

SORPTION OF VAPORS  
BY  
WOOD AND CELLULOSE



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The Sorption of Vapors by Wood and Cellulose.

T H E S I S

Submitted in Partial Fulfillment of the  
Requirements for the Degree of Doctor of Philosophy.

by

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## GENERAL INTRODUCTION

The sorption of vapors by wood and cellulose is a continuation, and elaboration, of an investigation started in this laboratory by Pidgeon and Maass <sup>(1)</sup>. Their work was confined to the sorption of water vapor by wood and cellulose, over an extended range of vapor pressures and temperatures. Further, a detailed study was made of the penetration of <sup>(2)</sup> water vapor into wood. These investigators confined their attention to various samples of two coniferous woods, and to a pure cotton cellulose, and examined these throughout the complete range of vapor pressures, and between the temperatures of 12°C and 42°C.

While a considerable number of investigations on the fibre saturation point of wood have been made, the complete sorption isotherm has rarely been determined. Tiemann (3), Myer and Rees (4), Dunlap (5) and Stamm (6) have determined saturation points by various methods. Quite extensive work on cotton cellulose is due to Urquhart and Williams (7), who have produced complete absorption and desorption isotherms over a large range of temperatures. However, a new experimental technique for the

determination of the moisture equilibria of woods was developed by Pidgeon and Maass (1). They evolved a method which gives reproducible results, and which is free from the objections which characterize much of the work done along these lines. Their method has been used in the study of an extended field of analagous investigation, in the following dissertation. Modifications have been introduced to meet special needs in the experimental methods.

The previous attention of this laboratory was confined to a fairly complete study of two coniferous woods, and to a pure cotton cellulose, and that only as far as water vapor was concerned. The work here to be described, deals with a greatly extended range of species. Obviously it has been impossible, and indeed unnecessary, to deal with each wood and cotton in as great detail. Further, a study has been made of the sorption of a number of vapors, other than water vapor.

The purpose of this investigation may then be described briefly as follows. The complete water vapor equilibria for cotton are first of all necessary when the comparative aspect is introduced. It is felt that in an investigation of this kind,



there is a possibility of thereby eventually obtaining information as to the essential nature of the fundamental cellulose molecular aggregate, from the quantitative aspects of sorption. This is particularly so in the range of extremely low vapor pressures. Such information, correlated to sorption in wood, could then be used to specify the part played by cellulose in the wood substance.

A comparative study of different woods was undertaken, as it was felt that the water vapor equilibria of a wood should be more or less of a definite type, depending on the essential structure of the wood, and varying from species to species. Thus, the water vapor equilibria of a wood are possible means by which one may classify the various woods. Such a classification would not be arbitrary. It would depend on the essential similarities and dissimilarities of the various species, and would be based on the actual nature of the absorbing system. Such a physico-chemical classification would be of interest in itself.

After consideration of the sorption of water vapor by woods and cellulose, one naturally proceeds to the sorption of other vapors. The sorption of any

particular vapor by wood and cellulose is of interest. The rate at which sorption occurs is of importance. The modifying influence of the non-cellulose substances in wood, and also its definite structure, will respond to this treatment. Thus by comparison of the results for wood and cellulose the affect, if any, of the lignin etc. may be indicated. There is always the hope that information may be obtained as to the actual chemical nature of these constituents. Thus the aim in this work on the sorption of various vapors is twofold, first, the results are of theoretical interest in themselves, second, compilation of data of this kind is, obviously, of practical importance. This is particularly true if a large number of different gases are considered. A detailed comparison of the mechanism of sorption with various gases, and substances, should also be fruitful in clarifying ideas as regards the actual nature of the systems under consideration, from the point of view of colloid chemistry. Before this is accomplished the term sorption should preferably be used. However it is necessary to indicate the process that is taking place, from the point of view of whether, vapor is being taken up by the system, or being taken out of the

system. To avoid confusion it was thought best to follow the nomenclature used by others (7), and arbitrarily use the term absorption, when equilibrium values are obtained by increasing the vapor pressure from that pertaining to a previous equilibrium value, and desorption, when the sequence of pressure changes is reversed. These two terms, absorption and desorption, therefore, do not negate nor imply solid solution, surface adsorption or compound formation.

#### DETAILED INTRODUCTION

Bearing in mind the general aim outlined above there follows now a survey of the specific field covered.

Considerable work was done to definitely establish the reliability of the various procedures for causing sorption, from the point of view of their reproducibility.

The influence of the preceding history, in its relation to absorption and desorption, was given attention. For instance, if absorption and desorption are determined at a given vapor pressure, does the final equilibrium value, at this pressure, depend on



the way in which this absorption or desorption occurs? Again, will a direct passage from zero vapor pressure, to that under consideration, give the same value as a procedure which involves several intermediate sorption values? This establishment of method was investigated with representative specimens of heart and sap woods, and with two different cottons. In this way the applicability of the results should be quite general.

The determination of percentage sorption against time is important from the experimental point of view, in governing the time required for the establishment of equilibrium. Apart from this, these relationships are of interest in connection with the structure of the absorbing material. Thus, the sorption of water vapor, against time, should give results which are more or less characteristic of the particular wood or cellulose. If the wood samples are of such a thickness, that each fibre is cut at least once, the time intervals recorded, represent actual sorption in time, and the results are of comparative importance. If each fibre is not cut at least once, there are two factors to be considered—first, the penetration of vapor into the sample, and second, the sorption.

The moisture equilibria for two different pure cellulose samples have been determined. One is an ordinary type absorbent cotton, the other, rag cotton from Eastman Kodak Co. Following an investigation of these cottons, the complete moisture equilibria of twenty different Canadian woods were determined. Three woods were chosen from the list of twenty, the choice being governed by the three showing the greatest divergence from the average sorption curve. This re-determination of the sorption isotherms, on new samples, a year after the first samples were investigated, had for its object the testing of reproducibility of sorption isotherms, characteristic of a particular species.

Following this comparative study of a number of different Canadian woods, work was undertaken on the subsequent ability of the wood to sorb water vapor, after the removal of certain of the non-cellulose constituents. This was done by measuring the complete sorption isotherms. The extraction was carried out by a carefully regulated standard process.

Some effort has been made to follow the reversibility of sorption of water vapor by cotton, extracted and unextracted wood, following different heat treatments.

Any modification of the elastic gel system, following moderate heat treatments, would be expected to show itself in a change in the ability to take up water vapor.

The vapors, other than water vapor, for which the sorption values have been investigated, are, sulphur dioxide, ammonia, hydrochloric acid and carbon dioxide. Of these gases hydrochloric acid has received, by far, the greatest attention. With the other three vapors the sorption experiments have been carried out over a limited vapor pressure range. It is felt that the results obtained, in addition to being of interest from the point of view of this dissertation, will also indicate profitable lines for extended investigation in this particular field. The action of hydrochloric acid on wood and cellulose has been given considerable attention. The sorption of hydrochloric acid by cotton cellulose was followed over a range of gas pressures, up to one atmosphere, only a few determinations being made. In the case of wood the complete system, from 0 to 76 cms. pressure of gas, was determined.

The next system to be examined was wood-water vapor-hydrochloric acid. A series of runs was made



in which a certain definite amount of absorbed water is present in each sample. These samples were then subjected to pressures of hydrochloric acid gas. A number of determinations were made in this manner, varying the initial amount of water present. Only one species of wood has been investigated in this connection. It was felt that the sorption of hydrochloric acid, by wood containing a definite amount of water, might serve as an indirect method of throwing light on the essential difference between absorption and desorption values. Two samples with approximately the same amounts of sorbed water, one due to absorption the other due to desorption, were compared in regard to their behavior with hydrochloric acid. Further, the ease of removal of hydrochloric acid from wood, both with and without water present, is of interest. Also an investigation has been made of the water absorbing powers of a wood previously exposed to hydrochloric acid.

The system cotton-water vapor-hydrochloric acid has also been investigated. The range of water contents while not quite as extensive as with wood, is sufficiently great to indicate the nature of this ternary system. The physical and chemical changes, undergone

by the cotton when subjected to this treatment, have been given consideration. The return to original weight and the entire water vapor equilibria have been followed for cotton treated in this manner. In dealing with ternary systems, the measurement of sorption against time was followed, and the affect of an increasing amount of water, on this factor, indicated.

A few experiments were also carried out on the ternary systems involving carbon dioxide, in the presence of definite amounts of previously absorbed water.

#### Experimental Method.

The method employed has as its basis a quartz spring balance suspended in an evacuated glass system. This glass system must be capable of maintaining a high vacuum. In connection with the system there is a bulb containing water, this serves as a source for vapor. The vapor pressure may be determined indirectly by controlling the temperature of this bulb, or it may be read off directly, on an oil manometer which is a part of the system. The remainder of the apparatus consists of a phosphorous pentoxide tube and connection to the pumping system and MacLeod gauge. The pumping system

is made up of a Languir mercury condensation pump, backed by a "Cenco Hyvac" pump. This is a general outline of the type of equipment which has been utilized. That it serves the desired purpose is readily seen from the following considerations.

There are several requirements which must be met. Sorption in the first place, is seriously inhibited if air is present, chiefly due to the great increase in the time required to attain the true equilibrium condition. Also the presence of air might be decidedly undesirable from the possible effect on sorption. The presence of sorbed air would almost certainly vitiate the accuracy of results for the sorption of certain vapors such as carbon dioxide. This requirement is met by the use of a vacuum <sup>tight</sup> glass system.

Furthermore, constant vapor pressure must be maintained throughout sorption as hysteresis is shown in the sorption of water vapor ~~under~~ changing vapor pressures. Thus, the experimental arrangement must permit of a definite pressure being held. This necessity is met by the presence of a water bulb, kept in a constant temperature bath, this bulb is in direct communication with the sorbing sample, and holds the vapor pressure invariable.



The experimental equipment must be such that the unavoidable adsorption by the walls of the container in no way affect the measurements. This requirement is met by the use of a quartz spiral, the extension of which indicates the amount of sorption. Quartz does not adsorb water appreciably. This direct method makes it immaterial whether the walls adsorb vapor or not.

Further, the possibility of using small samples of wood or cotton is important. A small sample will show less hysteresis than one which is large, also the times involved in the attainment of equilibrium will be much less. The importance of a uniform structure in the wood specimen can not be overemphasized. A small sample ensures a much more uniform structure than might result, if a large one were required. The utilization of relatively small samples is made possible by the use of the quartz spring balance.

The importance of the above requirements, for the type of investigation undertaken, is brought out by comparison with other methods, such as used by Urquhart and Williams(7), which lead to results whose comparative values may be of interest, but whose absolute values are open to question. The experimental equipment, and method, of these investigators was such, that a definite

quantity of water vapor was added to, or removed from, the system. The state of equilibrium was indicated by a manometer, and the amount absorbed determined by measuring the volume of the water vapor added or removed. Further, this method made use of large samples of cellulose, the average weight being around 10gms. as compared to a sample weight of approximately 0.1gms. in this investigation. This method of measuring sorption will, obviously, be in error as adsorption by the walls is a factor over which there is no control, and concerning the extent of which there is no information.

Furthermore, Urquhart and Williams state: "It is perhaps noteworthy that after water had been admitted to the cotton the pressure gradually fell to its equilibrium value, while after the removal of water from the cotton the pressure rose to its equilibrium value, indicating that the gain or loss is initially sustained by the outer layers of the material, and that the diffusion to or from the interior, necessary to restore a proper balance, is a more leisurely process than the absorption or desorption of water by these outer layers". This is not surprising since measured amounts of water were added to the cellulose and then the pressure at "supposed equilibrium" determined. The addition of a quota of water was not made uniformly as far as the

whole mass of cellulose was concerned. Consequently the outer parts of the cellulose were able to absorb this water first, with the result that this water had to be desorbed to supply the farther portions. But if there is any hysteresis, uniformity of water distribution would be impossible under these conditions, since the desorption pressure is less than the absorption pressure. Consequently the values determined on a basis of absorption would be too high.

The disadvantageous features of the above method have been eliminated, through the type of apparatus used and the methods herein described. There is direct measurement of weight, and the process of sorption occurs in the presence of a constant and unvarying vapor pressure. The results obtained are not in error by the amount of vapor adsorbed by the glass walls of the container, and further, they represent true absorption or desorption equilibrium conditions.



