15.51	73.82	-	14.05
15	12.78	60.68	6.18	12.24
12	10.51	50.31	5.57	10.26
10	9.21	43.75	3.95	8.10
0	4.58	21.72	2.62	6.03

TABLE XXIX.

Rate of establishment of equilibrium.

Spruce sapwood (A). Transverse thickness ..... 1.5 mm.

Vapor pressure in apparatus ....4.58 mm. Hg.

Temperature of thermostat .... 33° C.

Time. (min.)	S. (%)	Time. (min.)	S. (%)
Sample 1.	dry	**Sample 2.**	
1.5	1.42	1.5	1.23
3.0	2.27	4.6	1.47
7.0	2.55	8.1	2.33
10.0	2.84	14.5	3.06
17.0	3.41	21.5	3.19
25.0	3.41	60	3.19
40.0	3.41	76	3.19
52.0	3.41	97	3.19

Sample 6.

Time (min.)	S. (%)
0	Dry
4.0	2.57
10.0	2.96
18.0	3.24
32.0	3.24
41.0	3.24

TABLE XXX.

Rate of establishment of equilibrium.

Spruce heartwood (A). Transverse thickness .... 1.5 mm.

Vapor pressure in apparatus .... 4.58 mm. Hg.

Temperature of thermostat .... 33^{o} C.

Sample 3.

Time (min).	S. (%)
0	
1.6	1.82
3.5	2.67
12.1	3.51
22.1	3.68
40.0	3.85
60.0	3.85
18 hrs.	3.85

Sample 7.

Time (min)	S. (%)
0	
4.0	3.12
7.0	3.20
12.0	5.47
19.0	3.91
27.0	3.91
36.0	3.91

RATE FOR STANDARD SAPWOOD SAMPLE. # 9 wood meal

Temperature of thermostat .... 23^{o} C

Time. (min)	S (%)
3.5	3.23
7.0	4.06
12.0	4.24
15.0	4.43
21.0	4.72
24.0	4.72
31.0	4.72

TABLE XXXI.

Rate of establishment of equilibrium.

Vapor pressure in apparatus .... 4.58 mm.Hg

Spruce Sapwood (A). Sample 6.

Rate at 42°. C.

Time. (min)	S. (%)
2.0	0.67
4.5	1.81
6.5	2.00
9.0	2.09
12.0	2.18
20.0	2.18

Rate at 29°. C.

Time. (min)	S. (%)
3.0	2.28
6.0	3.23
11.0	3.52
18.0	3.61
25.0	3.72
50.0	3.72

Rate at 23°c C.

Time. (min)	S.
5.0	3.3
7.0	4.32
9.0	4.60
11.0	4.71
14.0	4.90
19.0	5.07
29.0	5.07

Rate at 18°C.

Time (min)	S (%).
3.5	4.47
6.0	5.15
9.0	5.62
12.0	5.90
15.0	6.10
19.0	6.37
27.0	6.37
48.0	6.37

Rate at 12° C.

Time (min)	S (%).
2.5	3.61
5.0	5.42
8.0	6.45
11.0	7.12
16.0	7.78
20.0	7.87
24.0	7.87
38.0	7.87

TABLE XXXII.

Rate of establishment of equilibrium.

Vapor pressure in apparatus .... 4.58 mm. Hg.

Spruce heartwood (A) Sample 7.

Rate at 42° C.

Time. (min)	S (%)
3.0	1.47
5.5	1.91
7.5	2.08
10.0	2.16
13.0	2.16
21.0	2.16

Rate at 29° C.

Time. (min)	S (%)
4.0	3.12
7.0	3.20
12.0	3.47
19.0	3.91
27.0	3.91
36.0	3.91

Rate at 23°C.

Time. (min)	S (%)
2.0	2.60
6.0	3.92
8.0	4.01
10.0	4.35
12.0	4.56
18.0	4.78
30.0	4.97

Rate at 18°C.

Time. (min)	S (%).
4.5	4.77
7.0	5.47
10.0	5.89
13.0	6.16
16.0	6.25
20.0	6.34
30.0	6.43
47.0	6.60

Rate at 12° C.

Time. (min)	S (%).
3.0	4.24
6.0	4.67
9.0	5.87
12.0	6.84
18.0	7.44
39.0	7.44

TABLE XXXIII.

Rate of establishment of equilibrium.

Standard cotton cellulose .

Vapor pressure in apparatus .... 5.48 mm. Hg.

Rate at 42°C.

T. (min).	S (%)
1.5	0.57
4.0	0.73
6.0	0.88
8.0	0.97
11.0	1.11
35.0	1.30

Rate at 33°. C.

T. (min)	S (%).
8.0	1.67
15.0	1.78
24.0	2.00
50.0	2.16

Rate at 29°C.

T. (min)	S (%).
2.0	0.97
9.0	1.62
17.0	2.23
24.0	2.32
31.0	2.32

Rate at 23°C.

T. (min).	S. (%)
1.5	0.80
5.0	1.73
8.0	1.95
13.0	2.17
17.0	2.31
22.0	2.49
26.0	2.49

Rate at 18°C.

T. (min).	S. (%)
3.0	2.13
5.0	2.71
8.0	3.03
11.0	3.31
14.0	3.46
18.0	3.57
27.0	3.63
50.0	3.78

Rate at 12° C.

T. (min).	S. (%)
2.0	0.88
4.5	2.14
7.02	3.02
10.0	3.36
14.0	3.93
19.0	4.13
26.0	4.13

TABLE XXXIV.

Rate of establishment of equilibrium. Drying.

Pressure of water vapor lowered from a higher value to 4.58 mm.

Temperature of thermostat 33°C.

Sample 2. Spruce sapwood.

T. (min).	S. (%).
2.0	7.38
5.0	5.30
9.0	4.93
18.0	4.18
23.0	4.18
39.0	3.94
58.0	3.45
99.0	3.45
20 hrs.	3.45

(Adsorption value .. 3.45)

Sample 3. Spruce heartwood.

T. (min)	S. (%)
1.5	10.15
2.5	8.57
5.5	6.63
14.0	5.56
20.0	5.24
29.5	5.05
46.0	4.59
90.0	4.20
20 hrs.	4.2

(Adsorption value .4.00)

Sample 6 Spruce sapwood. Thermostat . . . 29°C.

V.P. 4.58 initially pumped out through P_2O_5 tube.

Time. (min).	S. (%).
5.0	1.33
10.0	0.86
13.0	0.66
19.0	0.57
26.0	0.29
32.0	0.19
120.0	0.00

Initially S. 3.72%

TABLE XXXV.

PENETRATION OF WOOD BY WATER VAPOR .

Spruce (A).

Vapor pressure in apparatus ....4.58 mm. Hg.

Temperature of thermostat .... 23° C.

Sample 10. Sapw00d. Thickness .... 4.8 mm.

One transverse end open.

T. (min).	S. (%).
1.0	1.39
5.0	2.52
8.0	3.19
11.0	3.25
16.0	3.71
20.0	3.78
25.0	4.20
31.0	4.32
40.0	4.380
52.0	4.53
Final	4.53

Both transverse ends open.

T. (min).	S. (%)
3.0	2.06
6.0	2.59
11.0	3.39
13.0	3,66
16.0	3.85
19.0	3.99
22.0	4.18
27.0	4.32
50.0	4.52
Final	4.52

Sample 15. Sapwood. Thickness .... 9.5 mm.

One transverse end open .

3.0	1.11
6.0	1.77
9.0	2.31
12.5	2.22

Both transverse ends open.

5.0	2.13
10.0	3.16
17.0	3.50
23.0	3.80

Table XXXV. (cont.)

T. (min)	S. (%).	T. (min).	S. (%)
27.0	3.07	28.0	4.18
32.0	3.15	48.0	4.50
42.0	3.33	66.0	4.62
61.0	3.33	99.0	4.76
93.0	3.83	160.0	5.03

Sample 19. Sapwood. Transverse thickness ..... 14.0 mm.

One transverse end open.		Two transverse ends open.	
2.0	1.06	2.0	0.95
4.0	1.40	4.5	1.79
7.0	1.73	10.0	2.13
10.0	2.18	16.0	3.230
15.0	2.68	20.0	3.47
19.0	2.85	25.0	3.81
24.0	3.07	33.0	4.08
29.0	3.24	40.0	4.66
34.0	3.30	61.0	4.66
41.0	3.53	Final	4.66
50.0	3.73		
60.0	3.80		
94.0	4.02		

Table XXXV (cont.)

Sample 25. **Sample 26.**

Samples with both transverse ends open.

Thickness .... 20.0 mm.

Sapwood. **Heartwood**

T. (min)	S. (%)	T. (min)	S. (%)
4.0	1.62	3.0	1.03
8.0	2.28	5.0	1.34
12.0	2.90	9.0	1.49
15.0	3.12	13.0	2.01
18.0	3.34	16.0	2.11
23.0	3.69	19.0	2.21
27.0	3.87	24.0	2.52
32.0	4.07	30.0	2.73
37.0	4.22	38.0	3.01
47.0	4.38	48.0	3.19
63.0	4.65	64.0	3.60
93.0	4.86	94.0	4.12

Sample 20. 14.0 mm. in thickness. **Sample 21.** 14.0 mm.

Heartwood One transverse end open.

Both transverse ends open.

1	0.23	3.0	0.83
5.5	0.69	6.0	1.27
8.0	0.75	9.0	1.48
11.0	0.81	12.0	1.87
14.0	0.93	15.0	1.98

Table XXXV. (cont.)

T. (min)	S. (%)	T. (min).	S. (%)
17.0	1.16	18.0	2.20
21.0	1.24	22.0	2.47
26.0	1.51	27.0	2.64
34.0	1.57	35.0	2.90
41.0	1.68	42.0	3.14
63.0	2.21	64,0	3.70
100.0	2.56	100.0	4.02
176.0	3.20	172.0	4.47

Sample 14.

Heartwood. Thickness .. 9.5 mm.

Both transverse ends open.

2.5	0.61
7.0	2.39
14.0	2.70
18.0	3.30
26.0	3.80
33.0	4.10
46.0	4.40
65.0	4.96
91.0	4.96
160.0	5.21

Sample 17.

Sapwood. 6.5 mm. Thickness.

Both tangential ends open.

5.0	1.36
9.0	1.46
13.0	1.79
16.0	1.88
20.0	2.05
24.0	2.31
35.0	2.48
44.0	2.74
55.0	2.82
73.0	3.16
128.0	3.50
2.30	3.68

Table XXXV. (cont.)

RADIAL PENETRATION.

Sample 12. Sample 16.

Sapwood. Radial thickness . .6.5 mm. Heartwood.

T. (min).	S (%).	T. (min)	S. (%)
3.0	0.57	3.0	0.34
7.0	0.76	8.0	0.34
13.0	0.95	19.0	0.46
19.0	1.03	28.0	0.46
25.0	1.39	44.0	0.86
39.0	1.65	53.0	0.91
54.0	1.77	73.0	1.26
78.0	1.96	127.0	1.43
167.0	2.73	230.0	1.77
234.0	2.85		
360.0	3.30		

Sapwood. Sample 23 Heartwood Sample 22.

Radial Thickness 5.0 mm.

2.0	0.33	1.0	.034
4.5	0.41	5.0	0.34
10.0	0.61	10.0	0.46
23.0	0.94	20.0	0.58
49.0	1.47	48.0	0.76
83.0	2.08	82.0	1.04
124.0	2.63	124.0	1.15

TABLE XXXVI.

Rate of establishment of equilibrium and penetration.

Spruce (B).

Temperature of thermostat . . . . 23° C.

Vapor pressure in apparatus . . . . 4.58 mm. Hg.

Sample 1b. 1.5 mm.

Heartwood.

T. (min)	S. (%)
15.	1.26
4.0	3.00
7.0	3.56
10.0	3.87
13.0	4.03
16.3	4.27
19.0	4.32
23.0	4.32

Sample 2b. 1.5 mm.

Sapwood.

T. (min)	S. (%)
2.0	1.69
5.0	3.59
8.0	4.1
11.0	4.54
14.0	4.77
17.0	5.00
20.0	5.07
24.0	5.07

Sample 3b. 1.5.m

Sapwood,

T. (min)	S (%)
3.0	2.36
6.0	3.41
9.0	3.95
12.0	4.57
15.0	4.73
18.0	4.96
21.0	5.08
25.0	5.08

Sample 4b. Heartwood.

Both transverse ends open

- Thickness 5.0 mm. -

1.5	1.02
3.0	1.68
5.0	2.41
7.0	2.93

Sample 5b Sapwood.

Both transverse ends open

2.0	1.87
4.0	2.25
6.0	2.87
9.0	3.13

Table XXXVI. (cont.)

T. (Min.)	S. (%)	T. (min.)	S. (%)
10.0	3.13	13.0	3.43
17.0	3.39	16.0	3.75
21.5	3.84	20.0	3.85
24.0	3.90	23.5	3.85
28.5	3.90		

Sample 8b Heartwood		Sample 8b. Sapwood.	
- 9.5 mm thickness. -			
2.0	0.86	1.0	1.34
4.0	1.68	3.0	2.20
6.0	1.91	5.5	2.93
8.0	2.24	7.0	3.45
10.0	2.45	9.0	3.60
13.0	2.79	12.5	4.06
16.0	3.14	15.0	4.32
19.0	3.32	17.0	4.40
23.0	3.35	20.0	4.73
27.0	3.50	24.0	4.80
42.0	4.05	28.0	4.86
59.5	4.45	41.0	4.92
160.0	5.00	60.0	5.02
240.0	5.00	160.0	5.07
		241.0	5.07

TABLE XXXVII.

Rate of establishment of equilibrium and penetration.

Jack-pine.

Vapor pressure of water . . . . 4.58 mm. Hg.

Temperature of thermostat . . . . 23^0 C.

Sample 1j.		Sample 2j.		Sample 3j.	
-- Thickness 1.5 mm. --				--	
Heartwood.		Sapwood		Sapwood.	
T. (min)	S. (%).	T. (min)	S. (%).	T. (min)	S. (%)
2.0	2.48	2.5	2.75	3.0	3.92
4.0	3.62	5.0	3.80	6.0	3.84
7.0	4.23	9.0	4.17	10.0	4.51
11.0	4.89	12.0	4.77	13.0	4.71
14.0	4.96	15.0	4.77	16.0	4.77
17.0	5.08	18.0	4.98	19.0	4.91
20.0	5.08	21.0	5.06	22.0	5.11
23.0	5.15	24.0	5.06	25.0	5.17
26.0	5.30	27.0	5.13	30.0	5.23
41.0	5.56	40.0	5.13	39.0	5.23
52.0	5.81	55.0	5.21	54.0	5.23

Sample 3j Repeat.

1.5	2.19	1.0	2.19
4.0	3.31	4.0	3.45
6.0	3.97	6.0	3.97
10.0	4.37	9.0	4.31

Table XXXVII. (cont).

T. (min)	S. (%)	T. (min)	S. (%)
12.0	4.44	12.0	4.44
15.0	4.71	15.0	4.56
19.5	4.85	18.5	4.83
26.0	5.10	22.0	4.84
33.0	5.10	26.0	4.84

Sample 4j. Heartwood

5.0 mm. Thickness.

One transverse end open.		Both transverse ends open.	
2.0	0.61	2.0	1.97
4.5	1.28	5.0	2.87
7.0	1.59	8.0	3.33
8.0	1.66	11.0	3.93
10.0	1.74	14.0	3.93
13.0	1.96	19.0	4.53
16.0	2.19	25.0	4.61
19.0	2.42	31.0	5.22
27.0	2.95	38.0	5.30
42.0	3.17	60.0	5.3
51.0	3.32		
140.0	3.86		

Table XXXVII. (cont.)

Sample 5j.

Sapwood. Transverse thickness .... 5.0 mm.

One transverse end open.

T. (min)	S. (%)
3.0	1.82
5.0	2.61
8.5	3.07
11.0	3.46
14.0	3.75
17.0	3.81
20.0	3.91
35.0	4.31
43.0	4.57
140.0	5.05

Both transverse ends open.

T. (min)	S. (%).
3.0	2.04
5.5	2.72
9.0	3.69
13.0	3.86
18.0	4.08
23.5	4.26
30.0	4.83
55.0	5.05~~1~~
60.0	5.05

Sample 8j. Transverse thickness .. 9.5 mm.

Heartwood.

One transverse end open.

1.0	0.1
3.0	0.15
6.0	0.30
9.0	0.66
12.0	~~0~~0.81
16.0	0.91

Both transverse ends open.

1.0	0.35
4.0	0.96
7.0	1.21
10.0	1.43
13.0	1.78
16.0	1.92

Table XXXVII. (cont.)

T. (min)	S. (%)	T, (min)	S. (%)
20.0	0.91	19.0	1.92
27.0	1.01	22.0	2.07
32.0	1.16	26.0	2.27
42.0	1.16	31.0	2.33
54.0	1.36	37.0	2.48
76.0	1.72	50.0	2.58

Sapwood.
Sample 9j. Transverse thickness . . . . 9.5 mm.

One transverse end open.		Both transverse ends open.	
1.5	1.14	2.0	0.98
4.0	1.88	5.0	2.05
7.0	2.54	8.0	2.79
10.0	2.70	11.0	3.28
13.0	3.36	14.0	3.61
17.5	3.77	20.0	3.69
21.0	4.02	23.0	4.03
28.0	4.26	27.0	4.10
33.0	4.51	32.0	4.26
43.0	4.76	38.0	4.43
55.0	4.92	51.0	4.58
77.0	5.07		

Table XXXVII. (cont.)

Sample 14j Heartwood.

Transverse thickness . . . . 14.0 mm.

One transverse end open.		Both transverse ends open.	
T. (min).	S. (%)	T. (min).	S. (%).
3.0	0.55	2.0	0.45
6.0	0.55	4.5	0.83
11.0	0.78	7.0	0.92
16.0	0.87	11.0	0.97
24.0	0.87	15.0	1.06
34.0	0.97	19.0	1.06
45.0	1.10	24.0	1.24
60.0	1.20	31.0	1.38
180.0	1.56	42.0	1.56
		57.0	1.64
		75.0	1.64

Sample 15j Sapwood.

Transverse thickness . . . . 14.0 mm.

One transverse end open.		Both transverse ends open.	
2.0	1.61	1.0	1162
5.0	2.18	5.0	3.15
9.0	2.99	8.0	3.79
14.0	3.63	12.0	4.04
210	3.79	16.0	4.27
32.0	4.27	21.0	4.61

Table XXXVII. (cont.)

T. (min)	S. (%).	T. (min).	S. (%).
44.0	4.52	26.0	4.77
59.0	4.61	41.0	4.93
180.0	4.61	58.0	5.08

RADIAL PENETRATION. Thickness in radial direction . 6.5 mm

Sample 16. Heartwood.

3.0	0.82
6.0	0.87
13.0	0.94
18.0	1.05
21.0	1.11
30.0	1.11
40.0	1.23
59.0	1.35
75.0	1.35

Sample 10. Sapwood.

3.0	0.68
6.0	1.31
9.0	1.81
12.0	2.00
21.0	2.56
24.0	2.81
28.0	2.87
33.0	3.05
40.0	3.43
52.0	3.61

TABLE XXXVIII.

Rate of establishment of equilibrium at higher vapor pressures.

Sample 10 — Cotton cellulose.

4.8 mm. thickness.

Temperature of thermostat , 23°C.

Vapor pressure in apparatus 18.10 mm. Hg.

T. (min)	S. (%)	T. (min)	S. (%)
2.0	3.78	1.0	1.90
5.0	4.00	4.0	5.06
7.0	6.38	7.0	6.13
11.0	7.30	10.0	6.75
15.0	8.43	14.0	7.35
18.0	9.03	21.0	7.60
22.0	9.75	26.0	7.83
27.0	10.40	30.0	8.00
32.0	11.10	46.0	8.18
47.0	12.40	65.0	8.18
67.0	13.50.	161.0	8.76
162.0	15.60	196.0	8.76
195.0	15.85	196.0	8.76
300.0	16.35	300.0	8.76
Final	16.42	Final	8.76

Thermostat at ....29° C.

Sample 7. Heartwood.		Sample 6. Sapwood.		Cotton Cellulose.	
6.0	8.48	4.0	7.05	2.0	3.84
10.0	9.12	9.0	8.77	8.0	5.72

Table XXVIII(cont.)

T. (min)	S. (%)	T. (min).	S. (%)	T. (min)	S. (%).
13.0	9.79	12.0	10.21	12.0	6.26
17.0	10.60	16.0	10.58	16.0	6.80
24.0	10.95	22.0	10.91	21.0	6.65
28.0	11.20	27.0	11.52	25.0	6.65
33.0	11.45	32.0	12.02	30.0	6.65
40.0	11.70	37.0	12.11	40.0	6.65
49.0	11.70	45.0	12.30	60.0	6.65
62.0	12.20	60.0	12.68	Final	6.65
74.0	12.50	75.0	12.68		
84.0	12.50				

Miscellaneous.

Ashless filter paper.

1.0	1.30
5.0	2.06
7.0	2.73
9.0	3.05
12.0	3.11
15.0	3.11
Final	3.11

Lignin.

Glycol extracted.

4.0	1.82
9.0	1.98
15.0	2.12
27.0	2.12
34.0	2.12
47.0	2.12
Final	2.12

DISCUSSION OF RESULTS.

A discussion of the experimental results may fall into two sections:

Part I. which deals with the adsorption of water by wood purely from the point of view of the gas-solid interface. Such a discussion will bear on the colloidal nature of wood and cellulose and will consider the ultra-microscopic structure of the cell wall.

Part II. which deals rather with the larger structure which may be viewed under the microscope. Samples of wood are examined with a view of finding the rate at which vapors will pass through the internal structure.

PART I.

A. Moisture Equilibria of Spruce Wood (picea canadensis)

The equilibrium values for various samples of spruce wood determined throughout a considerable range of temperature and pressure are found in tables I to XXII. The values are reproducible within the range of experimental error, and remarkable regularity exists between the equilibrium values of different samples of the same species. In all cases a hysteresis effect is found the value attained by the adsorption of water from a drier state being lower than that obtained by the loss of water. It is, however, possible to obtain a result which may be regarded as the true equilibrium value at any given vapor pressure.

Variation of Adsorption with Vapor Pressure.

The typical graph connecting adsorption with vapor pressure is indicated in Fig. 5. (D) These values were obtained during an examination of wood meal (table XVIII) at a temperature of 23°C. The values for adsorption and desorption are both indicated but for reasons to be stated later the lower curve is regarded as the true adsorption isotherm. This smooth s-shaped curve is typical of the adsorption of a vapor which is condensible to a liquid which wets the adsorbent. There are three regions which may be mentioned. The first 1 - 2% of water is apparently very highly adsorbed causing a correspondingly low vapor pressure, which brings about a flattening of the curve near the origin. From an adsorption of 2% to 10% the curve follows practically a straight line indicating that adsorption is practically proportional to pressure in this region. As the saturation pressure is approached the curve again flattens out becoming asymptotic to the axis of adsorption. In this region a small increase

86. A

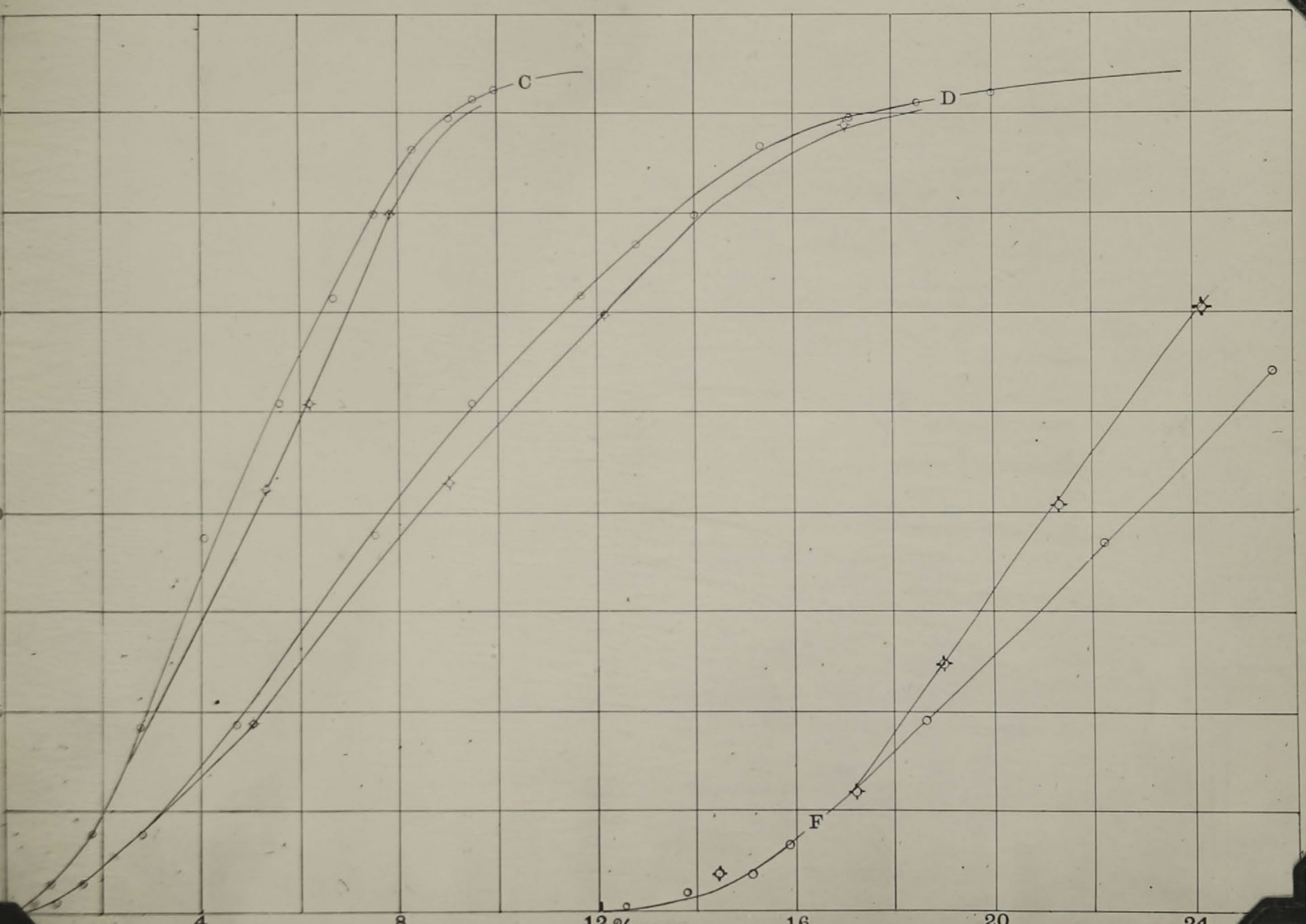

Fig. 5.