The investigation of vapors, other than water vapor, has necessitated no fundamental modifications in either the equipment or in the methods which are used. However, the relatively much greater pressures required, necessitated the substitution of a mercury manometer for the oil manometer. Further, it was found advisable to admit a quantity of the vapor, under investigation, into the system, without the presence of the liquid phase. Thus, no effort was made to hold the vapor pressure constant, as was done in dealing with water vapor. In the absorption of a gas where the possibility of hysteresis exists, the possible effect of a falling pressure, while absorption occurs, or rising pressure in the case of desorption, may be significant. Even should hysteresis occur with the vapors examined, and this remains to be shown, the general validity of the results is still satisfactory. This is appreciated on a consideration of the small size of the samples which are used, and in the light of the relatively large volume of vapor, from which sorption occurs. Also the vapor pressures which have been investigated, are much greater than is the case with water vapor. Thus, the fall in pressure, which accompanies absorption, or the rise with desorption, is not very significant in terms of the final

equilibrium pressure. Therefore the sorption value at the final pressure will very closely approximate the true equilibrium value at this pressure.

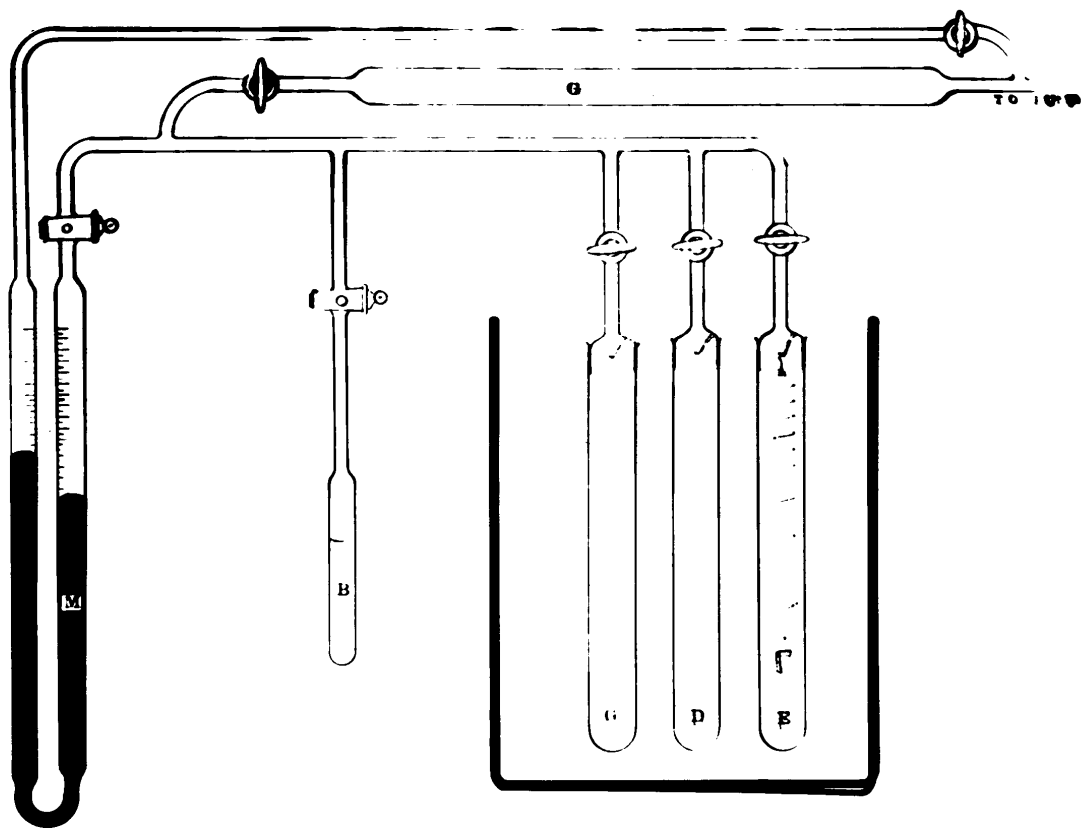
### Apparatus In Detail.

Figure 1 indicates the essential features of the system in which sorption occurs. Actually three different similar units have been constructed in this investigation.

The glass tubes G, D and E are removable, the ground glass joints are indicated in the diagram. The tubes are about eleven inches in length, with an inside diameter of one inch. A small glass hook, sealed into the glass head, serves as a support for the quartz spring balance. These tubes have functioned very satisfactorily as containers for spiral and sample. No tendency to leak at the large glass joint has been observed. In the case of the tubes most recently put into service, any possibility of leakage has been eliminated, due to the presence of a flange on the tube, this may be filled with mercury. Another improvement, not indicated in the diagram, is a change in the position of the connecting tube. By inserting this in the side of the tube itself the ground glass top may be removed without removal of the thermostating bath. The diagram indicates three sorption chambers

16(a)

Figure 1.



Apparatus.

in series. In practice it has been found convenient to make use of six of these together. This system has been confined to the study of the water vapor equilibria of woods and cottons. The advantages of this battery of six tubes are obvious. It enables the determination of the complete moisture equilibria of three different woods both sapwood and heartwood, at one time. Further, different samples of the same species may be considered under identical conditions. In the systems where other gases have been considered, single sorption units have been in operation.

The tube B contains water and serves as a source for vapor. It is surrounded by a Dewar flask maintained at a constant temperature, and thus the vapor pressure may be controlled.

The oil manometer M is shown. The oil used is "Cenco Hyvac" pump oil, and has a density about one fifteenth that of mercury, and also a negligible vapor pressure. This enables ready and accurate observation of the vapor pressures of water in the system. Where gases are used which require the measurement of greater pressures than can be indicated by this oil manometer, or with which chemical action may occur, substitution is made for the oil manometer M, of a mercury manometer.

This is capable of indicating pressures up to 76 cms. of mercury.

The position of the phosphorous pentoxide tube G is indicated in the diagram, it is used in determining the dry weight of the sample. Further, the tube takes up water very readily, thus avoiding the actuation of the pumping system for the removal of small amounts of water vapor.

Most of the glass tubing used in the assembling of this apparatus is 9 mm. in diameter, with stopcocks having a large bore. This is important as it reduces the affect of lag in pressures during the "drying" of the sample.

The bath surrounding the sorption tubes is indicated by the heavy lines. It was found that the accuracy of the optical measurements was affected by the use of a bath with a cylindrical surface. Thus the bath in use consists of a container with a flat plate glass surface. An aquarium, of suitable size to accommodate a battery of six sorption tubes, has been found quite satisfactory. The bath is equipped with a stirrer which ensures thorough and rapid circulation. The heating element is controlled by a toluene mercury therme-regulator through a relay. This

regulates the temperature in a satisfactory manner, the maximum fluctuations being in the neighborhood of  $0.02^{\circ}\text{C}$ . Further, a cooling coil of lead piping, through which a variable stream of cold water circulates, permits of the use of temperatures which are below those of the room, thus increasing the temperature range over which investigation may be conducted.

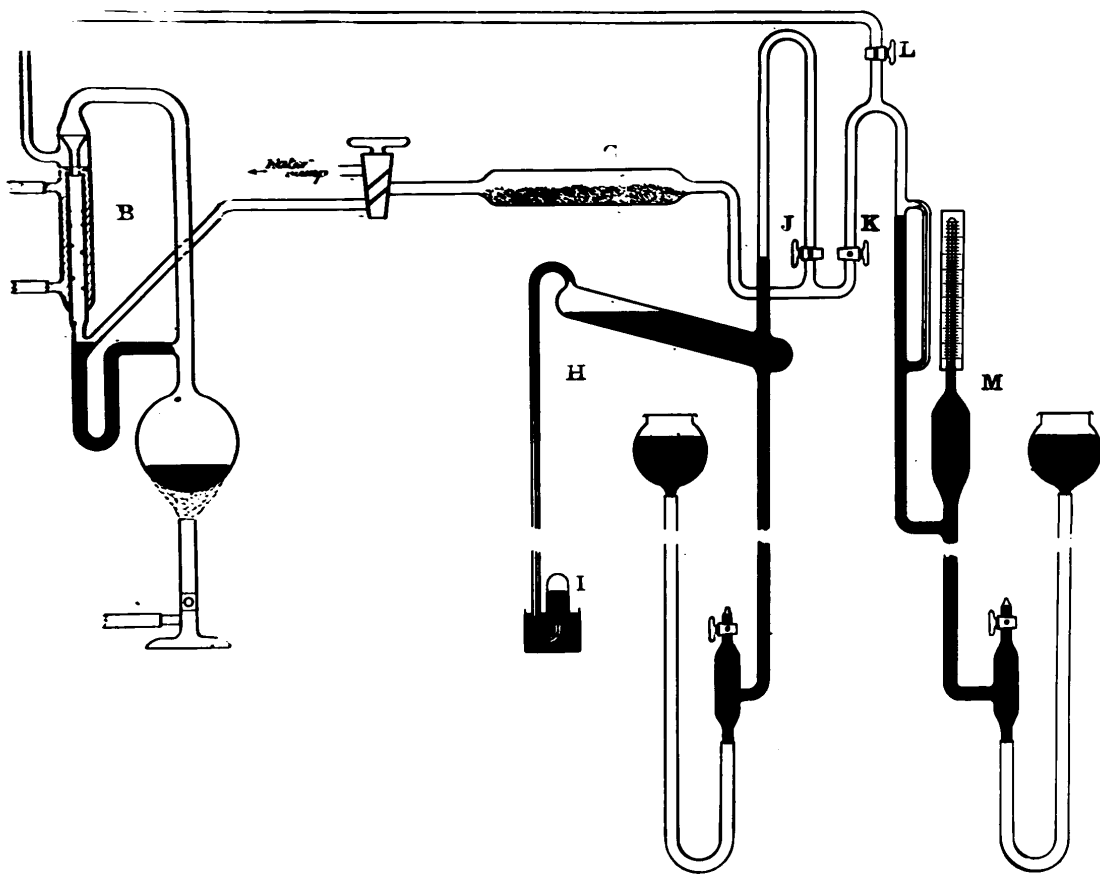
Figure 2. indicates the essential features of the pumping system. A is the connection which leads to the system to be evacuated. B is a Langmuir mercury condensation pump. M is a MacLeod gauge capable of indicating pressures down to 0.0005 mm. of mercury. This diagram indicates that the mercury condensation pump is backed by a Töpler pump. It was found more convenient to substitute a Hyvac pump. In all experiments the pressure is first lowered to at least 0.001 mm. before a run is commenced.

Observation of the extensions of the quartz spring balance is made by a cathetometer. The instrument used is capable of giving readings accurate to 0.02mm. It was found most convenient to focus the cross hairs on the extreme ends of the spiral for each extension. The optical system is such, that at a distance of about sixteen inches a distinct image is readily visible.



19(a)

Figure 2.



Pumping System.

The spiral is attached to the glass hook by means of a small wire loop. The length of this is such that the upper end of the spiral is below the ground glass joint. A silver wire stirrup supports the sample (fig. 1.). Direct support of the sample is possible if an appropriately placed V shaped cut is made in the wood specimen, thus eliminating corrections for any additional weight.

Spirals were constructed from quartz after the method of McBain and Bakr (8). Quartz spirals are particularly suitable, as quartz shows negligible hysteresis under the temperature conditions of experiment. The spirals used in this investigation were considerably finer than those previously described. Considerable care is required in drawing out fibres of suitable thickness and then of winding these. Considerable experience is necessary before suitable spirals can be made.

, The spiral, first of all, is calibrated throughout the working range by observing the deflections caused by known weights. The curve which results from plotting deflection against weight, gives a straight line which passes through the origin in most cases. For very great deflections, the linear relationship falls

off and the range over which it is to be used is limited to that in which no measurable deviation is observed.

Over two dozen spirals have been used. On the average a deflection of 1 mm. corresponds to a weight of 0.0030 gms. Thus, with the particular cathetometer employed, a weight of 0.0001 gm. can be easily detected, and the total weight of a sample weighing 0.1 gm. can be determined accurately to within 0.1%. Since the maximum differences observed are not greater than 30% of the total weight, the theoretical accuracy is well within 0.5% of the differences noted.

The selection and preparation of suitable samples is carried out as follows. In the case of cotton cellulose the two different cottons are kept in stoppered bottles, and samples may be withdrawn as required. With the woods, storage until it is desired for investigation, presents a problem. Suitable portions of wood are taken and wrapped in waxed paper and then stored in a desiccator to prevent drying out. On removal of the wood specimen, for the procurement of a sample, the outside portion of the piece is discarded, and a section, of suitable thickness, taken from the fresh surface. Care is taken to avoid including

any obviously unusual structure in this sample, that is, the section is taken from a portion of the wood which is representative and uniform throughout.