Adsorption Isothermals of Spruce and cellulose.

in pressure brings about a very large increase in adsorption, that is ds/dp becomes infinitely large. The shape of the curve in this region demonstrates the difficulty of obtaining an accurate value for the fibre saturation point; in fact it is seen that no such sharply defined point exists, but rather there is a range of adsorption values exhibiting a vapor pressure approximating that of the saturation pressure. A value has been obtained by careful extrapolation which will serve as a basis of comparison with the work of other investigators.

Fibre saturation point of Spruce wood at 23° = 24%

The difficulty of obtaining a ganeral relation to fit the whole isotherm will be evitent. For a considerable portion of the curve the simple equation of the straight line holds as rigidly as any other, while for the part which is convex to the pressure axis various modifications of the parabolic equation are applicable. These relations would not prove to be of great use so that no attempt to develop them has been made.

The theoretical signifigance of the different portions of the adsorption isotherm will be discussed in a later section.

Variation of Adsorption with Temperature.

In Fig.6 are seen the adsorption isothermals of spruce sapwood between 12° and 42° C. In common with the general case adsorption declines with rise in temperature. At temperatures below that of the room the complete curve is indicated, while at higher temperatures the curves are incomplete, as the method does not allow a vapor pressure corresponding to that of the room temperature to be exceeded.

While adsorption falls off with increase in temperature the vapor pressure required to produce the same relative humidity will also be greater. In fact the increase occurs in the same ratio as the adsorption falls off. This can readily be seen in a qualitative way. The adsorbed water exhibits a vapor pressure which is a constant fraction of that of pure water, so that as temperature is increased the increase in vapor pressure of the adsorbed water is proportionately the same as that of the pure water. Since the vapor pressure of adsorbed water and the amount of adsorption are inversely proportional, the vapor pressure of water will increase in the same ratio as adsorption decreases. Hence it follows that if the relative vapor pressure be kept constant adsorption will be independent of temperature.

Practically it is found that this is not entirely the

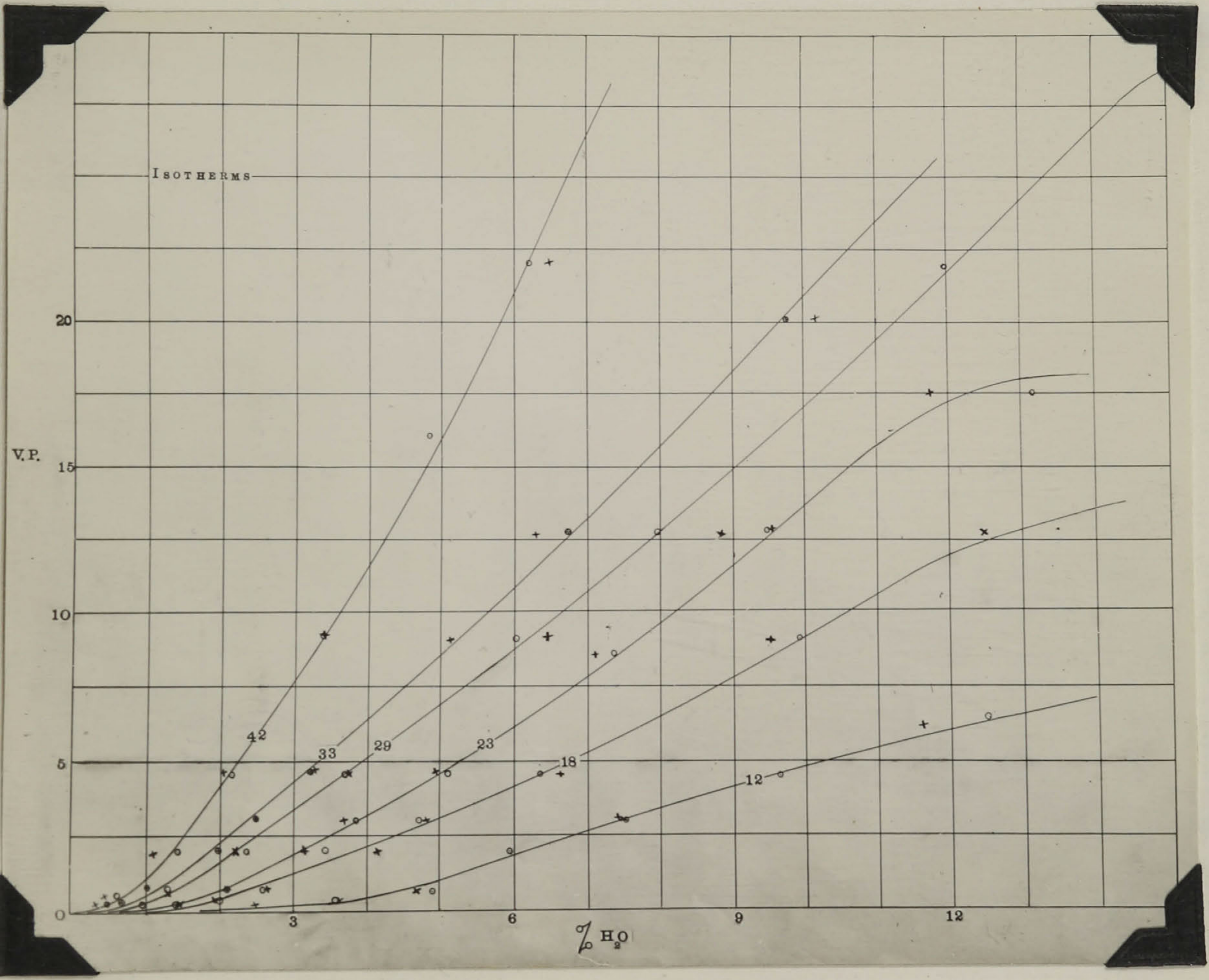

Fig. 6.

Adsorption isotherms of Spruce. (Picea canadensis)

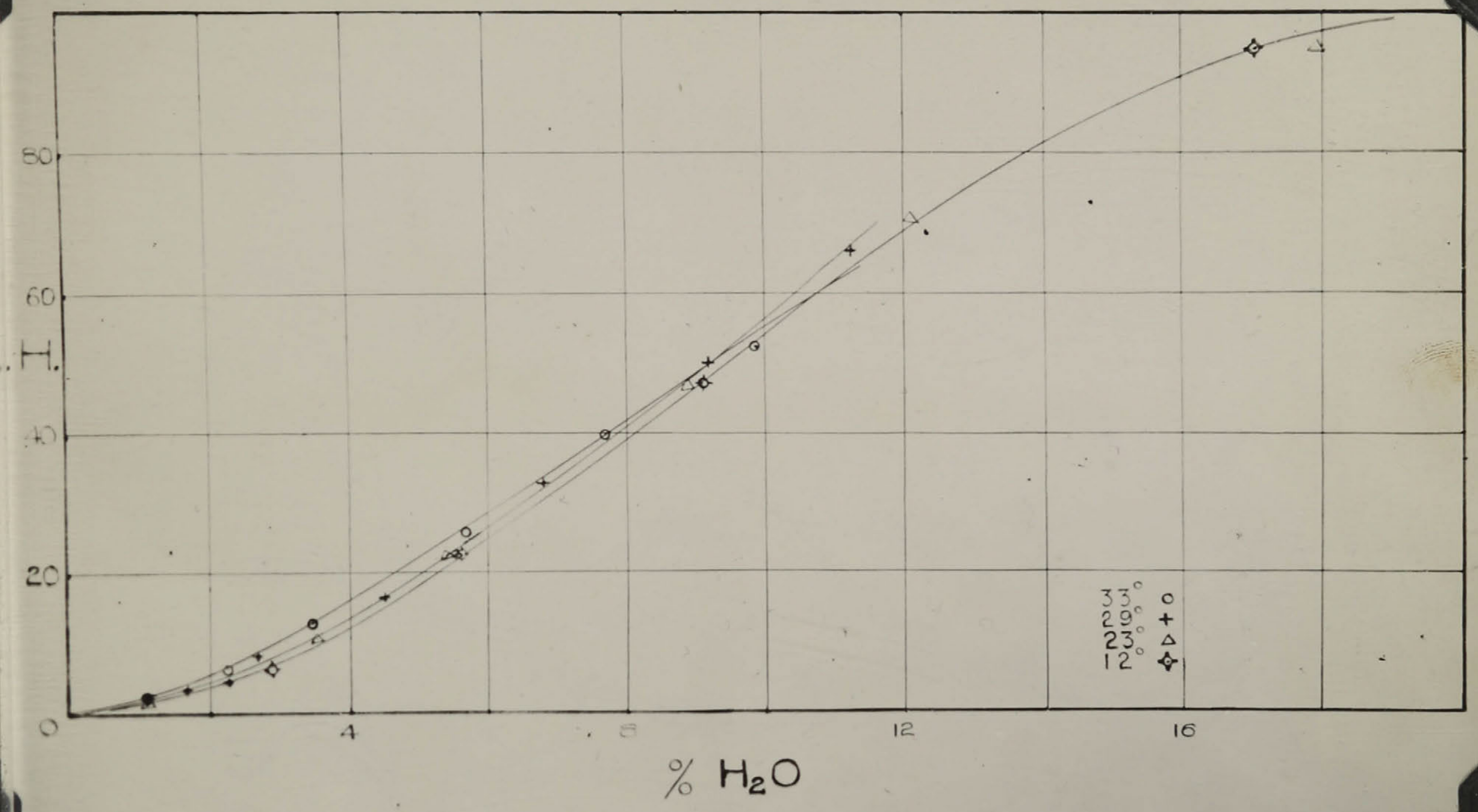

Fig. 7.

Adsorption isotherm.

though nearly so. In Fig.7 the isotherms of Fig.6 have been plotted on the basis of relative vapor pressures in place of the absolute values. It will be seen that the isotherms of lower temperature tend to exhibit excessive adsorption in the vicinity of the origin. In the upper portions, however, there is no difference distinguishable from the experimental error.

Adsorption Isosteres.

If the vapor pressures corresponding to a given amount of adsorption are plotted against the coresponding temperature an adsorption "Isostere" is obtained (Wo. Ostwald), that is a curve wich represents the variation of vapor pressure with temperature for any constant ampunt of adsorbed water. In Fig. 8 isosteres have been plotted for adsorption values from 1% to 8%. From what has been said above it will be evident that these isosteres will be exponential curves similar to the typical vapor pressure curve. If, in place of vapor pressures, the logarithms are plotted against temperature, the resulting graph should be approximately a straight line. In the second part of Fig.8 where this procedure has been adopted, it appears that a straight line is produced for isosteres representing an adsorption value greater than 2%. Below this value the lines are no longer straight

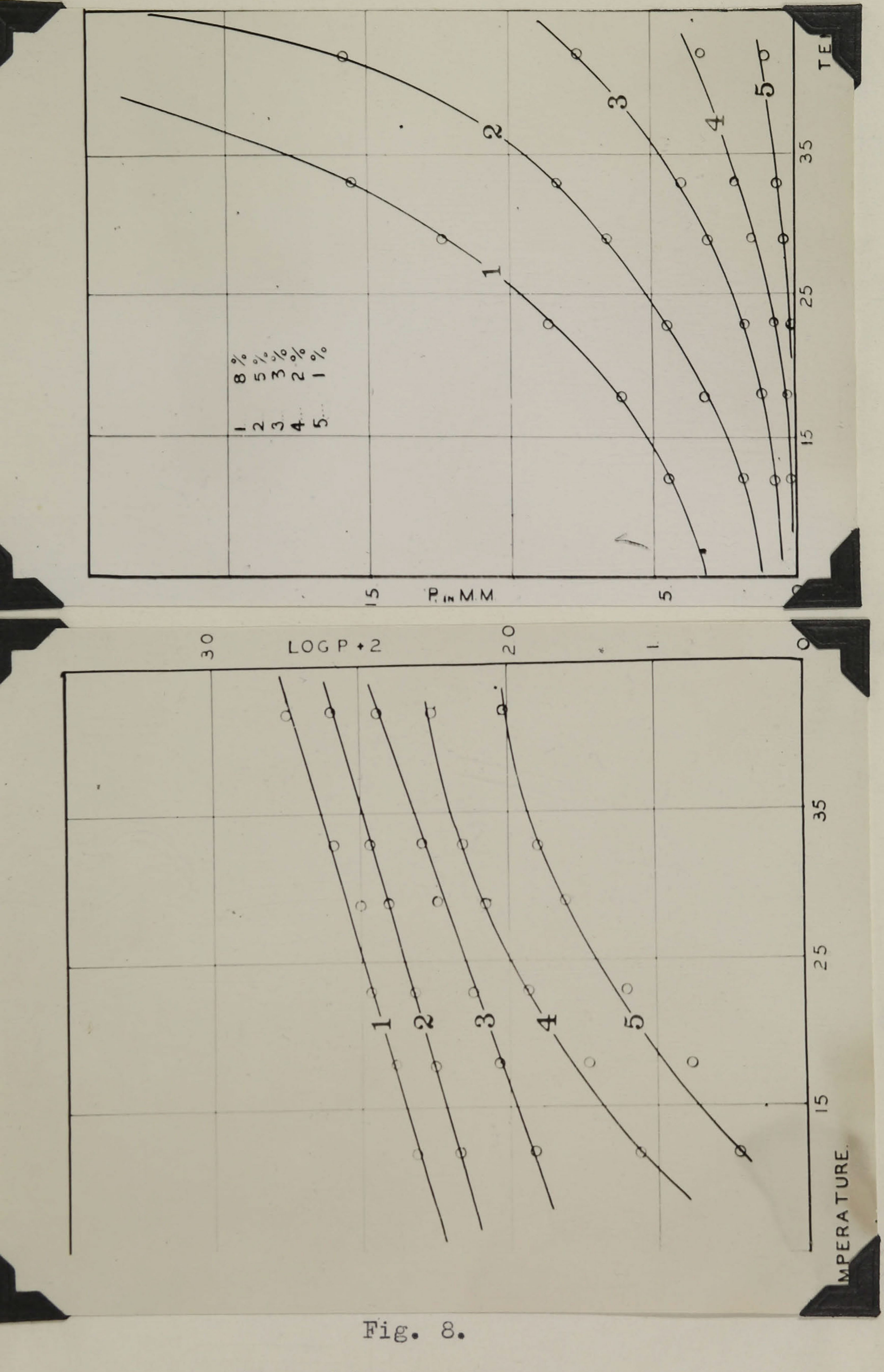

Fig. 8.

Adsorption Isosteres.

become convex to the pressure axis. These isosteres fall in the region where as already mentioned, the adsorption isotherm indicates a discontinuity which is probably caused by the introduction at this point of some additional factor in the mechanism of adsorption. This point will receive further discussion. It would be expected that the adsorption isosteres for values near the saturation point would also exhibit anomalous behaviour but a sufficient number of experimental values in this region are not available.

From purely theoretical reasoning Williams (Ref. 24) has derived an isostere equation of the following form:

$$\log a/c = B + A T$$

where c is the equilibrium concentration outside the adsorbent,
T is the absolute temperature ,
a amount of a sorption,
B and A and functions of a but not of T.

If the concentration c is replaced by p the pressure the equation takes the form-

$$\log a/p = B' + A T$$

Now if a is constant, B' and A are also constant so that if log p is plotted against 1/T the resulting graph should be straight line. The results for spruce when submitted to this procedure give curves similar to those of Fig.8 (right) so that for a considerable range of adsorption they may be expressed by this general equation. The curved isosteres which are obtained at low values of adsorption are probably due to the combination of two effects or forms of adsorption, one of which acts at low relative vapor pressures and which is superseded by the other at higher pressures. If it were possible to obtain a set of isostere values completely in the region of powerful adsorption (which has been referred to above) it is likely that it would follow the equation of Williams.

The independence of the isothermal of temperature may be pointed out by an application of the Clausius-Clapeyron argument.

Let there be a quantity of gas (a) adsorbed by a solid, so large that on the adsorption of further gas the amount present may be taken as unaltered. With (a) a pressure (p) is in equilibrium. At a temperature higher by dt we have the same (a) but at a pressure greater by dp.

Let q_a be the isosteric heat of adsorption
(1 cc. of gas at 1 atmosphere pressure)

If the gas be water vapor and a certain amount evaporates the following relation will hold:-

$$\frac{v_2 - v_1}{w\, q_a}\, dp = \frac{dt}{T}$$

here $v2 - v1$ is the increase in volume when an amount of water (w) evaporates from the adsorbent. According to Boyles law:-

$$w = \frac{p}{p_s} . d_s \ (v_2 - v_1)$$

where p_s and d_s are the pressure and vapor density at the saturation point.

hence:-

$$\frac{dp}{dT} = \frac{p}{p_s} \frac{d_s \ q_a}{T} \quad \ldots\ldots\ldots\ldots\ldots \quad 1)$$

at the saturation pressure $p = p_s$ so that:-

$$\frac{dp}{dT} = \frac{d_s \ q_a}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 2)$$

It is assumed that q_a does not vary with the amount of water taken up (the heat of adsorption varies greatly when the amount of adsorption is small but little when adsorption is high).

from 2) and 1)

$$\frac{dp}{dT} = \frac{p}{p_s} \frac{dp_s}{dT}$$

Integration of this form brings out the fact that p/p_s is a constant. That is for a given adsorption the vapor pressure at various temperatures is a constant fraction of the saturation pressure, which is a re-statement of the fact that adsorption is independent of temperature and is a function only of relative vapor pressure.

Isobars.

Isobars may be plotted in a manner similar to the isosteres. The amounts adsorbed at some constant vapor pressure for various temperatures are plotted. These curves are of course identical in character to the isosteres being simply the converse form.

Effect of Heartwood and Sapwood on Adsorption.

A careful examination of the adsorption of water by heartwood and sapwood has been made as will be seen in the tables of results. It seems, however, that while the rate of penetration of the two woods may be very different their adsorption isothermals are identical. The following are equilibrium values of heartwood and sapwood examined concurrently under the same conditions of pressure and temperature.

V.P.	.29	.77	1.95	3.01	4.58	6.54
Sample						
# 2 S.	1.37	1.45	2.49	2.98	3.75	4.95
#3# H.	.85	1.28	2.55	3.00	4.10	4.83

V.P.	.29	.77	1.95	3.01	4.58	6.54
Sample						
# 4 S	1.29	1.45	1.79	3.01	3.43	4.62
# 5 H	.80	1.27	2.17	2.43	3.44	4.35
# 6 S	.67	1.04	2.00	2.48	3.34	4.28
# 7 H	1.04	1.56	2.25	2.95	3.22	4.25

It will be seen that while agreement is poor in the initial values, at higher pressures the results are quite similar, considering the accuracy obtainable in adsorption measurements by gravimetric methods.

In Figure 6, the values for heartwood have been plotted and it is evident that no general trend from the curve as drawn for sapwood exists. It would seem then, that whatever changes occur in the transformation of sapwood into heartwood they do not materially affect the moisture equiibrium, hence all discussion will apply indiscriminately to heartwood or sapwood.

Effect Of Natural Drying:

Spruce sample (B) was obtained from a log which had been exposed for some time (at least 1 year) on a pile in the open The results of these measurements are listed in table XXII, a few of which are reproduced be low for purposes of comparison.

Temperature of thermostat.......... .... 23° C.

V.P.	Spruce (A)	Spruce (B).
4.58	5.07	5.07
9.21	9.77	6.89
12.78	11.83	9.35

It seem that at lower pressures there is no difference between the two woods while at higher pressures the air dried sample shows much lower adsorption, and it may be presumed that the final saturation value would be much lower. This may be almost stated as a general rule, that if differences in adsorption are found they will be greatest in the vicinity of the saturation point. (see Fig. 9 Spruce and Jack-pine.)

The effect of long continued drying is to lower the value attained on adsorption, this is exemplified in the case of pine, (sample 3j, table XXXVII) The sample was dried after which it was exposed to a vapor pressure

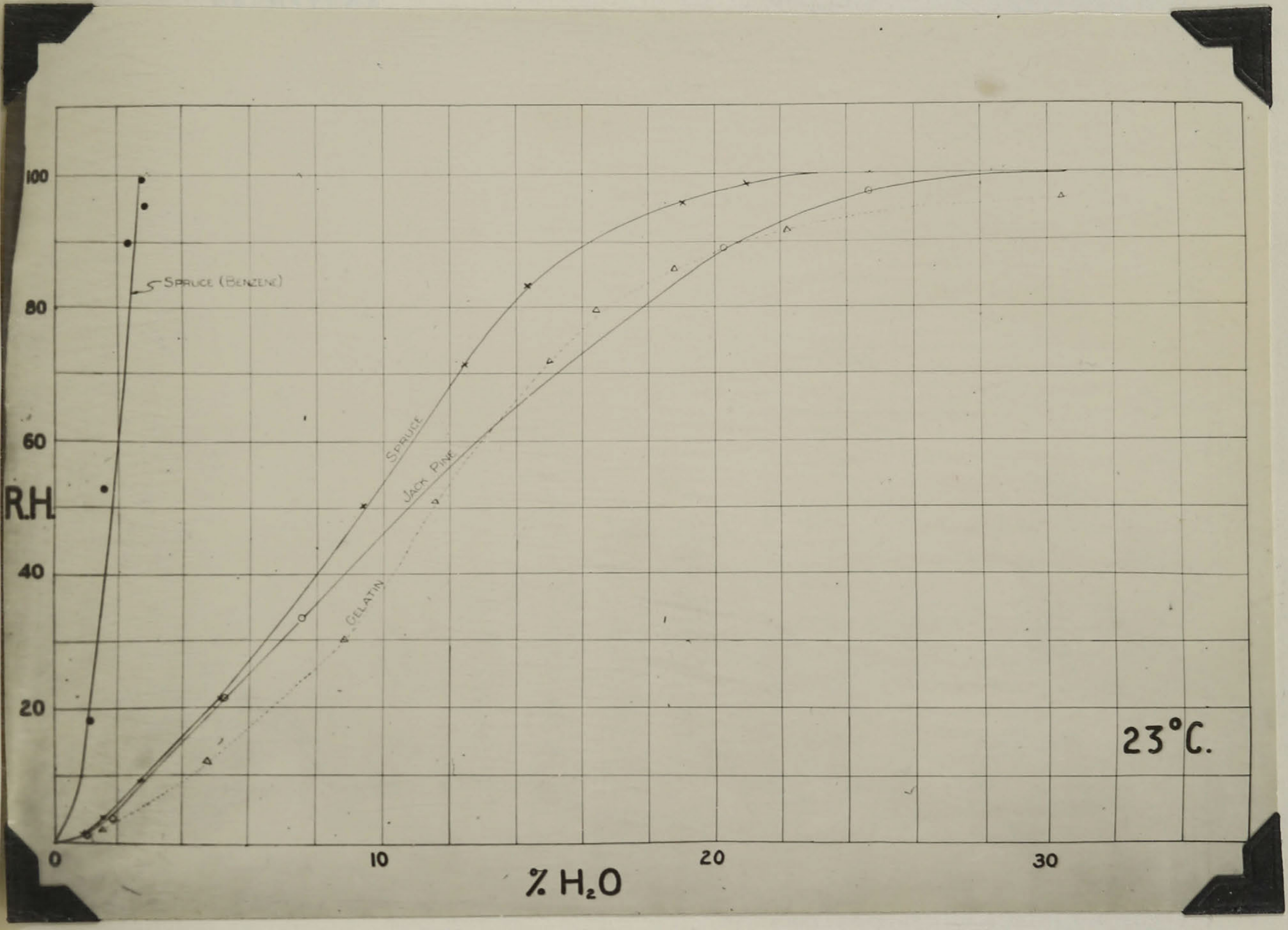

Fig. 9.

Adsorption isotherms of Spruce and Pine.

of 4.58 mm. Hg. After the establishment of equilibrium the sample was again thoroughly dried and the process repeated. If this is is done several times the equilibrium value attained between each drying slowly diminishes in magnitude.

1st. adsorption	. . . . . 5.23%
2nd. "	. . . . . 5.10%
3rd. "	. . . . . 4.84%

If, however, at any time a very high adsorption takes place, such as near the fibre saturation point, the sample seems to be restored to its original condition. A list follows of the saturation values of Spruce sample 2. at 33°C and a pressure of 4.58 mm. Hg. Between the determinations at these stated conditions, the samples were both dried and thens subjected to higher vapor pressures. It will be seen that in this case there is no reduction in the amount of adsorption.

1.	2.	3.	4.
3.45%	3.45%	3.61%	3.49%

Moisture Equilibria of Jack Pine . (Pinus banxiana)

The equilibrium values for pine have been determined at 23° (table XXIII) . Heartwood and sapwood have been examined the values for the former being considerably higher at low humidities. This effect is considerably more marked than in the case of spruce as the following table will show.

R.H.	Heart.	Sap.
1.40	1.02	0.98
3.67	2.14	2.05
9.26	3.28	2.83
21.72	6.23	5.21
33.43	7.43	7.60
50.31	9.38	9.16
90.35	18.70	20.35
97.20	24.60	24.60

This behaviour is rather unusual as the greatest differences are ordinarily exhibited near the saturation point.

In Fig. 9 the complete isotherm for pine sapwood is shown together with that of of spruce. It will be seen that pine posseses a much higher saturation value than spruce while in the initial stages the two curves are identical. It has already been mentioned that this is probably the typical behaviour of many woods, as it is in this region that condensation is taking place in the larger capillaries of the wood which will vary considerably between different species. The lower part of the curve deals more with true adsorption and since it is probable that the fundamental wood substance is the same in all species, the curves in this region will tend to co-incide. Thus the wide variation in fibre saturation points which have been found by various investigators may be simply the upper end of adsorption isothermals which would be similar at lower vapor pressures.

An hysteresis effect was found as in the case of spruce and cotton cellulose but in every case, the true equilibrium was taken as represented by the desorption value.