The sample is dried by long evacuation in the presence of phosphorous pentoxide at a pressure of about 0.0005 mm. mercury. After approximately 12 hours, a constant weight is observed. This weight is arbitrarily considered as the "dry weight", and the percentage increase due to sorption is always calculated on this basis. This point is completely reproducible, and may be checked several times, even after the sorption of water vapor. However, this reproducibility is not always found when other gases are used. It is only true when the sorbing system suffers no permanent change.

Attention must be paid to the purity of the gas admitted to the system in which sorption is determined. In most cases the gas is kept in the liquid phase in a bulb (fig. 1), having undergone previous chemical purification. With water, the chief precaution is the entire removal of all dissolved gases. This is ensured by alternately freezing and evacuating the water in the bulb. Generally three freezings are sufficient to completely remove all gaseous impurities. Some

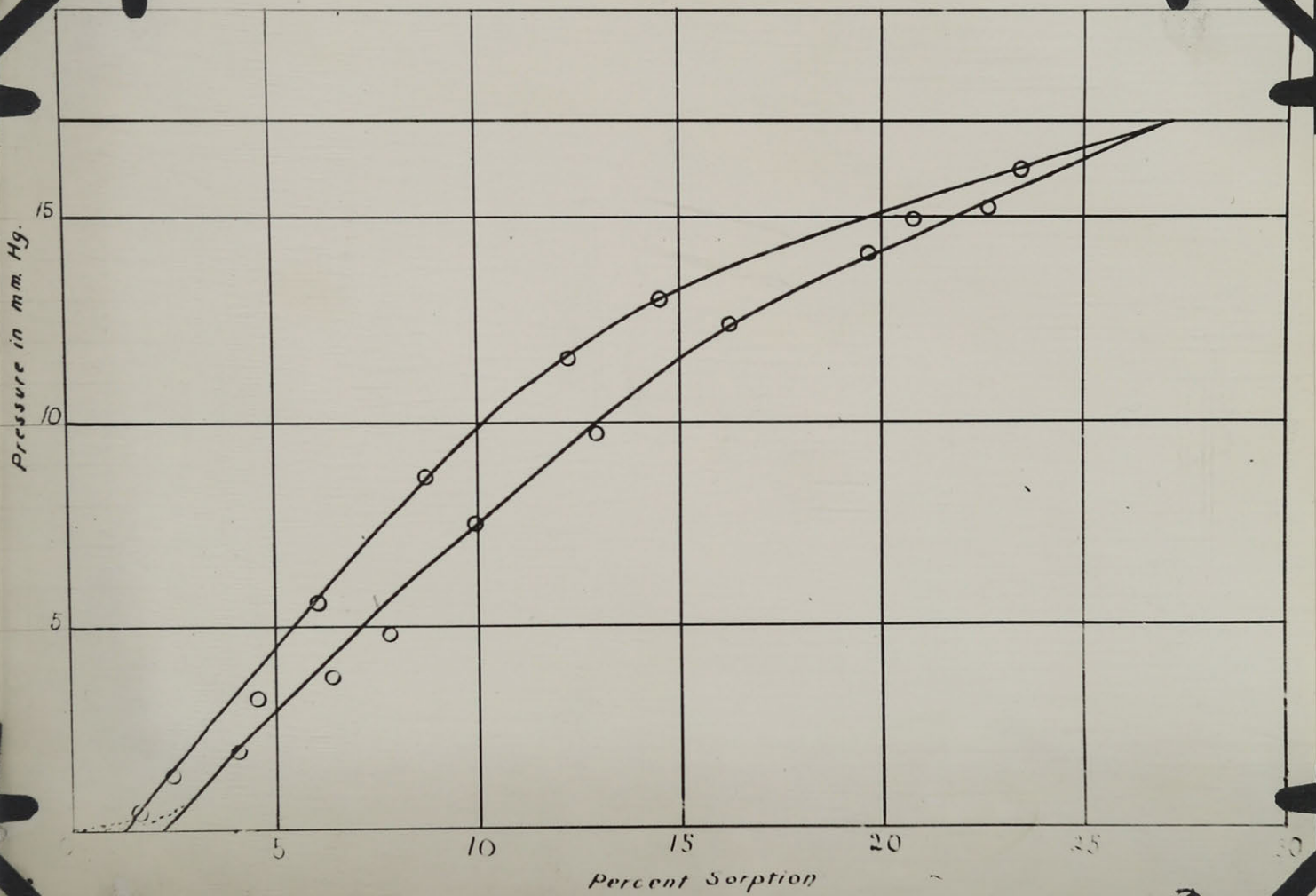
care has to be exercised or the water bulb will break. Slow freezing, with a carbon dioxide ether mixture, from the bottom upwards has been found satisfactory.

#### Development of Method.

Figure 3. indicates typical sorption isotherms for water vapor. It is seen that there are two curves, which tend to coincide near their extremities. Percentage absorptions are plotted as abscissas, and either the direct vapor pressure in mm. of mercury, or the relative humidities as ordinates. The form of the curves is similar in both cases. The use of relative humidities, in this connection, is much more general than plotting results against the absolute vapor pressures. Since the sorptions at relative humidities have been found to be independent of the temperature this makes possible the comparison of data from results obtained at different temperatures. In order to make use of the comparative aspect, and employ absolute vapor pressures, all determinations must have been made at the same temperature. The two curves, shown, illustrate the hysteresis which exists in the sorption of water vapor by wood and cellulose. Hysteresis

Figure 3.

Water Sorption Isotherm for Hemlock.  
(Heartwood).





indicates the existence of two true equilibrium sorption values, at one relative humidity, or vapor pressure. One value is obtained by the taking up of vapor from a lower pressure, or results from increasing vapor pressures. The other results from the removal of vapor or follows from a lowered pressure. In absorption there is less water held by the sample, than is the case if a desorption value is considered at the same vapor pressure. It is significant that hysteresis disappears as 100% relative humidity, or the saturation vapor pressure, is reached. This will be discussed later.

It is evident, therefore, that considerable attention must be paid to the details of experiment in order to determine either real absorption or real desorption values. The samples, investigated, are of such a thickness, that each fibre has been cut at least once. With such samples the times to equilibrium vary, depending on first, whether the equilibrium value being determined is absorption or desorption, and second, whether the relative humidity is low or high. In the region of 25% relative humidity, absorption equilibrium conditions are ordinarily obtained in about thirty minutes. Desorption equilibrium values require upwards of forty five minutes.

As the relative humidity increases, or the absolute vapor pressure, the times to attain equilibrium also increase. In all cases, to attain equilibrium with the taking out of water vapor, desorption, the time is greater than required for the taking up of water, absorption. In the upper regions of the curves absorption requires from one to two hours, while desorption takes nearly double this time interval.

The equilibrium times become great in proximity to the saturation value. No experimental attempt is made to determine this value, it is calculated by extrapolation of either of the two curves. Actually grave difficulties are met in its experimental determination. McKenzie was able to report a saturation value of 43.2% after seventy nine days with "absorption" still slowly taking place.(9). The reason why saturation values cannot be determined experimentally may be seen from the following discussion. If the temperature of the thermostat is lower than the temperature for free water condensation by a slight amount, then indefinite amounts will condense. The best that can be done experimentally is to have a thermostatic control which has

this temperature as a mean value so that alternately water condenses and evaporates. But evaporation will be from water held between fibres influenced by the angle of contact and governed by the closeness of packing of the cellulose fibres in cotton or the gross structure in wood. The extrapolated values for saturation cannot be looked upon as true saturation values, (which perhaps do not exist at all). The extrapolated values are, however, of interest in comparison from sample to sample.

The problem confronting the investigator, is the choice of a method which will give true equilibrium values, either absorption or desorption values, depending on which is desired, in the shortest possible time. The method adopted, must of course, be capable of giving results which are definitely reproducible. Thus the first attention of this work was towards the development of a technique which would give reproducible results, in as short a space of time as possible.

In practice, equilibrium values are determined in the presence of a constant vapor pressure, however, a cycle of operations is involved, the essential features of which follow.

After determination of the dry weight, the sample is allowed to become saturated with water vapor. This is indicated by condensation of water vapor

on the walls of the sorption vessel, and after some five hours saturation is sufficiently complete. A quantity of water/vapor is quickly removed, the amount removed is such that the equilibrium vapor pressure will be a few mm. below that at which the first sorption value is to be determined. Thus a sudden desorption has been effected. Without waiting for the complete establishment of equilibrium the vapor pressure is raised to that to be investigated. Absorption occurs at this constant pressure. The determination of each sorption value involves first, desorption from a greater value, and second, absorption up to that which is desired. This gives as a final value the desorption value, for the final vapor pressure. The important experimental feature is the desorption below the final value. In each case care is taken that actual desorption below this point has taken place. This is done quickly by sudden lowering of the vapor pressure and at the same time observation of the loss in weight. When the weight is distinctly less than that to be determined, the absorption process is initiated. This cycle of events is repeated until the complete equilibrium curve is obtained.

Since desorption equilibrium values are desired, and since this method gives such values, and gives them reproducibly, this system has been followed as being by far the most convenient. That the above process gives a desorption value is seen by the following typical data.

After keeping a sample at 100% relative humidity, (17.36 mm.Hg.) the pressure was reduced to 12.67 mm. and held there until equilibrium had been established, resulting in a sorption of 16.54%. This is a true desorption value. The sample was again subjected to 100% humidity. The pressure was reduced to 11.14mm. and held until the quartz spiral showed loss of weight below 16.54 %. The pressure was then raised to 12.67mm. The final sorption reached 16.47% and is within the experimental error of the desorption value. It is known as a cycle value, and is seen to be identical with the desorption value. The difference involved gives a saving in the time during which the pressure has to be maintained constant at the final value, namely, 12.67mm.

Another cycle value was obtained as follows. Starting with 100% humidity, by lowering the pressure to 8.09mm. and then raising it to the desired pressure

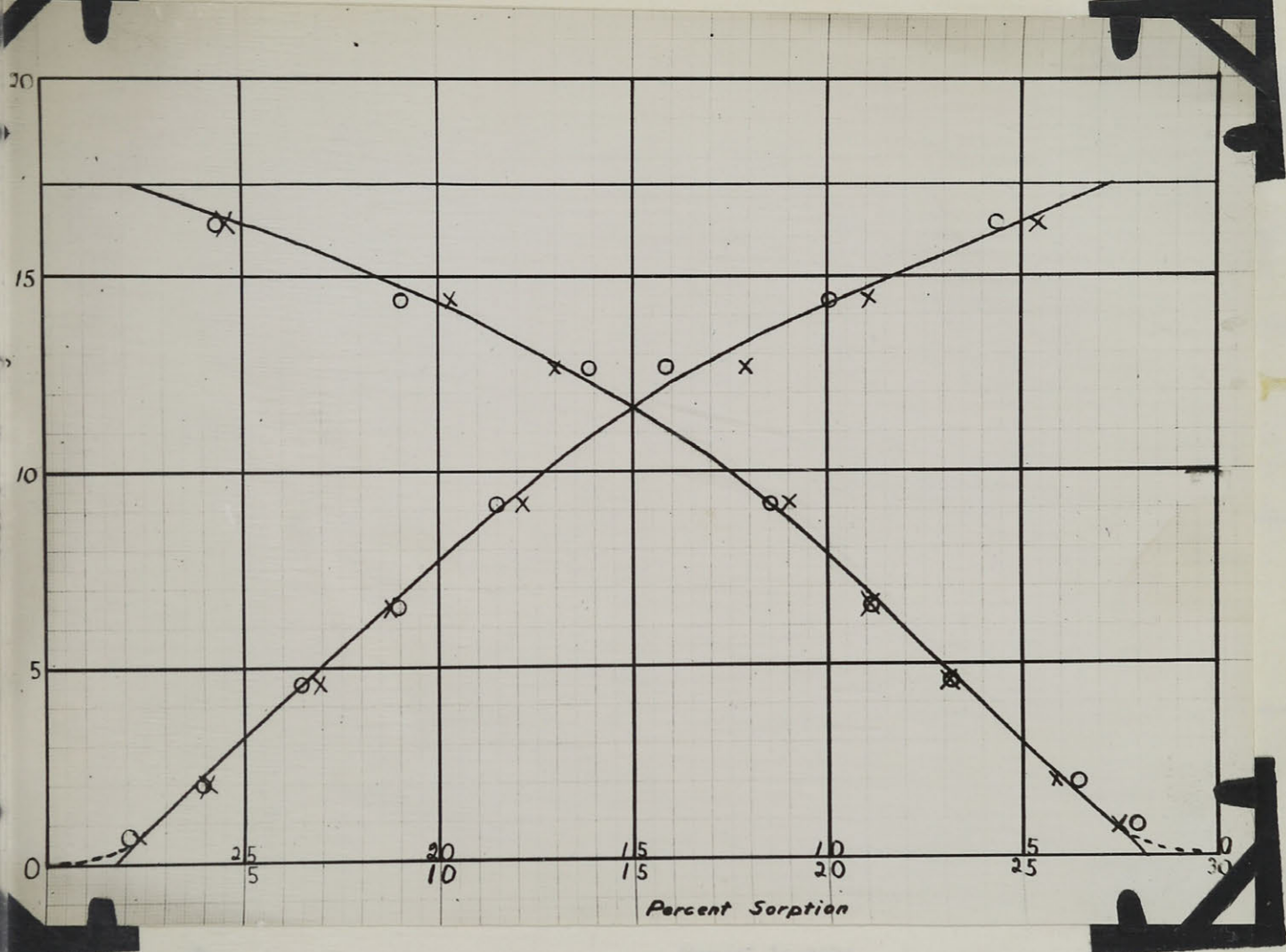
of 9.14mm. this gave a cycle value of 12.1% as compared to 11.9 by direct desorption. For convenience the complete desorption isotherms for the twenty Canadian woods, tabulated below, were determined by the cycle method, which it is seen approximately gives desorption values. When it is remembered that some sixteen equilibrium values had to be obtained for each specimen, it will be understood why a technique was evolved in which the time during which the pressure had to be maintained constant, was cut down to a minimum.

Care had to be taken, in the first place, that the first pressure-lowering was maintained for a sufficient length of time to allow loss of water vapor, in amount, below that which is characteristic of the final desorption value. By taking consecutive points on the curve this could be established in each case. Due precautions were observed that the pressure lowering was never carried to a point considerably below the final pressure, since in this case the cycle value is found to lie between the absorption and desorption values, an example will illustrate this. After subjecting the sample to 100% humidity the vapor pressure was lowered to 4.57mm, and then brought up to



Figure 4.

sorption Isotherms for Black Cherry.



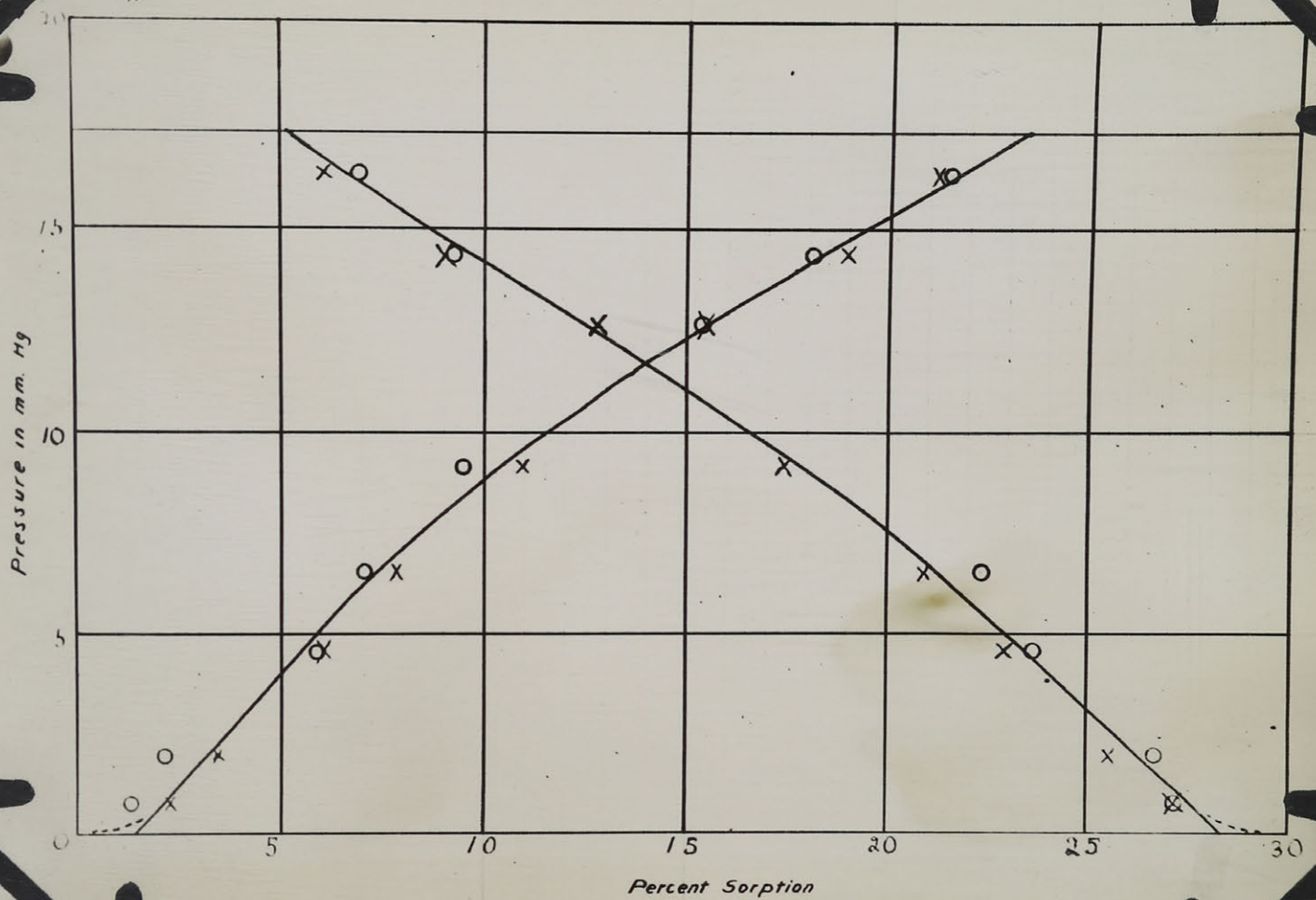
Sapwood.

Heartwood.

30(b)

Figure 5.

Water sorption Isotherms for Sugar Maple.



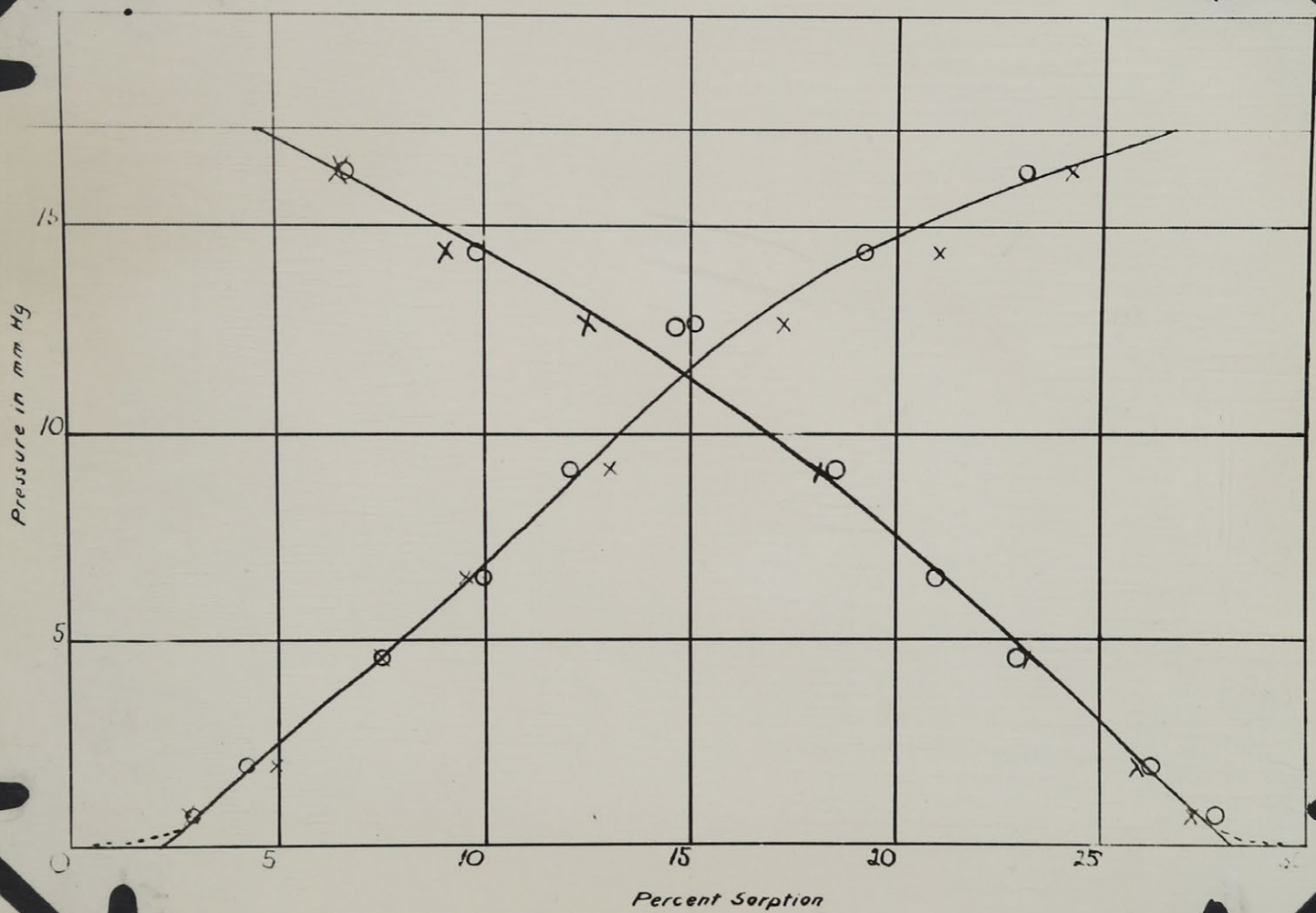
Sapwood.

Heartwood.



Figure 6.

## Water sorption Isotherms for Hemlock.



Sapwood.

Heartwood.

the sapwood of the hemlock has somewhat greater sorption values than the heartwood. In the case of black cherry they are the same, and in the maple the heartwood has decidedly greater sorption values.

After having elaborated this question of reproducibility, the data for the twenty Canadian woods are now tabulated. Instead of comparing all the data, either in the form of a tabulation or curves, it is more convenient to indicate, as has been done, in Table 1. five points that were taken from the sorption curves drawn in such a way as to represent each sorption isotherm. (The experimental data for all the isotherms are tabulated in the appendix ). In column one are given the amounts of sorption at zero vapor pressure, extrapolated from each curve. In column five is given the saturation sorption value, extrapolated from each sorption isotherm to 100% humidity. The three other columns give, as their headings show, the sorptions at three intermediate points.

Table 1.

## Sorptions Values for Canadian Woods.

Relative Humidity %.	0.0	17.3	51.8	86.4	100.0
----------------------	-----	------	------	------	-------

Vapor Pres. mm.of Hg.	0	3	9	15	17.36
-----------------------	---	---	---	----	-------

Red Pine(*Pinus resinosa*).

Sapwood.	1.85	5.10	10.10	17.60	26.10
----------	------	------	-------	-------	-------

Heartwood.	1.00	4.45	9.50	16.50	23.00
------------	------	------	------	-------	-------

Red Oak(*Quercus borealis*).

Sapwood.	1.00	4.45	9.70	17.20	22.50
----------	------	------	------	-------	-------

Heartwood.	2.30	5.70	10.10	16.20	21.10
------------	------	------	-------	-------	-------

Ironwood(*Rhamnidium ferreum*).

Sapwood.	1.10	5.65	10.65	18.00	24.00
----------	------	------	-------	-------	-------

Heartwood.	1.10	5.65	10.65	18.00	24.00
------------	------	------	-------	-------	-------

White Pine(*Pinus strobus*).

Sapwood.	0.50	4.60	9.00	17.75	24.25
----------	------	------	------	-------	-------

Heartwood.	0.80	4.10	8.60	18.25	27.00
------------	------	------	------	-------	-------

Black Spruce(*Picea mariana*).

Sapwood.	0.85	5.20	10.45	20.00	25.00
----------	------	------	-------	-------	-------

Heartwood.	1.00	5.20	10.45	20.40	26.85
------------	------	------	-------	-------	-------

Table 1 (continued).

Relative Humidity %.	0.0	27.3	51.8	86.4	100.0
Vapor Pres. mm. Hg.	0	8	9	15	17.36
White Elm( <i>Ulmus americana</i> ).					
Sapwood.	0.80	4.45	9.95	19.35	24.20
Heartwood.	2.25	6.10	11.50	20.00	24.95
Soft Maple.					
Sapwood.	1.25	4.65	10.95	19.00	25.20
Heartwood.	0.95	4.65	11.45	20.35	24.85
Basswood( <i>Tilia glabra</i> ).					
Sapwood.	0.60	3.65	7.70	15.10	23.25
Heartwood.	0.55	4.05	9.50	19.25	26.10
Balsam( <i>Abies balsamea</i> ).					
Sapwood.	1.00	4.65	10.10	19.20	24.50
Heartwood.	2.35	5.40	10.75	20.00	24.80
White Spruce( <i>Picea glauca</i> ).					
Sapwood.	1.90	5.65	11.75	21.00	28.15
Heartwood.	1.60	5.65	11.75	21.00	28.15

Table 1 (continued).