The fibre saturation point as found by extrapolation of the adsorption isothermal at 23°C. is

Moisture Equilibria of Cotton Cellulose.

A complete survey of the equilibrium values for standard cotton cellulose hae been made (tables XXV and XXVI) a sample being examined concurrently with spruce sapwood and heartwood (#6 and #7) The adsorption isothermal for cellulose follows the same general form as that of wood, but the amount of adsorption is much less. In Fig. 5 (C) the isotherm at 23° C. has been plotted with that of spruce. At all vapor pressures the value for cellulose is approximately two thirds that of wood (average of 6 determinations is.61) In the same manner as wood the adsorption by cellulose is independent of temperature.

The value obtained for the saturation point by extrapolation of the isothermal at 23°C. is 11·3%

There are several possible explanations of the lower values for cotton cellulose. If we assume that the cellulose in wood behaves in a similar way to the cotton cellulose it follows that the non-cellulose parts of wood are responsible for the increased adsorption. consider the case of coniferous wood containing 42% cellulose and attribute to this part an adsorption equivalent to that of cotton cellulose; it is then possible to calculate the amount of water adsorbed by the constituents other than cellulose. The values so obtained are indicated in the following table.

P.	Cotton.	Wood	Non-cell.	Extracted cell.
1.0	1.18	1.70	3.10	2.50
2.5	1.85	2.58	5.00	4.05
5.0	2.75	3.95	7.55	5.70
7.5	3.58	5.15	9.90	7.32

It will be seen that the values obtained are considerably in excess of those of wood. In an attempt to directly measure the adsorption of some other wood constituents. lignin was examined. This constituent comprises about 25 to 35% of the wood substance. It was extracted by a method developed in the Dept. of Cellulose Chemistry of this university employing ethylene glycol as the solvent. The value obtained for this substance at 4.5 mm. pressure and a temperature of 23°C, is 2.12% (Table XXXVIII) The corresponding value for wood is 5.07% so the increase in adsorption cannot be due to lignin. Aside from lignin and cellulose the remaining constituents of wood are the hemicelluloses and certain soluble carbohydrates and resins. It does not seem probable that these substances will show excessive adsorption so it seems that the difference can not be attributed to the non-cellulose portions of wood.

The natural conclusion is that the difference is due to something inherent in the two types of cellulose. Cellulose was extracted from wood by chlorination followed by treatment with sodium sulphate. The values obtained are indicated in table XXVII and are partly reproduced above for comparative purposes. It will be seen that the values are considerably higher than for wood and are, in fact, of the same order of magnitude as the values calculated from the difference between wood and cotton cellulose. This fact makes available another explanation.

The cellulose obtained from wood by removal of the lignin by chlorination is commonly differentiated into three types.

Alpha cellulose	insoluble in 17.5% alkali.
Beta cellulose	soluble in the above but re-precipitated by acetic acid.

Gama cellulose Soluble un alkali but not repprecipitated by the addition of acid

Cotton cellulose is considered to be largely alpha cellulose. It may well be that the beta and gama celluloses have a much greater affinity for water than the alpha cellulose which would at once account for the higher adsorption of wood and of extracted cellulose. The solubility of these two forms in alkali lends favorable evidence to this idea.

There remains the possibility that the increased value for wood is due to a more complex ultra-microscopic structure which causes capillary condensation at lower vapor pressures. It is known that cotton belongs to the class of gels possesing very coarse capillaries so that the amount of water taken up would be largely done so by true adsorption or absorption and capillary condensation would play no part. This does not, however, accord so well with the observed results as it fails to explain the increases adsorption of extracted cellulose and also if this were the case it would be expected that in the lower regions the adsorption isothermals for wood and cotton would co-incide. As this does not take place at any point it points to the previous suggestion of a difference in chemical attraction rather than a physical difference in structure.

Summary of Results of the Fibre Saturation Point.

Saturation points obtained by extrapolation of Adsorption isothermals at 23° C. Results expressed as percent of dry weight of wood (subject to restrictions of p.)

Cotton cellulose	11.8
Spruce sapwood	24.0
Jack pine sapwood	31.0

The literature does not contain reference to any previous determinations of the fibre saturation point of these particular species of wood which are typically Canadian woods. For purposes of comparison several other species are represented below together with the name of the method by which the point was determined.

Sitka spruce.	Moisture content	30.5
"	Shrinkage	28.0
"	Modulus of rupture	27.0
"	Electrical conductivity	29.0
Redwood	" "	30.5
" extracted	" "	31.0

The values for electrical conductivity are due to Stamm and have appeared in the [illegible] Journal of Industrial and Engineering Chemistry April 15, 1929. The value for extracted wood are interesting and may be compared with the value obtained for extracted cellulose in this research . . . . 11·8 %

The most accurate determination of the saturation point for cotton cellulose has been made by Urquhart and Williams (ref 28)

Soda boiled Cotton 22.4%

It will be noticed that this value is greatly in excess of those obtained in the present research. This is no doubt due to the presence of condensed water which these investigators admitted to be visible in their apparatus at the saturation point.

ANALYSIS OF ADSORPTION ISOTHERMS.

The behaviour of gels during the adsorption of gases or vapors divides them roughly into two classes, non-swelling and swelling. In Fig.9 a comparison has been made between the adsorption isothermal of wood and of gelatin, which may be taken as a typical swelling gel. The similarity in general character is at once apparent. The wood substance may be considered as a swelling or elastic gel. The adsorption of water is then completely reversible, as the gel dries the process occurs smoothly without any discontinuities as are found in non-elastic gels, (like the opacity point of a silicic acid gel) the gel finally dries to a hard solid.

A description of the most commonly accepted theory of gel structure will afford a picture by which the phenomenon of adsorption may be explained. It is generally assumed that gels possess a heterogeneous structure, a network of ultra-microscopic capillaries separates the actual particles of the gel. In the case of a gel which is saturated with water these capillaries are filled with liquid, as the gel dries the liquid is removed from these spaces. In the case of non-elastic gels the particles, or micells as they are termed, experience irreversible changes by which they become progressively more rigid and less hydrophylic, hence upon drying a limit is reached at which they are too rigid to close up further and open capillary spaces are left. Upon being again brought into contact with water they only take ~~up~~it up in so far as they fill the capillary spaces without the micells, which have become coarser and more rigid, being again subdivided and the gel softened anew. In the case of swelling gels, on the other hand, the micells do not lose their power of taking up liquid reversibly. That is, when they are packed closely together on drying, the walls remain suple and the micells do not become coarser and lose their identity. When liquid is added again they now move apart to their original condition causing the whole gel to swell.

The adsorption of water by follows this behaviour closely, The micells may be the cellulose molecules themselves, or more probably agregates of these molecules. (Herzog, by x ray measurements has calculated the volume of the cellulose molecule as .68 Mu^3, while micellular particles are generally many times this value.) The micells are probably orientated in the cellulose fibres as swelling is much greater in the longitudinal than in any other direction.

The dry wood is then a highly dessicated colloidal gel consisting of an aggregate of minute particles held together by their mutual attraction. Owing to the fineness of the micells the surface area will be large compared to the volume (Stamm (Ref. 13) calculates the surface per gram of wood substance as 310,000 sq. cm.) On this surface the vapor is first adsorbed, the pressure exerted by the water molecules being less than the saturation value by virtue of the attraction between water molecule and [illegible] micell. The amount of water required to saturate this surface will be taken up rapidly by the process of true adsorption of a gas on a solid, and for any given vapor pressure the equilibrium adsorption value may be attained in either direction, that is, there is no hysteresis effect. This is well shown, in the case of wood, by the shape of the adsorption isotherm near the origin. The first 1 to 2% of water is taken up reversibly and at a reduced vapor pressure (see Fig 5 F.) causing a flattening of the curve in this region.

As more water is added eventually the opposing surfaces will unite to form a column of water in a capillary, the pressure at which this takes place will depend on the diameter, the largest capillaries being the last to fill. In this part of the curve there is essentially a free water surface, the vapor pressure of which is governed by the radius of curvature. As more water is added, it would be expected that the vapor pressure would remain practically constant until the capillaries were filled, any increase in vapor pressure being due to the filling of a larger capillary. This is the case for a non-swelling gel where the walls are rigid, but as wood belongs to the elastic class the walls of the capillaries move apart causing an increase in the radius of curvature of the surface. Hence vapor pressure increases with adsorption, and from the curves it will be seen that this takes place in a linear fashion.

As the vapor pressure approaches the saturation point, a very small lowering will be sufficient to cause liquid condensation. Hence it is conceivable that at this point the larger pores in the wood, such as are microscopically visible, are becoming filled with water. In this way very small changes in vapor pressure will entail great changes in adsorption and the isothermal which expresses this will flatten out near the saturation point.

Thus it will be seen that this picture of the colloidal nature of wood affords a plausible theoretical explanation of the observed facts. The reason why the adsorption isothermals of different woods often co-incide in the lower parts of the curve is at once apparent, for the taking up of water in this region depends on the fine invisible structure of the wood substance, which is probably fairly constant between different species. Condensation near the saturation point will probable . be occuring in the lumina of the fibres themselves the diameter of which varies widely

Further evidence in favor of this view is adduced from a consideration of the rates of adsorption at different relative vapor pressures . If dry wood adsorbs water at a vapor pressure of .1 mm. Hg, the time required for the establishment of equilibrium is approximately nine minutes. This value is of the order of magnitude comparable with usual rates of adsorption which seldom exceed several minutes. The longer time in the case of wood is probably due to some absorption which takes place together with the adsorption.

Along the straight portion of the adsorption isothermal the time required for the establishment of equilibrium is approximately the same, showing a value of 20 minutes which increases slightly at higher vapor pressures. According to the idea submitted above the increased time over the case for pure adsorption will be due to the time required to fill the capillary spaces between the micells of the wood. This time will be proportional to the rate of condensation and the rate at which the vapor diffuses to the condensing surface.

For the upper part of the curve, near the saturation point, the time required is very great, the establishment of equilibrium being incomplete even after the elapse of three hours. This is again due to the time required to fill the larger capillaries, and the time required for gaseous diffusion. This latter factor is probably a very considerable one near the saturation point as approximately 20 litres of vapor at the temperature and pressure of the experiment are required to saturate one gram of wood. (500 volumes at N.T.P.)

The rates which have been discussed above are listed in the following table:

Results for spruce sapwood.

T.. 33°C.

V.P. .105 mm.

TIME.	S
1.0	.14
3.5	.14
9.0	.28
Final	.28

T .... 33°C

V.P. 4.58 mm.

TIME	S
1.5	1.23
4.5	1.47
8.5	2.35
14.5	3.06
21.5	3.19
Final	3.19

T ... 23°C.

V.P. 18.11 mm.

TIME	S
2.0	3.78
7.0	6.3
15.0	8.4
32.0	11.1
67.0	13.5
162.0	15.6
195.0	15.85
300.0	16.35
Final	16.42

It is convenient at this point to mention the rates of establishment of equilibrium of cotton cellulose. A survey of table XXXIII will indicate that the time for cotton is very similar to that of wood about 20 minutes. In table XXXVIII, however, a different behaviour is manifested In this experiment, which was performed at a vapor pressure of 22 mm. Hg, the cotton cellulose reached equilibrium in 21 minutes, while the wood, in common with behaviour indicated above, required 75 minutes. It is possible that cotton has a more uniform inter-micellular structure so that the time required to fill them is the same at different vapor pressures.

Size of Inter-micellular Capillaries.

If it is assumed that the pressure of the system is controlled by the curvature of water surfaces in capillaries, the pressure at any point depends on the corresponding diameter of the capillaries. Thus by the use of the formula connecting lowering of vapor pressure with curvature of surface, it should be possible to calculate the size of the capillaries.

The appropriate formula is obtained as follows:-

The expression invovling darius of curvature, surface tension and rise in a capillary is,

$$\lambda = \frac{\rho g r}{2} (h + 1/3 r) \; . \; . \; . \; . \; 1)$$

where h is the height,

r is the radius of curvature

λ is the surface tension,

ρ is the density, and

g is the gravity constant

When r is very small, h is corresponding large, so that in the expression (h 1/3r) 1/3 r may be neglected, hence

$$\lambda = \frac{g r h}{2} \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; 2)$$

The relation connecting reduction of vapor pressure with height is:

$$\log \frac{p_o}{p_h} = \frac{M\,h}{1000.1033\;R\;T} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; 3)$$

By a combination of (2) and (3) the following expression is obtained:

$$r = \frac{M\;2\,\lambda}{\rho\;g\;1000\;.\;1033\;R\;T\;\log\;{}^{p_o}/_{p_h}} \quad . \; . \; . \; . \; . \; . \; . \; . \; 4)$$

In which p_o is the pressure at $h = 0$ in this case corresponding to the saturation pressure p_s .

p_h is the pressure at height h, in this case the vapor pressure coresponding to a radius of curvature r.

M, R, and T, have their usual signifigance.

It is customary to assume that the surface tension is the same as that of the liquid in bulk, whereas for the thin films under consideration this is probably not the case. However, making this assumption we may find that theoretical radius of the capillaries at different stages in the swelling process.

Values for Spruce are as follows:-

Adsorption.	Vap. Press.	r.
2.30 %	1.6 mm. Hg.	4.5×10^{-8} cms.
8.85 "	10.5 "	16.2×10^{-8} "
20.00 "	20.5 "	381.0×10^{-8} "

The first value is taken at the point at which hysteresis disappears and thus it may be considered as the smallest capillary in the colloidal structure. The diameter corresponding to this radius is 9×10^{-8} cms which represents the distances between two opposing surfaces. of adsorbed water into the smallest pores. At relative vapor pressures smaller than this value the results of the calculation of r become smaller than the size of the molecules themselves, hence it may be assumed that in this region the taking up of water consists of adsorption on the dry walls and not on capillary condensation. For all vapor pressures above this region the radius of curvature increases becoming comparatively very large as the saturation pressure is approached,

Hysteretic Lag Between the Taking Up and Loss of Water.

The appearance of a hysteresis effect has been generally noticed . The relation of the desorption and ~~adsorption~~ adsorption curves to one another is shown in Fig. 5 for spruce and cotton cellulose. The effect is not continued to the origin but disappears at an adsorption of approximately 2.5%. The significance of this fact has already been discussed. The two curves apparently co-incide at the saturation point although this cannot be determined experimentally. Certain cases failed to show this hysteresis effect as will be seen in Fig 10 (p. 112). In this experiment the same value was attained from either direction when the temperature was 33°C. At a lower temperature however an apparent permanent hysteresis was observed. A careful survey of the effect of gain or loss of water has been conducted the results of which are found in tables XVII to XXI . In practically all cases a definite hysteresis was found which decreases as temperature increases. In spite of a few exceptions it must be considered that this phenomenon is a characteristic one and a fundamental explanation must be sought.

A mechanism which is applicable to the case under discussion has been suggested by Zsigmondy (Ref. 3) and was first applied to silicic acid gels. it is assumed that when the walls of the micells have become dried they are less easily wetted. Thus as water is being taken up the radius of curvature of the surface is less then when water is lost in which case the walls of the capillary have already been wetted by the liquid. If this is so, as water is taken up the radius of curvature of the liquid surfaces is greater and hence the vapor pressure is greater for the same content. When water is removed from the sample the walls will be already wet so the true radius of curvature for the capillary tube will be assumed, if the liquid completely wet~~t~~s the solid surfaces, the curvature will be considerably greater causing a lower vapor pressure for the same amount of water taken up. So that wherever the taking up or loss of liquid takes place by the filling or emptying of small capillaries, a hysteresis effect will be noticed.

Applying this picture to the case of wood, for the first 2% it has been pointed out that water is taken up by true adsorption on the large specific surface presented by the wood structure. Accordingly, in this region the adsorption will be completely reversible, a fact which has been found to be experimentally true. For all adsorptions above 2% till near the saturation point pronounced hysteresis is found , this would be expected if the theory of gel structure is accepted, as the taking up of the adsorbate is caused by the filling of capillaries.. Near the saturation point the hysteresis decreases and presumably disappears when the actual saturation point is reached. This is explicable on the grounds that the capillaries which are becoming filled in this region of the curve, are so large that the liguid surfaces which are presented, differ little from a plane surface.

The natural conclusion of the above is that the true equilibrium value for any given vapor pressure will be attained by the loss of water. That is the desorption isotherm is the true one. This idea has been adopted by another investigator, Coolidge, in his work on the adsorption of vapors by charcoal (Ref. 36) noticed a hysteresis effect and considered that the true value was represented by the lower curve, In general, however, the tendency has been to regard the true adsorption value as the mean of the results obtained by loss and gain of the adsorbate.

A rather convincing piece of evidence for the view-point is afforded by the following experiment.

Spruce sapwood. 23° C.

The following steps are passed through:		V.P.	S.
Step 1.	Sample adsorbs water from dry state	4.58MM.	5.36%
" 2.	vapor pressure rises to	20.0 "	10.50%
" 3.	pressure r eturned to	4.58"	6.03%
" 4.	Pressure to zero for 10 minutes .	-	3.80%
" 5.	pressure raised to	4.58"	6.03%

This process is immediately explicable on the grounds of Zsigmondy's theory. When the walls of the micells are very dry, the value attained by the sample at a constant vapor pressure of water is 5.56% . If the pressure is considerably elevated and the adsorption increased to 10%, on returning to the previous pressure the adsorption value will now be 6.03% showing the hysteresis effect, which has been attributed to the fact that the walls of the capillaries are now wet. If now the pressure is lowered to zero and the sample dried for a short time, the value the value obtained on re-exposure to a vapor pressure of 4.58 mm. is found to be identical with that obtained by loss of water namely 6.03%. Hence if the walls of the capillaries have been previously wetted by increasing the adsorption above the expected saturation value, the true value may be reached either by adsorption or by desorption.

The process indicated above constitutes a simple and rapid method of obtaining the true adsorption value for any given vapor pressure. As will be seen in Fig.10 the rate of adsorption is very slow and it is inconvenient to obtain the required values by this method. The following method, based on the theory outlined above, has been used to overcome this difficulty. If it is desired to obtain the amount of adsorption corresponding to a vapor pressure of 5 mm. Hg. The tube (B) (See apparatus) is heated to a temperature corresponding to a much higher vapor pressure, in this way the sample is saturated with water , the tap to the water tube is then closed and the sample is rapidly dried below the expected value. When the sample is again exposed to the required vapor pressure the true equilibrium value will be attained by the adsorption of water in a very short time. This procedure has been followed in the present research.

Adsorption of Condensible Vapors Which do not Wet the Adsorbent.

One case of this type of adsorption has been examined namely benzene and wood. The isothermal so-obtained is plotted in Fig. 9. The amount of adsorption is much less than in the case of water, and a great difference in character is noted near the saturation point. Near a relative vapor pressure of 100% there is no flattening of the curve as in the case of wood. This indicates that in the case of benzene, at no time is condensed liquid present, and the increase in weight is due purely to adsorption of molecules of gaseous benzene on the surface of the wood structure. The form of this isothermal is typical of the case of the adsorption of a gas above its critical temperature, since the liquid does not wet the solid there is no tendency for it to be formed. This case is very interesting for there have been few determinations of the adsorption of a non-wetting liquid. The shape of the curve in the vicinity of the saturation point suggeststhat supersaturation may exist which will be removed only when suitable nuclei for condensation exist.

PART II.

GENERAL

In order to utilize the rate of establishment of equilibrium as a comparative measure of the rate of diffusion of vapors through wood, it is absolutely necessary that the various samples of wood be exposed to a constant vapor pressure in every case. The most convenient way to obtain this is to immerse the water tube in a stirred mixture of melting ice. In order to standardize conditions,all the samples which will be discussed have been examined at 23°C. and at a vapor pressure of 4.58 mm. Hg.

Standard Sample.

Toseparate the effect of thickness on the rate of vapor diffusion, it is necessary to have a standard against which to compare these rates. That is the rate at which a free surface adsorbs water vapor. A longitudinal thickness of 1.5 mm. has been chosen since this is so much less than the average fibre length that every fibre is cut through at least once . It is assumed in such a sample that every surface is accessible to an entering vapor, so that the structure of the wood plays no part in affecting the rate of penetration. In Fig. 10 the rate at which such a sample adsorbs water is shown. It will be seen that the rate at different temperatures is similar , while the rate of loss of water is much slower and tends to increse at lower temperatures. This standard time is much the same with different samples as the following table will show,

Time in minutes, from the dry state to equilibrium at a vapor pressure of 4.58 mm. Hg.

Spruce. No.	2.	4.	6.	9.	Average.
Sapwood	18.0	20.0	21.5	26	21.2
Heartwood	21.0	17.5	21.5		20.0

The question as to whether this time represents adsorption absorption or the process of filling up capilary spaces has been discussed previously. A decision in this matter is not necessary for this part of the discussion, as it is only necessary to assume that the walls of the wood structure require this time to become saturated when directly exposed to water vapor at the given pressure. If this rate is measured carefully and an average value obtained, any increase in the time

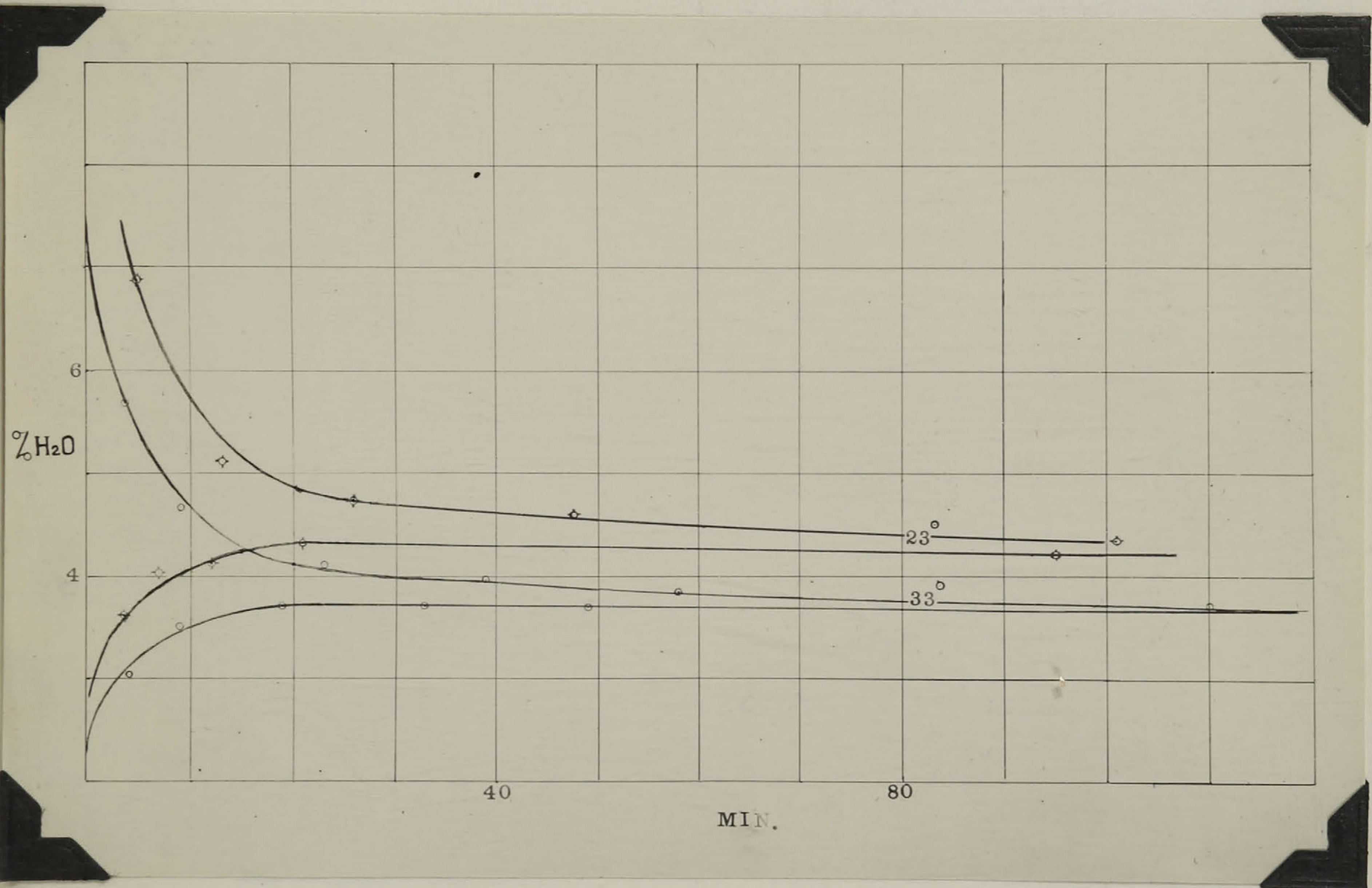

Fig. 10.

required to establish equilibrium in the case of thicker samples will be due to the time taken to diffuse through the wood structure.

Method of Comparison.

it was necessary to find some convenient basis of comparison of the rates for different samples. The uncertainty of the final saturation point makes it a poor criterion on which to base comparisons of the diffusion rate. It is therefore assumed that all samples of the same wood would finally attain the the value reached by the standard were the experiment protracted until equilibrium was completely established.

This assumption has been tested in the case of samples which are saturated in a reasonable time and it has been found to be valid. If the saturation value is measured or assumed the time to half value may be obtained from the curve.

Directions in which Diffusion has been Measured.

The most important passages in the tree occure in the longitudinal direction as it is in this way that a passage for the food carrying liquids must be found. The general structure of wood has been described previously, reference to Fig. 1 will at once indicate the importance of the longitudinal direction. Thus it is that by far the greater number of determinations have been made in this direction. Samples whose longitudinal dimensions are various multiples of the average fibre length have been chosen and the rate of establishment of equilibrium examined with both one and two transverse faces open.

A number of experiments have been performed in the radial direction, by blocking off the transverse and tangential faces.

The tangential direction has little interest and beyond one experiment it has not been examined.

A. Longitudinal Diffusion through Spruce. (Picea canadensis)

Samples with a longitudinal dimension of 5, 9, 14, and 20, mm. have been examined both for heartwood and sapwood. The results are listed in tables XXXV and XXXVI. A discussion of these results is best conducted by reference to the time curves which have been plotted in Fig. 11 and Fig. 12.