Relative Humidity %.	0.0	17.3	51.8	86.4	100.0
Vapor Pres. mm. of Hg.	0	3	9	15	17.36

Yellow Birch(*Betula lutea*).

Sapwood.	0.65	3.85	9.55	20.65	24.40
Heartwood.	1.50	4.85	10.45	21.60	25.40

Hemlock(*Tsuga Canadensis*).

Sapwood.	2.10	5.55	12.25	20.50	26.70
Heartwood.	1.80	4.95	11.90	21.10	25.40

Black Cherry(*Prunus serotina*).

Sapwood.	1.70	4.80	11.50	21.80	27.20
Heartwood.	1.80	5.05	11.30	21.60	27.70

Sugar Maple(*Acer saccharum*).

Sapwood.	1.40	4.15	10.20	19.40	23.40
Heartwood.	1.60	4.80	13.40	21.30	24.80

White Birch(*Betula papyrifera*).

Sapwood.	0.90	3.95	10.30	22.00	26.50
Heartwood.	1.25	4.50	10.65	23.00	27.65



Table 1 (continued).

Relative Humidity %.	0.0	17.3	51.8	86.4	100.0
Vapor Pres. mm. of Hg.	0	3	9	15	17.36

Beech(*Fagus grandifolia*).

Sapwood.	1.40	5.60	12.20	18.15	25.10
Heartwood.	1.85	5.95	12.75	22.75	28.80

White Ash(*Fraxinus americana*).

Sapwood.	1.35	5.85	11.40	18.90	24.75
Heartwood.	0.95	5.70	11.85	19.90	24.95

Eastern Cedar(*Juniperus virginiana*).

Sapwood.	1.65	5.75	10.65	13.35	22.35
Heartwood.	1.85	6.05	12.60	22.25	27.80

Aspen(*Populus tremuloides*).

Sapwood.	0.60	4.05	9.80	20.50	27.75
Heartwood.	1.90	5.15	10.80	22.00	30.60

Larch(*Larix occidentalis*).

Sapwood.	3.40	7.20	12.45	21.60	26.50
Heartwood.	1.80	6.25	12.95	23.00	28.95

An attempt has been made to correlate the variation in the sorption of the various woods, with some of their other physical properties, such as density and hardness, but without success. The most important generalization, to be found, is the great similarity in the amount of sorption for all the woods examined to date. This point will be elaborated, shortly, in connection with the sorption isotherms for cotton and for extracted wood.

It is of interest to note that of the twenty woods examined, in eleven the heartwood has the greater sorption, in six they are approximately the same, and in only three is there distinctly greater sorption in the sapwood. This means that as a rule the heartwood has a greater sorption than the sapwood.

Below is given a table (Table 2) in which all the values, given above, have been averaged. These, therefore, may be taken as the average sorption values for woods. Here it is again brought out that the heartwood has a greater sorption than the sapwood. By inspection the average is seen to be very close to any of the values given in Table 1.

The values obtained for extracted wood are for two samples which gave practically identical values. The

extraction was carried out in the usual manner, The wood was refluxed, at the boiling point, for four periods of twenty four hours, in a 1% sodium hydroxide solution in an atmosphere of nitrogen. The sodium hydroxide solution was replaced each day by a fresh solution.

The desorption values for cotton (1). were determined on a rag cotton obtained from Eastman Kodak Co., and which had been subjected to careful purification. The values for cotton (2). are the desorption values obtained by Urquhart and Williams (7)

Table 2.

Average Sorption Values for Woods  
and for two Cottons.

Relative					
Humidity %.	0.0	17.3	51.8	86.4	100.0
Vapor Pres.					
mm. Hg.	0.0	3.	9	15	17.36

Average Sorption Value for Wood.

Sapwood.	1.30	4.90	10.50	19.0	25.10
Heartwood.	1.50	5.20	11.10	20.4	26.10
Average.	1.40	5.05	10.80	19.70	25.60

Table 2(continued).

## Desorption Values for Extracted White Spruce.

Relative

Humidity %.	0.0	17.3	51.8	86.4	100.0
-------------	-----	------	------	------	-------

Vapor Pres.

mm.Hg.	0	3	9	15	17.36
Sapwood	1.70	5.25	10.70	21.25	25.10
Heartwood.	1.75	5.00	10.10	19.10	26.80
Average.	1.70	5.10	10.40	20.20	25.90

## Desorption Values for Unextracted White Spruce.

Sapwood.	1.90	5.65	11.75	21.00	28.15
Heartwood.	1.60	5.65	11.75	21.00	28.15

## Desorption Values for Cotton Cellulose.

Cotton(1).	0.90	2.80	5.70	12.15	18.50
Cotton(2).	1.40	3.30	6.85	13.30	(22.60).

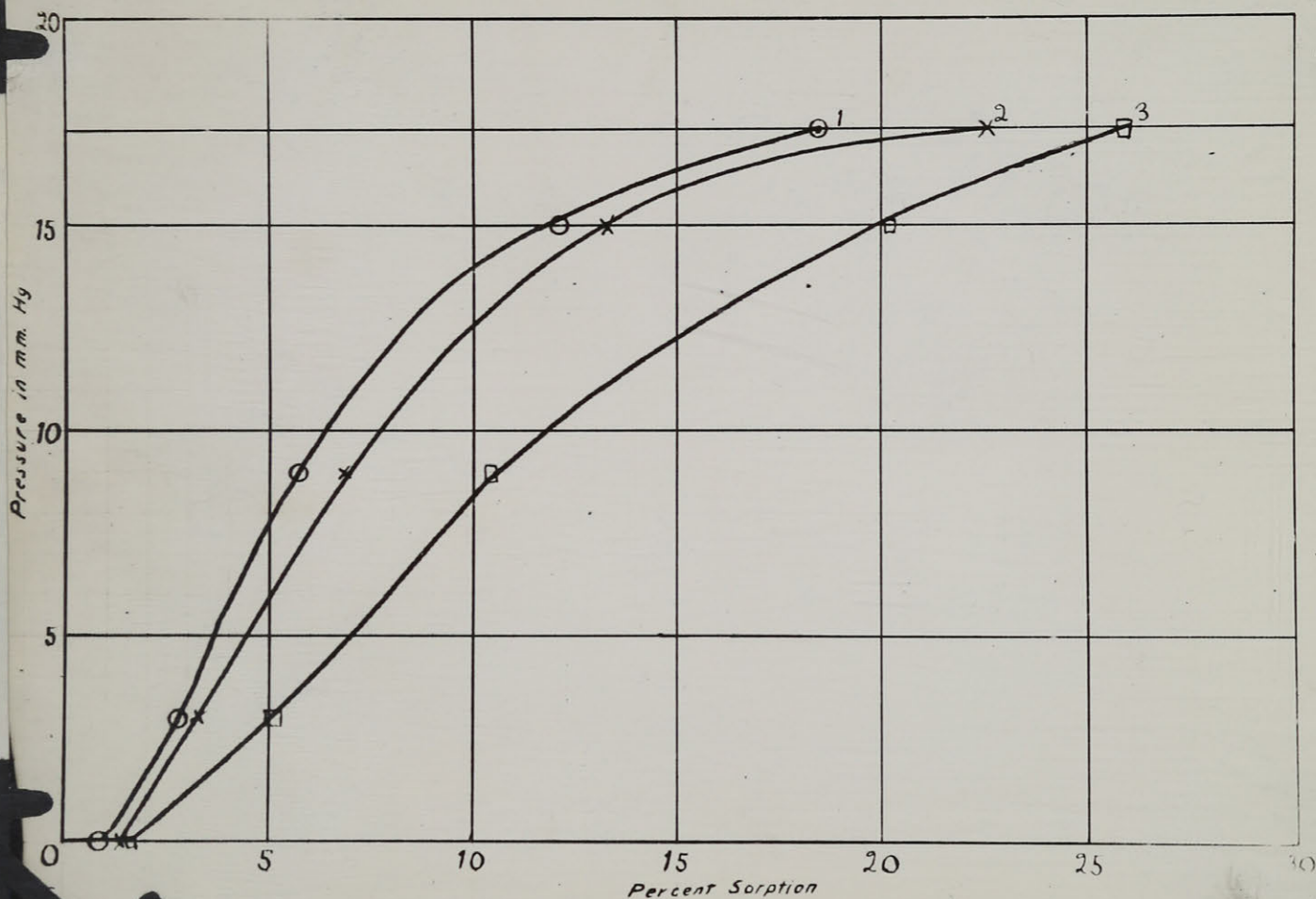
The method used by Urquhart and Williams in determining the value at 100% humidity is entirely different from that described here. This value is open to serious question, as determined by these investigators.

Figures 7 and 8 give a graphical representation of the data listed above.

It is clearly brought out from the above table, that the extraction, which has removed all the carbohydrates resins etc. and left only the cellulose

Figure 7.

Average Sorption Values for Wood and Cellulose.



Curve 1 Rag Cotton.

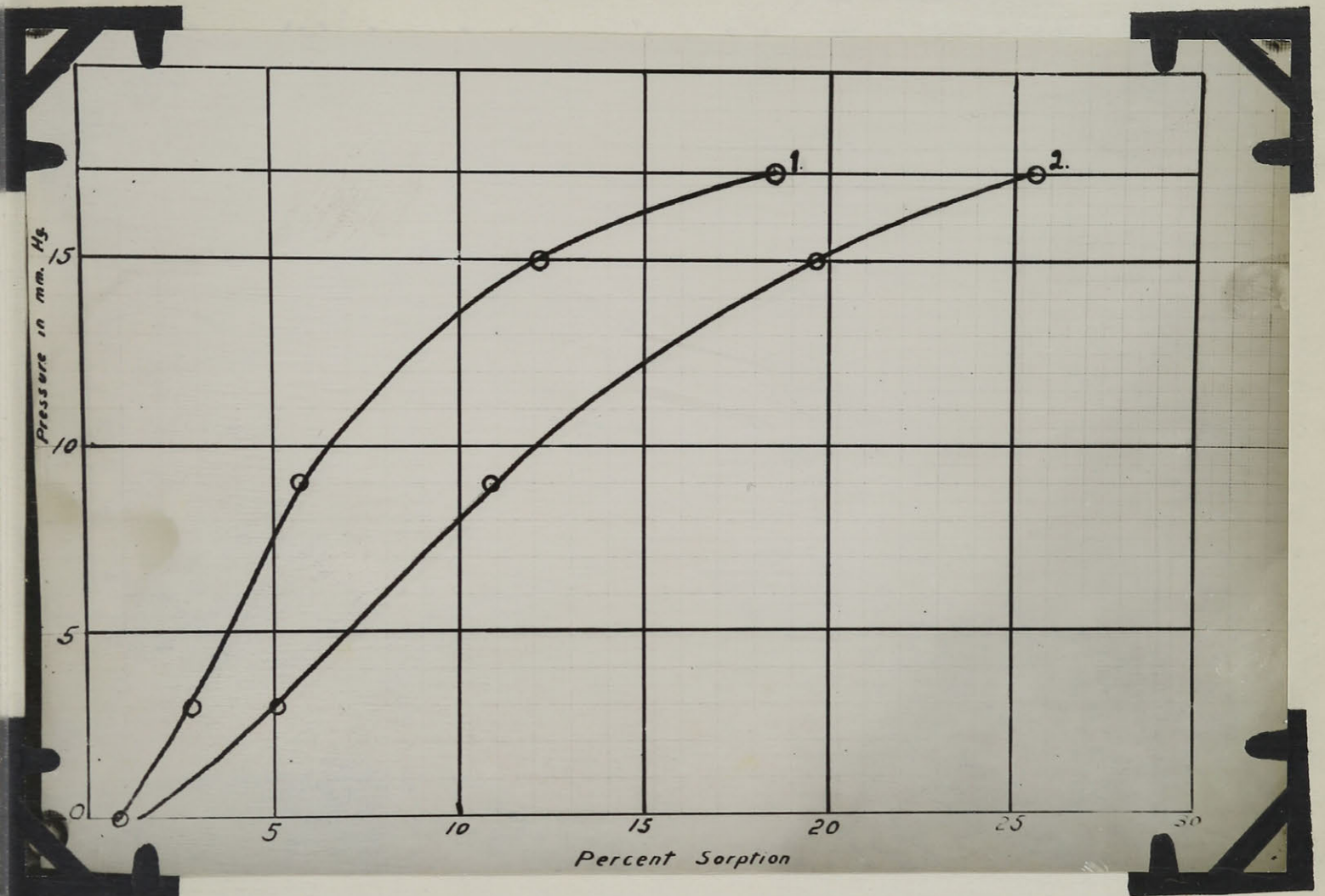
" 2 Cotton by Urquhart and Williams.