It is at once apparent that there is a great difference in the rate for heartwood and sapwood. In the case of the latter, even up to a longitudinal dimension ~~length~~ of 9.5 mm. there is little difference in rate from the 1.5 mm. sample; while in this case, with an average fibre length of 3.5 mm , there must be at least

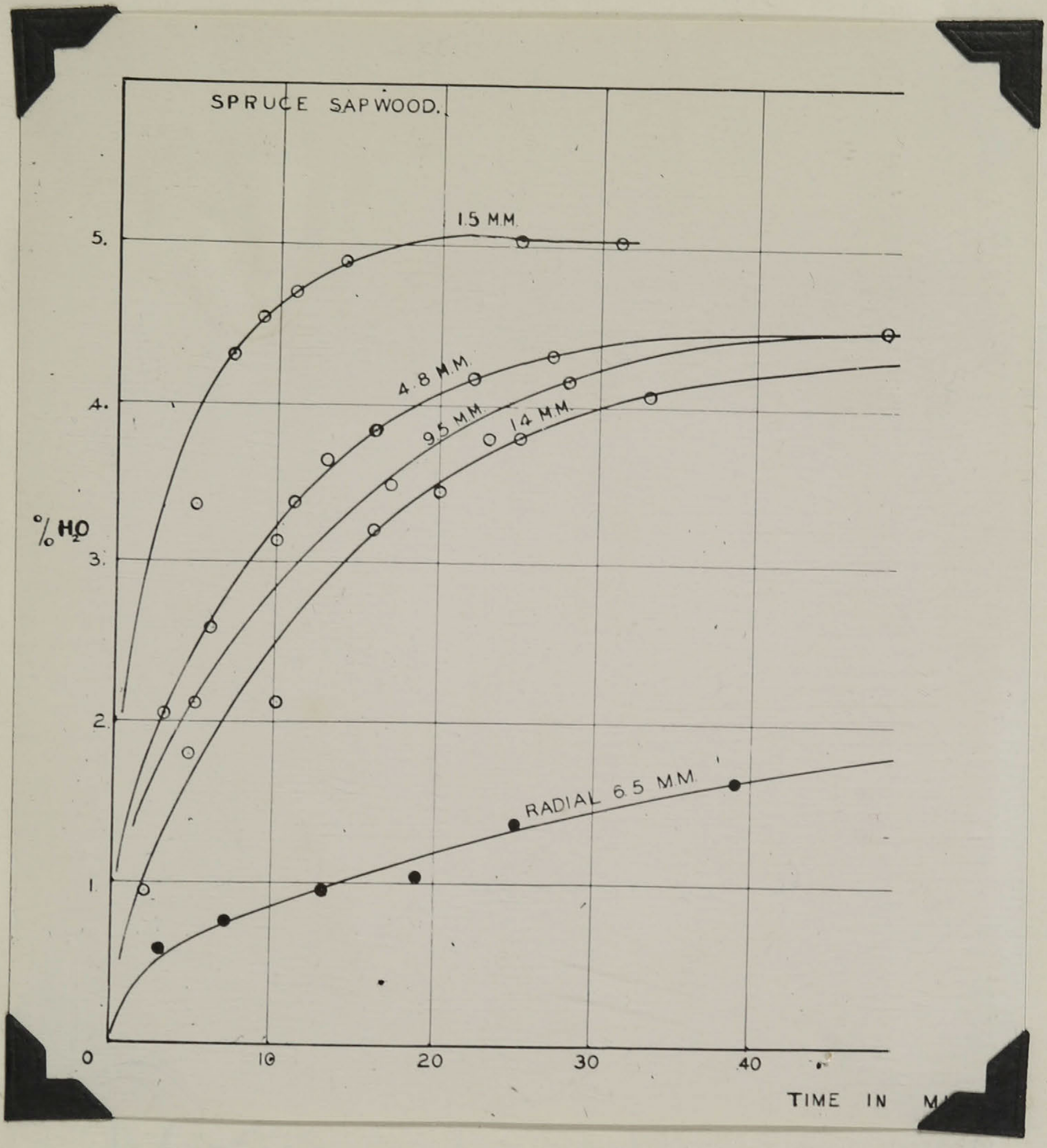
SPRUCE SAPWOOD.
1.5 M.M.
4.8 M.M.
9.5 M.M.
14 M.M.
RADIAL 6.5 M.M.
% H₂O
5.
4.
3.
2.
1.
0
10
20
30
40
TIME IN MI

Fig. 11.

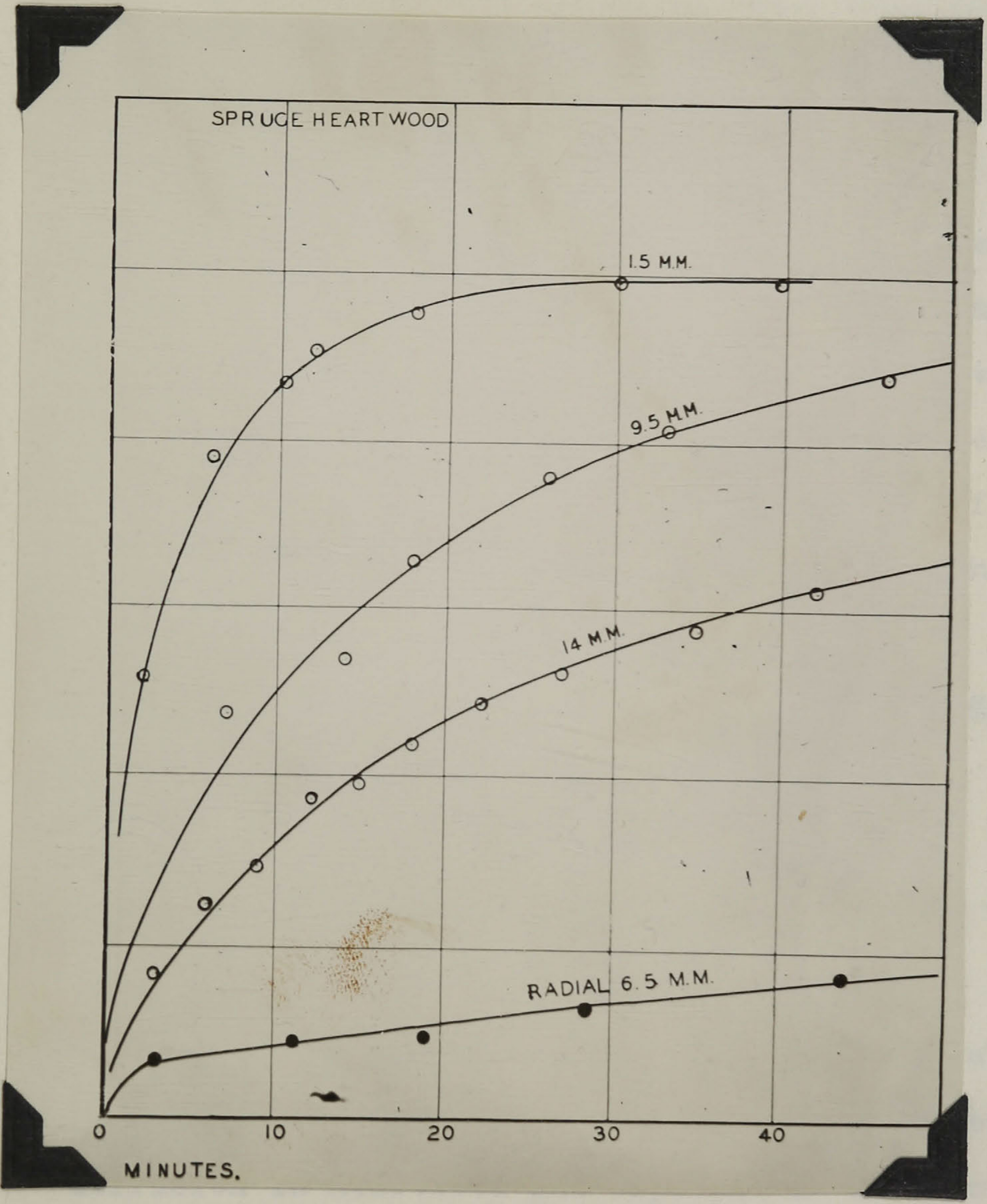
SPRUCE HEARTWOOD
1.5 M.M.
9.5 M.M.
14 M.M.
RADIAL 6.5 M.M.
0
10
20
30
40
MINUTES.

Fig. 12.

one fibre completely enclosed in the body of the wood and which can be reached by the vapor only by passing through the openings between the fibres.

In the ease of heartwood (Fig. 12) The rates for thicker samples are quite different. For the standard sample of 1.5 mm. thickness the rate is similar to that of sapwood so that the difference which is so obvious in the case of thicker samples must be due to the resistance offered to the entering vapors by the opening between the fibres. The marked difference between rates of diffusion in the two kinds of wood is well shown by a consideration of the time to half value.

Spruce.

Long. Thickness	Time/2 Heartwood.	Time/2 Sapwood.
1.5 mm.	2.2 min.	2.3 min.
5.0 "	-	3.2 "
9.5 "	9.9 "	4.3 "
14.0 "	18.1 "	8.0 "

Since a small change in the time to half value corresponds to a very great difference in rate the difference between diffusion in heartwood and sapwood is even more marked than the above would indicate.

Diffusion Through Dried Spruce in the Longitudinal Direction.

The results of time experiments on various samples of Spruce B (see p. 25) are indicated in table XXXVI. The values are not essentially different from those of green wood as the following table will illustrate

Thickness.	Heartwood. T/2	Sapwood T/2
1.5 mm.	2.1 min.	2.2 min.
5.0 "	5.5 "	4.4 "
9.5 "	10.4 "	4.5 "

These values check well with those obtained above for Spruce (A).

This fact has a bearing on the unsolved problem of the nature of heartwood. While this part of the tree has ceased to take an active part in the life process, it is difficult to state just how "dead" it is. If the changes which characterize the formation of heartwood take place by natural by natural ageing after the death of the wood, it would reasonably be expected that sapwood would undergo a similar change ; so that a sample chosen from the sapwood of a log which has been air dried for several years would prove more impermeable to water vapor than a fresh sample. This apparently is not the case as indicated by the unchanged rate of penetration, so the impenetrable condition of heartwood is evidently a change which takes place by the agency of life processes .

Diffusion Through Spruce wood in the Radial Direction.

In table XXXV are listed the results of several experiments in which the transverse and tangential faces were masked so that the penetration of the water vapor into the dry sample was restricted to the radial direction. The results are plotted for heartwood and sapwood in Fig. 12 and Fig. 11 respectively. A greater difference between the two kinds of wood is manifested than in the case of longitudinal diffusion. In fact, in the case of heartwood, after the first rapid adsorption which saturates all the readily accessible surfaces, the adsorption proceeds so slowly that even the time to half value must be obtained by extrapolation.

The magnitude of these values is indicated below:-

Sapwood	122 Min.
Heartwood	310 "

Diffusion in this direction must take place through the medullary rays which are comparatively few in number . Communication between the rays and the fibres which make up the bulk of the wood substance is established by means of the bordered pits.
Thus it is that in the case of heartwood, in which these pits are stopped up in some way, the small number of openings makes the wood almost impenetrable.

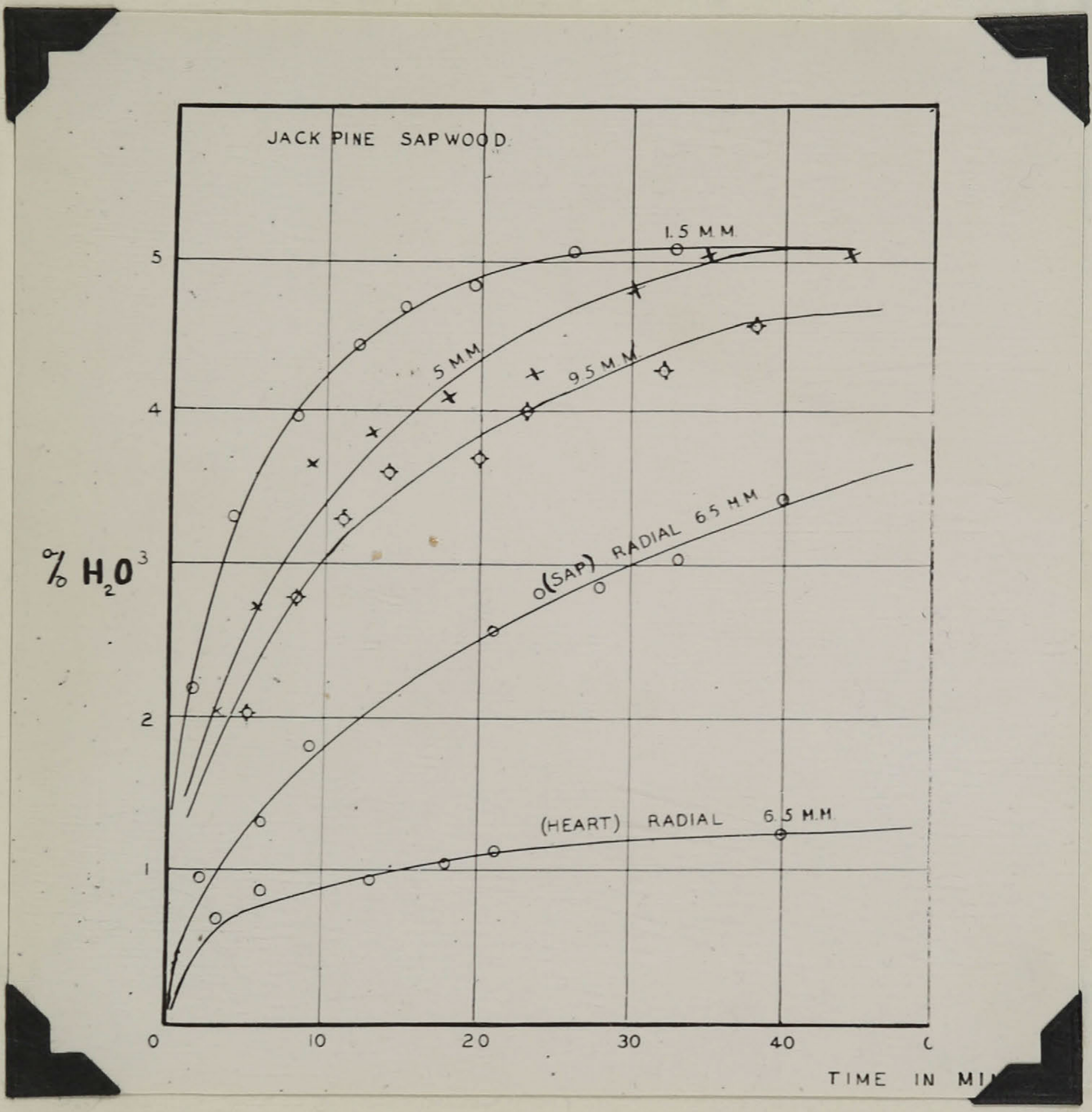
JACK PINE SAPWOOD
1.5 M.M.
5 M.M.
9.5 M.M.
(SAP) RADIAL 6.5 M.M.
(HEART) RADIAL 6.5 M.M.
% H_2O
0
1
2
3
4
5
10
20
30
40
TIME IN MI