" 3 Average Value for Wood.



Figure 8.

Sorption Isotherms for Extracted Wood and Rag Cotton.



Curve 1 Rag Cotton.

" 2 Extracted White Spruce.

and most of the lignin, has reduced the sorption by only very little. This reduction is mostly in the region of high relative humidity, where the gross structure of the material plays a part.

It follows definitely, that the experiments of Pidgeon(1). have been corroborated. These experiments showed, that the sorption of water vapor by wood is on a much greater scale, than the sorption by cotton.

This is true over the whole range of vapor pressures, both for the wood in its natural state, and for the extracted samples.

#### The Influence of Heat Treatment of Wood and Cotton.

The reversibility of the sorption of water vapor by cotton, has been given some attention. The experimental results, in this connection, will be found in the appendix. Following evacuation at 50<sup>o</sup> C and redetermination of the sorption values, only at low relative humidities, it is found that there is a slight loss in sorptive capacity. This is also true after treatment at 75<sup>o</sup> C, however, in this case, the values are a little closer to those obtained initially. A third heat treatment, two hour periods are always used, at 90<sup>o</sup> C and redetermination of

the sorption values resulted in exact duplication of the initial sorption values.

In the case of extracted white spruce the results are definitely different. Following treatment at 50<sup>0</sup> C. there is a marked increase in sorption. A further, yet definite, increase is again observed after heating at 75<sup>0</sup> C. However, after evacuation at 100<sup>0</sup> C. there is a return to the original set of values, an approximate duplication of the initial sorption values is found.

With unextracted white spruce the results are very similar to those noted above. However, following the highest heating instead of the initial values being reproduced, there is an apparent decrease in the amount of water vapor sorbed. While the magnitude of this difference is not great, the fact appears to be quite definite.

Thus, the moderate temperature changes involved result in no pronounced alteration in the colloid systems concerned. The close similarity in the behavior of cotton and the extracted wood, following the highest temperatures, is apparent. Further, the slight permanent effect noted with the unextracted wood is of interest. These results would suggest that the irreversible change might



probably be due to some definite alteration in the non-cellulose constituents of the wood.

If a sample of cotton or wood is saturated with water vapor, and then exposed to the vacuum, the original dry weight is exactly reproduced in all cases. If the drying process includes heat treatment, conditions are somewhat changed. Wood; white spruce, loses from 0.33% to 0.57% in weight if evacuated at a temperature of 50°C. for a period of two hours. On cooling, and permitting the sample to remain in contact with the phosphorous pentoxide tube, this loss in weight remains unaltered. Further, if the heat treatment is raised to 75°C. and then 100°C. no appreciable increase in the loss of weight is indicated.

Similar treatment of cotton results in slightly different behavior. If cotton is heated to 50°C. a loss in weight of 0.57% is observed. However, this loss in weight is not constant as is the case with wood, on opening contact to the drying tube a gain in weight is noticed. After roughly one hour the exact original weight is apparent. This was checked by reheating and then admitting air. Under these conditions no change in weight occurs in one hour.

That this increase in weight should be due to the sorption of water vapor from the phosphorous pentoxide seems highly improbable. However, the phenomenon of an increase in weight by cellulose over phosphorous pentoxide, following a change in the temperature , has also been noted by John and Wise (10).

### The Sorption of Hydrochloric Acid by Wood and Cellulose.

When cellulose is brought into an aqueous solution of hydrochloric acid it hydrolyzes, the cotton undergoes a marked change in physical properties. No measurements of the sorption of hydrochloric acid gas in cotton and wood, as far as the writer knows, have been carried out. In view of the change mentioned above, such an investigation is of considerable interest.

It should, perhaps, be mentioned that most carefully prepared hydrochloric acid was used, C.P. reagents were employed. The gas was bubbled through two wash bottles of concentrated sulphuric acid, and finally over two phosphorous pentoxide tubes. This ensured a perfectly dry sample of gas coming into contact with the wood and cotton under investigation.

The first experiments, attempted, were with a dry cotton, and it became apparent, that equilibrium was only brought about in a very long time. Below are the sorption values that were obtained. From the flattening out of the time curve they are supposedly equilibrium values, each is the result of a ninety hours experiment. It is seen that quite appreciable amounts of hydrochloric acid are absorbed, and the first question that arose <sup>was</sup> whether or not the absorption was reversible.

# Sorption of Hydrochloric Acid by Cotton Cellulose.

Equilibrium value at 5.40 cms. press. of gas 0.80%

" " " 70.20 " " " 2.00%.

## Sorption against Time.

Time(hours).	% Sorption.
17	1.26
28	1.49
52	1.61
64	1.83
70	1.90
87	1.95
94	1.95

(Final gas pressure 70.20 cms. Temperature 22°C.).

On applying the vacuum, the hydrochloric acid came off fairly readily until 0.80% was left. There had been little change in the appearance of the sample. Only at the higher hydrochloric acid pressure did it take on a greyish tinge. On heating in vacuo, at 50°C., the last trace of hydrochloric acid was driven off, and the original dry weight of the sample was reached. It was judged that the hydrochloric acid was absorbed by the cotton and could be desorbed, but the time required for equilibrium to

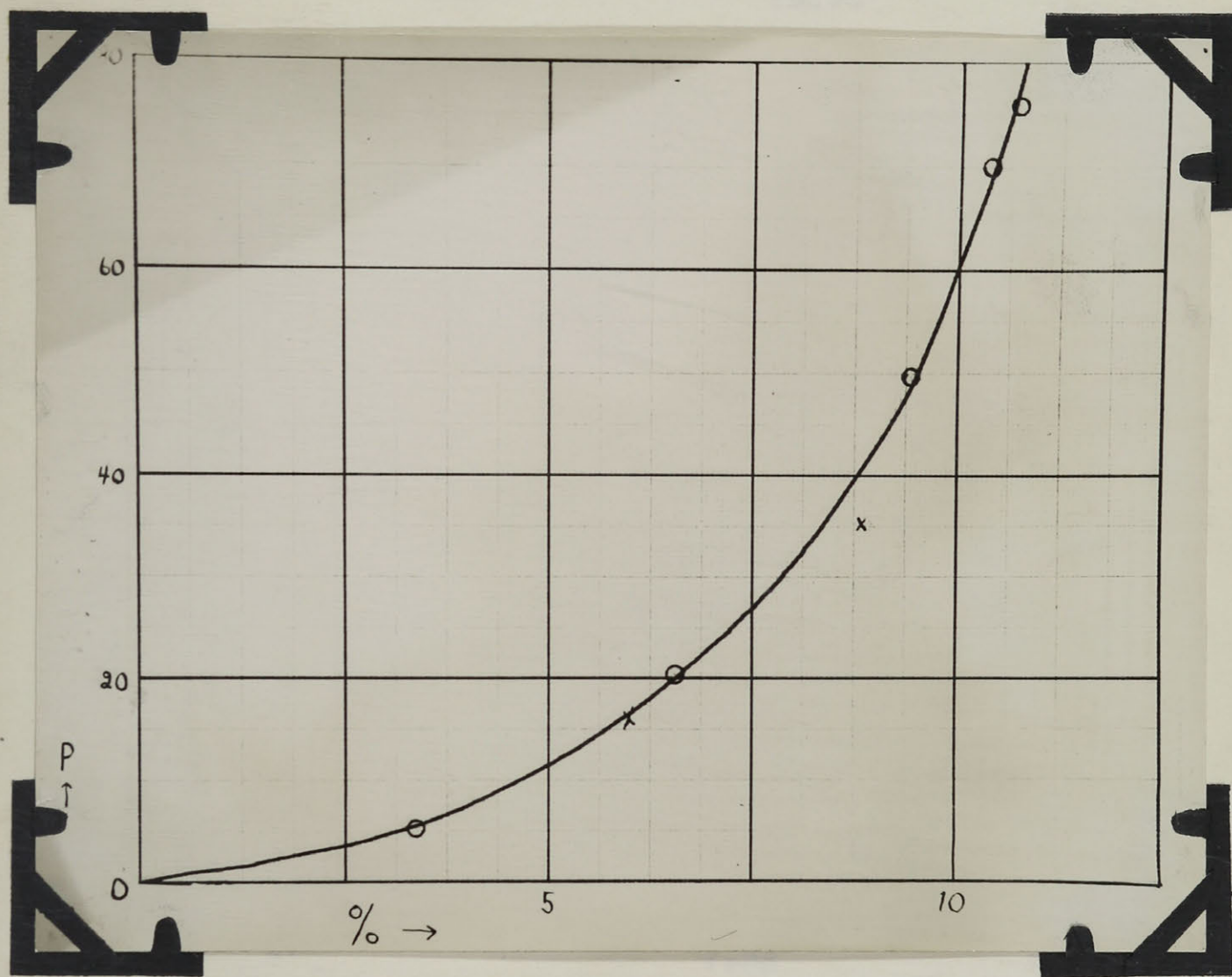
be reached, made it impractical to carry out a detailed sorption isotherm.

When the cotton was replaced by a sample of white spruce, heartwood, it was found that equilibrium was established much more rapidly, only one third of the time being required. The equilibrium values for sorption are given below, and also the data for a typical time curve. Column 1 indicates that two samples were used, and the sorptions obtained(col.2) at various pressures of hydrochloric acid(col.3) are shown in figure 9 to lie on a smooth curve. To test out desorption sample one, after having been maintained at a pressure of 76.90 cms., was kept until equilibrium resulted at a pressure of 35.40 cms. This gave a desorption value of 8.97%, which it is seen, lies fairly well on the absorption isotherm, indicating that there is little or no hysteresis. This, of course, will have to be confirmed when time permits, with further experiments. In a vacuum, the absorbed hydrochloric acid was taken out fairly rapidly until a residue of 2.24% was reached after twenty four hours.

45(a)

Figure 9.

Sorption Isotherm for HCl on White Spruce Heartwood.



Sorption of Hydrochloric Acid by White Spruce.

Sample.	% Sorption.	Pressure (cms.Hg).
---------	-------------	--------------------

1	3.38	5.50
---	------	------

1	7.60	20.09
---	------	-------

2	9.40	49.60
---	------	-------

1	10.37	70.60
---	-------	-------

2	10.71	76.90
---	-------	-------

Desorption Equilibrium Values.

1	8.97	35.40
---	------	-------

2	7.01	16.00
---	------	-------

.....  
Sorption against Time.

Time (hours).	% Sorption.
---------------	-------------

1/2	2.54
-----	------

2	4.08
---	------

3	4.43
---	------

4	5.23
---	------

5 3/4	5.53
-------	------

7 2/3	5.83
-------	------

10	6.02
----	------

21	6.72
----	------

24	6.93
----	------

27	7.32
----	------

31	7.42
----	------

(Final pressure 20.09cms. Temperature 22° C.).

## Desorption of Hydrochloric Acid against Time.

(Initial value 10.71% HCl).

Time(hours).	% Sorption.
1/4	8.57
1/2	7.67
1	6.82
1 3/4	5.63
3 1/4	4.83
7	3.13
13	2.74
23 1/2	2.24

.....

The form of the isothermal sorption curve is apparently quite different from the sorption curve with water vapor, and approaches more nearly to the form of a Freundlich adsorption. It is true that in terms of relative vapor pressures-as far as hydrochloric acid is concerned-it is only a tiny fraction of the saturation value that has been examined. But the criteria for similarity is found in the sharp upturn of the curve. Before discussing this phase any further it is worth considering the experiments carried out with wood samples containing a definite amount of water. Because in these cases,also, sorption



curves were obtained similar in character to that of hydrochloric acid in dry wood.

The experimental procedure consisted in suspending a sample from the spiral and first of all bringing it down to dry weight. Then water vapor was brought into contact, until a desired amount of absorption had taken place. The stopcock, leading to the water bulb, was then closed, and hydrochloric acid admitted to the desired vapor pressure. The latter was always many times that of the residual water vapor remaining in the apparatus, so that further absorption of water vapor could be neglected in comparison to the striking increase in sorption, which is to be discussed. A calculation shows that the maximum possible error is in the order of  $1/2\%$  of the dry weight of wood, and it is very unlikely that this would be reached. The direction in which error would take place would be, of course, to give an added apparent sorption of hydrochloric acid. As a matter of fact, the addition of hydrochloric acid will sweep any residual water vapor on to the walls of the containing vessel. This was made apparent in the case of highest water vapor pressure by the formation of a very fine mist. The experimental results follow.

# **Sorption of HCl by White Spruce containing Water.**

(Amount of water absorbed by wood 1.67%).

% HCl.	% HCl.	% HCl.	V.P.
	(Held by water).	(IN wood).	(cm.Hg).
5.38	0.86	4.52	11.60
8.83	1.04	7.79	40.60
11.22	1.16	10.06	74.70

.....

(Amount of water absorbed by wood 3.29%).

5.24	1.64	3.60	5.30
6.97	1.73	5.24	11.00
8.40	1.82	6.58	21.30
10.26	2.19	8.07	40.70
11.24	2.37	8.87	76.00

.....

(Amount of water absorbed by wood 5.05%).

10.50	2.49	8.01	11.70
13.08	3.04	10.04	41.00
14.22	3.36	10.86	73.00

.....

(Amount of water absorbed by wood 7.46%).

11.55	3.82	7.73	9.70
15.63	4.70	10.93	41.00
17.17	5.22	11.95	74.30

.....

## Sorption of HCl by White Spruce containing water.

% HCl.	% HCl.	% HCl.	V.P.
(Held by water).			(In Wood).
			(cm.Hg).

(Amount of water absorbed by wood			9.47%).
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15.74	5.16	10.58	11.50
-------	------	-------	-------

19.74	6.13	13.61	43.70
-------	------	-------	-------

22.46	6.84	15.62	73.80
-------	------	-------	-------

.....

(Amount of water absorbed by wood			12.30%).
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18.45	6.27	12.18	9.50
-------	------	-------	------

24.28	7.74	16.54	41.20
-------	------	-------	-------

27.04	8.61	18.43	72.40
-------	------	-------	-------

.....

The first column, in the above table, indicates the total amount of hydrochloric acid taken up by the system wood-water. The second column indicates the amount of hydrochloric acid calculated as dissolved in the water present, on the assumption that the water is unaltered. (The calculation is made from data found in Landolt Börnstein, page 1397). The third column represents the actual sorption by the wood. It is obtained by subtracting the amount of hydrochloric acid, calculated as existing in solution in the absorbed water, from the total amount of sorbed hydrochloric acid. The fourth column indicates the hydrochloric acid pressure at which the equilibrium point was determined.

It is of special interest to note that the equilibrium sorption values were reached more rapidly with wet wood than is the case with dry wood. The difference is most striking with wet and dry cotton. Whereas ninety hours were required with the dry cotton, three hours sufficed when water was present. The comparative data will be found in the appendix.

In the case of the ~~wet~~ samples evacuation brought the weight down to within 2% of the dry weight. After heating to 50<sup>o</sup> C. a semi-permanent increase of 1% was still observed. In the case of cotton, heating reduced the residual increase of 4.6% to an actual loss of 1.3% showing that some permanent change had taken place. However, a water absorption isotherm on such a sample showed very little change, except at the initial stage, where there was a decreased absorption. If the comparison is made with the initial absorption of a specially purified cotton, this is not so great. (The comparative data will be found in the appendix). In the case of wood, only the first part of the water isotherm was examined, and this, as with cotton, showed a small decrease in the water absorption of the hydrochloric acid treated wood.

By means of the data contained in the above tables a composite table can be formed, giving interesting information. This is given below.

Table 3.

The Sorption of HCl by White Spruce Heartwood.

<u>% Sorption.</u>							V.P. (cm.Hg).
<u>0%</u>	<u>1.67%</u>	<u>3.29%</u>	<u>5.05%</u>	<u>7.46%</u>	<u>9.47%</u>	<u>12.30%</u>	
3.20	3.20	3.35	6.40	7.00	9.30	11.15	5
5.70	4.25	4.90	7.67	7.85	10.20	12.20	10
7.40	5.60	6.52	8.87	9.15	11.50	13.95	20
8.27	6.80	7.50	9.45	10.00	12.55	15.30	30
8.90	7.72	8.05	9.98	10.70	13.35	16.35	40
9.35	8.55	8.37	10.37	11.20	14.05	17.20	50
9.86	9.25	8.60	10.62	11.55	14.75	17.90	60
10.36	9.90	8.79	10.80	11.70	15.40	18.35	70
10.54	10.10	8.87	10.87	11.90	15.80	18.50	75

This table is made up of values read off curves plotted for each of the runs which have just been given. Each column is headed by the percentage of water present. Since the first column gives values for the sorption of hydrochloric acid by dry wood, and since all the other values have been corrected for the acid held by the water, reading across in a horizontal manner one observes a range of hydrochloric acid sorptions at one gas pressure, but by samples with different amounts of absorbed water.

These results can be interpreted in a number of ways, and it is rather difficult to decide which is the correct interpretation. Suppose, first of all, one considers the water absorbed by the wood to be unchanged in its power to dissolve hydrochloric acid. Then the values in the table, which were calculated on this basis, show that in samples having less than 4% of absorbed water, the wood sorbs less hydrochloric acid, while above 4% it sorbs more hydrochloric acid, than the dry sample. On the other hand one might assume that the sorption of hydrochloric acid, on the wood, is unaltered, and that the absorbed water has changed in relation to its capability of dissolving hydrogen chloride. This would mean that the water absorbed in samples containing the highest percentages of water, dissolved hydrochloric acid better than ordinary water. The water absorbed to high percentages is, however, more likely to retain its usual characteristics than the first water that is absorbed. Doubtless the first 1 or 2% of water absorbed by wood will not have the same solvent action on the hydrogen chloride as ordinary water, but with increased water content the ordinary water properties should be approached more and more by the absorbed water.

Some experiments carried out on hydrochloric acid sorption by samples containing water left after desorption had taken place, are interesting in connection with what was said above. Two samples were first of all saturated with water vapor, then desorption was allowed to take place until a value was reached, as near as possible, to an absorption value. In the table below, 5.40% desorption is compared with a 5.05% absorption value, and a 7.88% water desorption value is compared with an absorption one of 7.46%.

Table 4.

<u>% Sorption.</u>				
<u>5.05 %</u>	<u>5.40 %</u>	<u>7.46 %</u>	<u>7.88 %</u>	V.P.
(Abs).	(Des).	(Abs).	(Des).	(mm. Hg).
6.40	4.30	7.00	5.35	5
7.67	5.35	7.85	6.00.	10
8.87	7.00	9.15	7.15	20
9.45	8.15	10.00	8.20	30
9.98	9.00	10.70	8.95	40
10.37	9.60	11.20	9.60	50
10.62	10.10	11.55	10.10	60
10.80	10.45	11.70	10.50	70
10.87	10.60	11.90	10.60	75

(The underlined values indicate the amount of water).

From the results of Table 3. the amount of hydrochloric acid sorbed increases with the amount of water present, above the 4% water sample. Thus, if the fact of the equilibrium water value being absorption or desorption is of no consequence, one would naturally expect the two "desorption" woods to take up the largest amount of acid, as each exceeds the "absorption" value by about 0.40%. However, both woods with the larger amount of water-but present as equilibrium desorption values-sorb decidedly less hydrogen chloride than the woods with less water-but water present through absorption. Apparently the wood has a lessened ability to take up acid when the water exists there following desorption.

In the above table (Table 4) is given the percentage sorbed on the dry wood, that is, after the hydrochloric acid dissolved in the water has been subtracted, as was described. Before discussing the reason for this, it is necessary to see whether any information can be obtained with regard to the nature of the hydrochloric acid sorption.

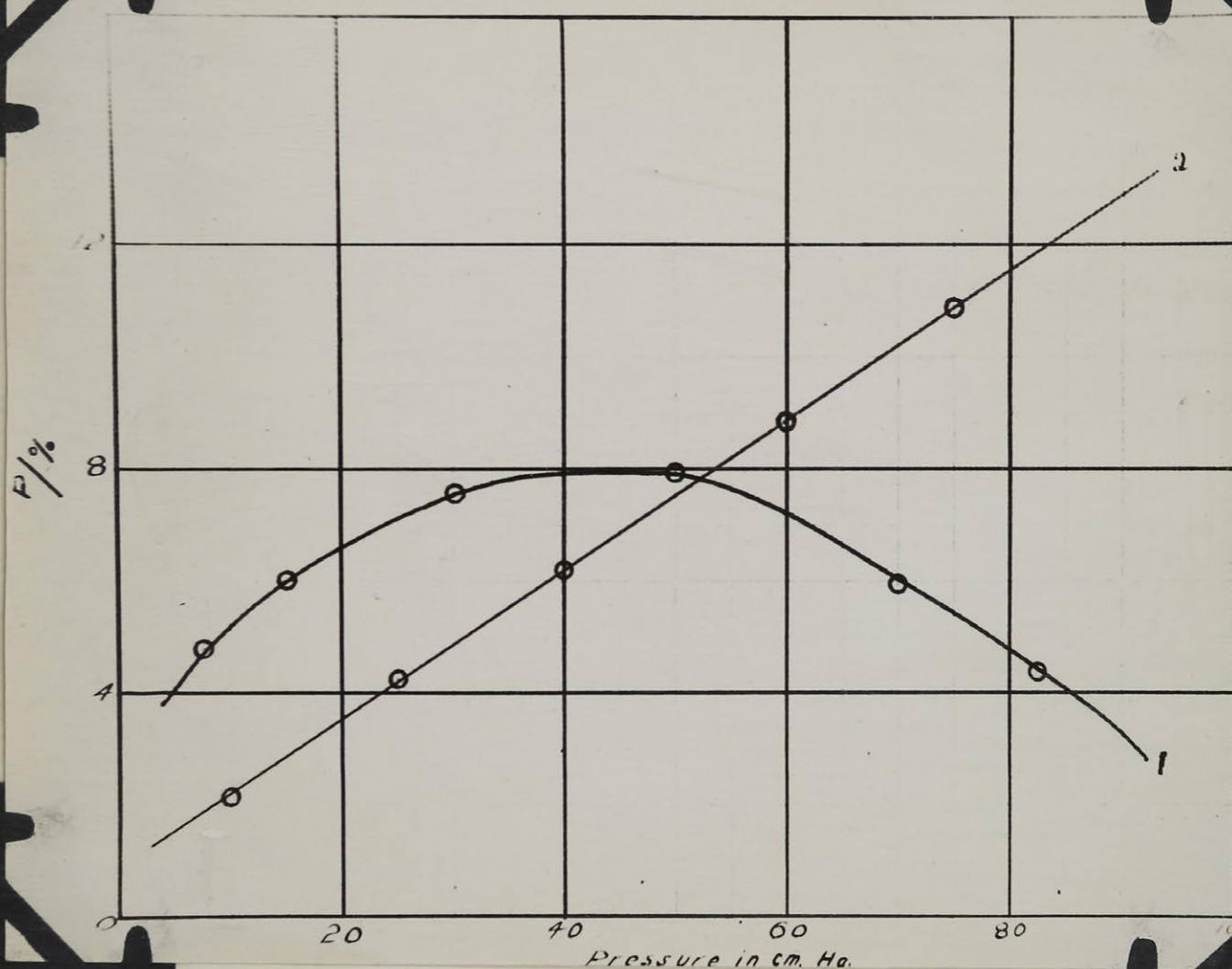
As was pointed out before, the absorption curve for hydrochloric acid has a different form from that



Figure 10.

Sorption Curves for Water on Cotton and HCl on Cotton + H<sub>2</sub>O .

(Plotted according to Langmuir's equation).