Fig. 13.

126 B.

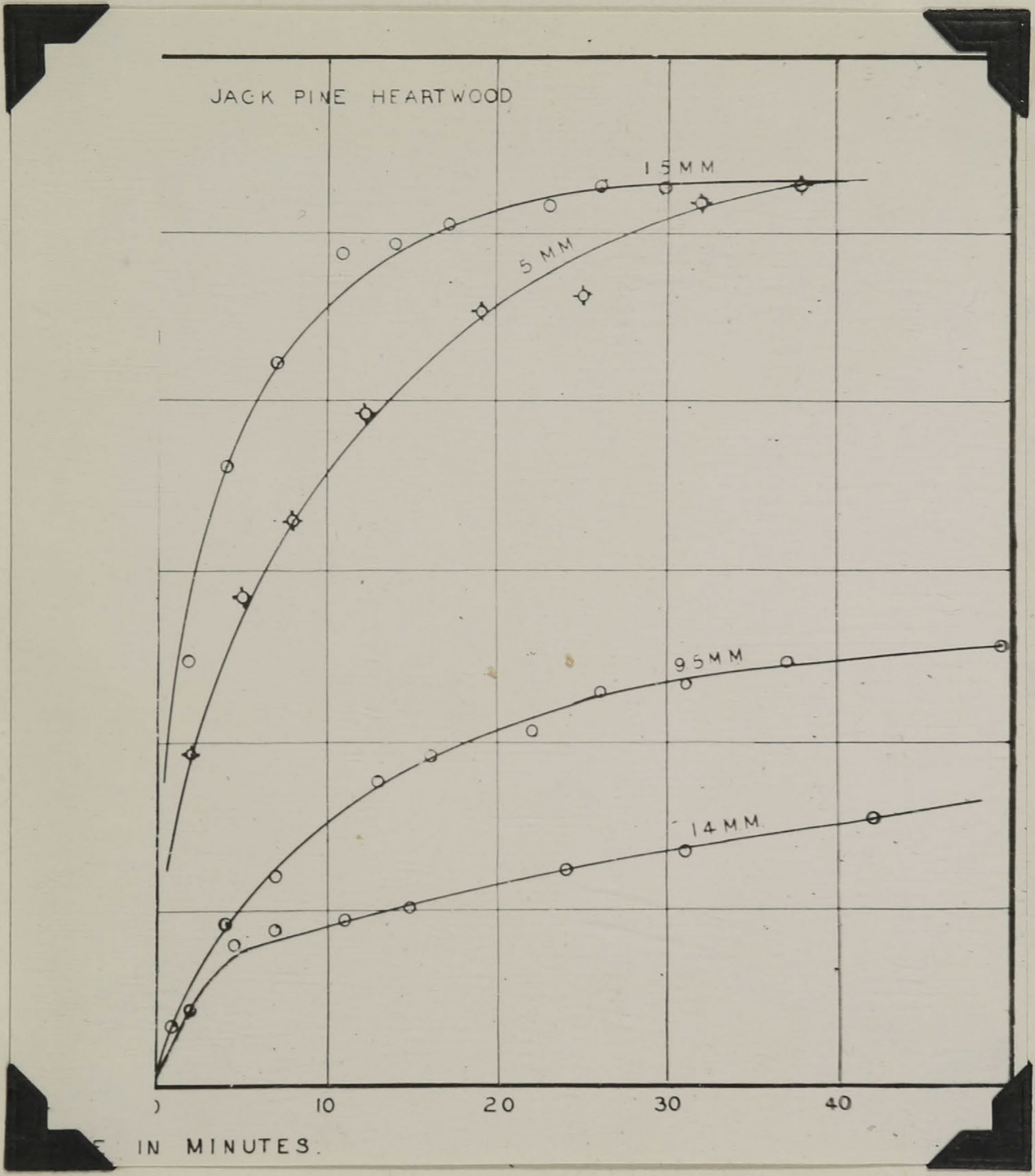
JACK PINE HEARTWOOD
15MM
5 MM
9.5MM
14 MM
0
10
20
30
40
E IN MINUTES.

Fig. 1d.

Diffusion in the Longitudinal Direction.

The values for sapwood show a marked similarity to those of spruce (see Fig. 13 and tables) while in the case of heartwood there is considerable difference. As seen from the curves the thicker heartwood samples are quite as impenetrable as the radial sections of spruce. For comparative purposes the values to half saturation are reproduced below together with those of spruce.

Sapwood. Thickness.	T/2 in minutes. Spruce (A)	Spruce (B)	Pine.
1.5 mm.	2.3	2.2	2.2
5.0 "	4.3	4.45	4.2
9.5 "	6.4	4.5	6.6
14.0 "	8.0	-	-
Heartwood.			
1.5 mm.	2.0	2.1	2.5
5.0 "	-	5.5	4.0
9.5 "	9.9	10.4	50.0
14.0 "	18.0	-	160.0

It is apparent that the natural process which produces heartwood from sapwood results in much greater stoping up of the pores. This is perhaps to be expected from the fact that the resin content of pine is much higher than that of spruce.

Radial penetration.

The curves for the rate of diffusion in the radial direction are plotted in Fig. 13. These values indicate that Pine is in general more penetrable in this direction, as the rate for sapwood is greater than that of spruce, and that of pine heartwood is the same as spruce while, from a consideration of the longitudinal penetration, it should be much slower.

Discussion of the Number of Fibre Lengths per Sample.

In order to give the results of time measurements a meaning in terms of the wood structure, it is necessary to find the number of fibre ends which must be passed to saturate each sample.

The fibre has not a constant length so that an average value must be accepted. According to Sutermeister the average for spruce is 3.53 mm.. If this value is accepted a sample whose longitudinal dimension is 5 mm. should contain at least 1 fibre length. If both ends of such a sample are open the greater part of the fibres will be accessible at one end at least. The closing of one end, however, should mask off at least half of the fibres so that they must be reached through the pores connecting them to the fibres whose end is open. In Fig. 15 it is seen that this is not experimentally borne out, the 5 mm. sample shows little change in rate when one of the transverse faces is blocked off. Apparently in this sample the average length of fibre is greater than 3.5 mm. A qualitative examination of sections of spruce under the microscope substantiates this result.

In Fig. 15 the effect of closing one end of a sample of 9.5 mm. longitudinal thickness is depicted. In this case there is a considerable reduction in rate takes place. It would appear that in this section at least one fibre, on the average is so placed that it may be reached only by passing through the bordered pits between the fibres..

The effect of closing one end is indicated in the following table of times to half value:-

Spruce A. Sapwood	1. Face.	2. Faces.
4.5 mm.	4.4 min.	4.3 min.
9.5 "	9.2	6.4
14.0 "	11.5	8.0
Pine. Sapwood.		
5.0 mm.	5.5	4.2
9.5 "	7.4	6.6
Heartwood.		
5.0 mm.	19.7	4.0
9.5 "	200.0	50
14.0 "	?	160.0

The table well-illustrates the extreme lack of porosity of pine heartwood. The closing of one transverse end has a tremendous effect in retarding the attainment of final equilibrium. It is to be concluded that the formation of heartwood in the case of pine involves almost a complete stopping up of the pores. There is much difference of opinion as to the mechanism of this change. It is considered by some that the torus, which is like the flap of a valve, is pressed over to one side thus firmly closing the passage. The above results would tend to support this view, at least in the case of pine, for the slow rate of penetration (when there must be considerable pressure difference across the openings) points to a very tight sealing of the openings.

SUMMARY AND CONCLUSIONS.

In this investigation the adsorption isothermals of wood and cellulose have been for the first time determined by a method free from inherent error. The isothermals have been indicated throughout their entire length from the origin to the saturation point.

A consideration of the isothermals at different temperature has established the fact that adsorption is independent of temperature and is a function only of relative vapor pressure. The theoretical reason for this has been indicated both qualitatively and mathematically.

By plotting the variation of vapor pressure with temperature, adsorption isosteres have been obtained which are exponential curves similar to the typical vapor pressure curve. For a considerable range of adsorption the points of log p plotted against $1/T$ fall on a straight line. It follows that the adsorption in this region may be expressed by the relation,

$$\log a/p = B' \quad A\ T$$

This relation has been deduced from purely theoretical grounds and its application to wood is significant.

The effect of various natural factors on the adsorption of water by wood have been carefully attention. There seems to be little difference between the final saturation value attained by heartwood and sapwood. The curves for pine show a marked divergence at lower vapor pressures finally co-inciding again at the saturation point. The effect of natural drying has been examined and it is found to reduce the amount of adsorption near the saturation point, which is itself considerably lowered. At lower humidities, however, there is little difference between dried and green wood.

This effect,both from practical and experimental grounds, may be considered as a characteristic one: that is, if differences are noted, they will be most marked at high relative vapor pressures. Thus it is seen that the saturation point of spruce is 24%, that of pine is 31%, while from the origin to a relative humidity of 25% the two isotherms are identical.

A theoretical analysis of the adsorption isotherm has led to an understanding of the observed facts in the light of the modern theory of gel structure.
The shape of the isotherm and the reversability of the adsorption place wood in the class of swelling gels.
It is considered that the wood substance is made up of small particles which are separated by ultra-microscopic

capillaries. In the process of taking up water the walls of these capillaries are first saturated with an adsorbed layer of the vapor, this is followed by the filling up of the pores with liquid condensed at reduced vapor pressure due to the small radius of curvature of the liquid surface. As the vapor pressure increases the capillaries increase in size causing the wood to swell, until near the saturation point the amount of liquid taken up is very large for a small increase in vapor pressure.. In this region it is considered that large pores such as are microscopically visible will be filling with water as the required reduction of vapor pressure to produce condensation is very small. This picture exactly fits the adsorption isothermal of wood, it explains the shape of the curve and the reason for the great variation between species at higher vapor pressures. Or rather it may be considered that the similarity of the curves in the lower regions proves the fundamental unity of wood substance

The theory as extended to apply to wood affords a theoretical reason for the hysteresis effect which was observed in almost all cases. It is due to the difference in curvature of surface during filling and emptying of the sub-microscopic capillaries with its attentant variation in vapor pressure for the same amount of adsorption.

The moisture equilibrium of cotton cellulose has been examined and new values obtained which are greatly less than those indicated in the literature. The values for cotton cellulose are much less than those for wood, while these for extracted wood cellulose are considerable greater. A consideration of the composition of the two varieties of celluloses at once disclosed the reason for the difference. Cotton cellulose is largely alpha cellulose while wood cellulse contains two additional varieties, beta and gamma cellulose. These latter , being soluble in alkali , have a greater affinity for water than alpha cellulose, hence their presence in wood is responsible for the increased adsorption.

In the second part of this research the experimental method has been extended to afford a means of examining the rate of diffusion of water vapor through the wood in various directions. The rate of penetration in the longitudinal direction has been given particular attention. It has been dempnstrated that heartwood is much more impermeable than sapwood and in the case of pine the difference is particularly striking. The rate of diffusion in the radial direction has also been examined.

This method makes it possible to obtain numerical values of a comparative nature .

It will be evident that the experimental procedure described in this investigation is one capable of wide application in the field of adsorption measurements. It is particularly adapted to the measurement of adsorption of condensible vapors, and posseses all the obvious advantages of direct measurement.

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