1. H<sub>2</sub>O on Cotton.

2. HCl on Cotton + H<sub>2</sub>O.

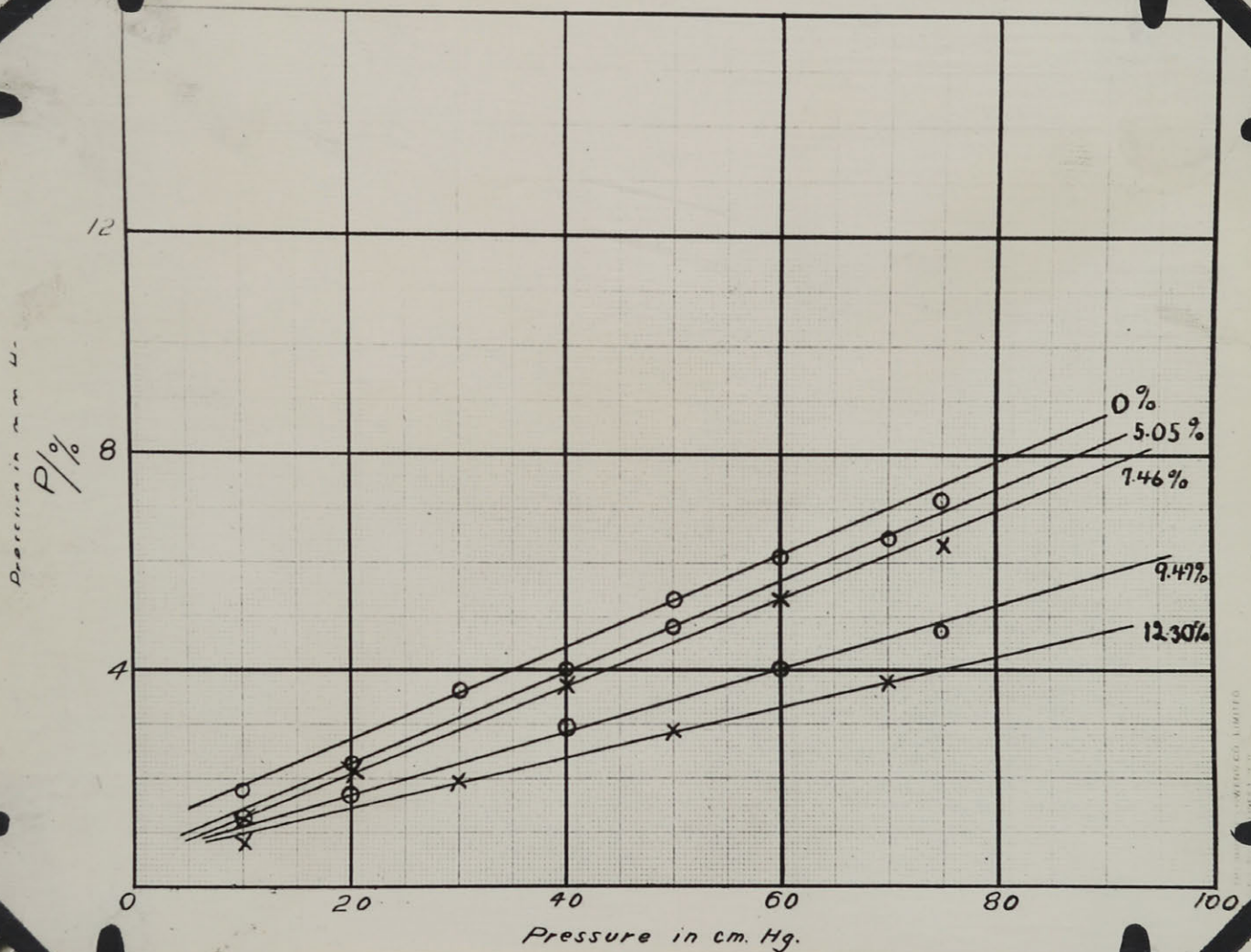
of the water sorption isotherms. If both of these are tested by applying Langmuir's adsorption formula

$$x/m = a b p / (1 + a p).$$

it is found that the water sorption ~~does not follow~~ this, whereas the hydrochloric acid sorption on dry cellulose does. In figure 10. curve 1. represents sorption of water in cellulose, "2" that of hydrochloric acid. According to McBain(11).the interpretation given is that in the case of HCl we are dealing with a straight surface adsorption, whereas in the case of water, part, at least, must be due to filling up of the interstices between the actual cellulose and part to absorption. If the hydrogen chloride sorption is surface adsorption, then the interpretation that can be given to the increased sorption of the wet samples (above 4% moisture content) is that the water increases the active surface of cellulose, on which adsorption takes place. In that case the application of Langmuir's formula to the data of Table 3 should also give straight lines. Figure 11 shows that this is the case. On each curve is indicated the percent of water. The only one not conforming to a straight line is the one just below 4% of sorbed water. The decrease in hydrochloric acid sorption below 4% water content, can then be

Figure 11.

The Sorption of HCl by wood with different amounts  
 of absorbed water.  
 (White Spruce).





explained by the active surface being partially used up by the adsorbed water. This effect will, of course, hold for all the other determinations, but is more than counterbalanced by the increase in active surface, caused by the addition of the larger amounts of water

The decrease in sorption, when water is left by desorption, can also be explained. The water, so held, is more intimately associated with the cellulose, as is shown by the lower vapor pressure of the water desorption point. This results in a greater decrease of the active sorbing surface available for the hydrochloric acid sorption.

The Sorption of Sulphur Dioxide, Ammonia and  
Carbon Dioxide by Wood and Cellulose.

Cotton cellulose takes up sulphur dioxide exceedingly slowly, over one hundred hours is required for the establishment of equilibrium. At a gas pressure of 76cms. and at 22°C. approximately 5.0% is sorbed. The last 0.80% of this is held very rigidly, ordinary evacuation does not, over a period of three days, remove this part of the sorbed gas. However, three hours of heating at 85°C. removed the last traces.

The sorption of sulphur dioxide evidently does effect some permanent alteration in the cellulose. The sorption values, indicated above are not reproducible. The second sorption, at an identical gas pressure, gives a sorption value of 3.09% as compared to 5.10% initially determined. Further, a water vapor sorption was determined on this sample (the experimental data is given in the appendix). The results show a slight change in sorptive capacity, in the region of high relative humidities. There is an increase in sorptive power comparable to that found in the case of hydrochloric acid treated cellulose.

A characteristically different behavior is noted when wood is considered. Spruce sapwood alone has been investigated.

There is a much greater amount of sulphur dioxide taken up by the wood, than is the case with cotton, 13.6% as compared to 5.0%. Further, the time to reach the true equilibrium condition is comparatively very small. Ten hours is the time interval at 76cms. pressure of the gas. Another marked difference is the much greater amount of the residual gas. After twenty four hours nearly 4% of the sorbed sulphur dioxide is still held by the wood. This is, however, readily removed on heating to 85<sup>0</sup>C.

In general, the results with ammonia are similar to those just mentioned. Approximately 4% of ammonia is sorbed by cotton cellulose at 76cms. pressure. Equilibrium takes roughly forty eight hours. However, the sorbed gas is very easily removed, one hour on the vacuum effects its complete removal.

As was the case with sulphur dioxide and wood, the latter takes up much more ammonia than does cotton. The equilibrium value is reached in about twelve hours, and indicates a sorption of 7.37% at 76cms pressure of ammonia. All but the last 1% of the sorbed ammonia is quite easily removed on evacuation. However, even heating to 95<sup>0</sup>C. still left a residue of 0.40%.

The work so far with sulphur dioxide and ammonia is merely introductory. However, even from such preliminary experiments, certain generalizations are apparent. With wood the attainment of equilibrium takes much less time than with pure cotton cellulose. The modifying influence of the non-cellulose constituents, as well perhaps, as its structure, evidently effect the sorbing system to a marked extent. Also the degree of sorption is quite different with the wood samples investigated. It is on a much larger scale.

Carbon dioxide is not appreciably sorbed by cellulose, up to a gas pressure of 76cms. Further, if the cotton cellulose contains 5.0% of absorbed water there is still absolutely no sorption evident. With wood, 1.07% of sorption takes place at a pressure of 42cms. Raising the pressure to 76cms. results in no increase in sorption. The sorbed gas is readily removed. Starting from 0 sorption and a pressure of 76cms. only 1.03% of carbon dioxide is sorbed. From 0 sorption and at 22cms. pressure, a sorption of 0.75% is observed. Apparently sorption becomes asymptotic to the value 1% somewhere between a gas pressure of 22cms. and 42cms. If wood contains 3.36% of water, there is absolutely no sorption of carbon dioxide by such a sample. The water completely inhibits the appreciable retention of carbon dioxide.

### Summary and Conclusions.

In the above heading the term conclusion must be taken as having a temporary character. Not only are the interpretations put to the results not unique in the sense that others of equal value might well be put forward, but also the necessity for more extended research is made apparent. Perhaps the most conclusive result that has been obtained is in regard to the sorption of water vapor in wood. In the first place, it was shown that the sorption of water vapor by any species of wood examined was very much greater than the sorption in cotton cellulose. In the second place, it was shown that the extent of sorption of one particular species of wood was a reproducible quantity<sup>it</sup>, that the variation from one species to another could very often be detected.

The similarity in the amount of sorption in sap and heart wood shows that there is very little difference in the character of what might be termed living and dead wood, the sorption in the sapwood is slightly less than in the heartwood.

The sorption of water vapor, according to the writers point of view, is a surface adsorption on the colloidal micelles which according to Clark(12)



very often consist of 8500 hexosan units. Consequently the amount of sorption can be looked upon as a measure of the extent of such a surface in the sample which is investigated.. To bring out what this is leading to, the following table has been compiled.

Table 5.

<u>Relative Humidity</u>	<u>17.2%</u>	<u>51.8%</u>	<u>86.4%</u>
	(% Sorption).		
Rag cotton.	2	4.35	10.15
(Sheppard&Newsome)			
cotton.	2	4.3	9.8
Hydrate cellulose A	2.96	7.20	13.50
" " " " B	2.0	8.75	15.50
" " " " C	3.80	9.20	17.02
(Campbell&Russel)			
Kraft pulp.	4.15	8.25	16.33
Wood(Hemlock).	4.6	9.1	19.70

.....

In the above table the cotton cellulose absorption values of the writer and of Sheppard and Newsome(13) have been chosen in preference to those of Urquhart and Williams(7) in view of the criticism of the method of these investigators mentioned in the introduction.

However, Urquhart and William's values do not differ enough from those quoted to alter the deductions about to be made. The values for hydrate cellulose are also taken from the paper by Sheppard and Newsome(13). The values for wood cellulose of Campbell and Russell have not, as yet, been published. This is unbleached cellulose prepared by the Kraft process and contains about 5 3% of lignin. Finally, the absorption values for Hemlock are given as obtained by the author.

In the first place it may be pointed out that so-called cellulose hydrate, or mercerized cotton, simply consists, according to accepted hypothesis, of cellulose with more free linkages for adsorbent purposes due to greater dispersion than in the original cotton. Hydrate cellulose A, B and C are in the order of the amount of dispersion. Then it may be pointed out that the sorption of extracted wood and of natural wood is practically identical. Extracted wood contains only lignin(from 20 to 25%) besides the cellulose. Methods of obtaining so-called lignin may involve a change in the latter's physical composition, however, that may be, Pidgeon and Maass (1) showed that such lignin has less water vapor sorption tendency than wood, and therefore than extracted wood. Thus the assumption may be justified that the

experiments with wood have shown that the cellulose present in the latter, has a far greater sorption capacity for water vapor, than cotton cellulose and perhaps, even than mercerized cotton.

The fact that dried wood shows less absorption than fresh wood(1) is in agreement with this point of view,, since a drying of the wood would tend to decrease the number of free linkages available for sorption.

The fact that the rate of sorption for wood is much greater , than the rate of sorption for cotton cellulose, is in agreement with the above. It is too early to venture to state just what part the lignin plays in the cellulose dispersion. Experiments will have to be carried out with extracted woods containing various amounts of lignin, in order to be able to assign an absolute value to the part in sorption played by the lignin and by the cellulose.

It is important to emphasize the fact that the cellulose found in wood is very similar to that which occurs in cotton. The x-ray spectra of ordinary wood is very similar to that of cotton and of extracted wood, the extractive process effects little change. Except insofar as the non-cellulose materials help to hold the cellulose fibres and constituent micelles

in position as a kind of cement, they have a negligible effect on the x-ray patterns. Thus, the considerations mentioned would seem to indicate that the lignin is present in a dispersed condition in the wood structure. Evidently no definite compound is formed with the cellulose crystals. Other investigators (14) have come to the conclusion that wood represents a complete intergrowth of carbohydrates and lignin, the latter being formed by adsorption and the formation of a gel on the surface of the cellulose fibres.

A realization of the fact of relatively great dispersion of the cellulose in wood seems to definitely favor the above concept as regards lignin. It would appear that the lignin was the dispersion medium, and that its protective presence stabilizes a fine dispersion of cellulose micelles.. In the process of paper-making the protective materials are removed. A temporary satisfying of the residual free surfaces occurs by loose union with water. As the drying process takes place definite agglomeration ~~takes~~ also occurs. If a Kraft pulp is desorbed the initial desorption values are quite close to those for the average wood. However, subsequent absorption gives

a series of values distinctly below those for a comparable wood absorption isotherm. This indicates that the initial behavior is typical of finely dispersed wood cellulose. After it has been dried there is an increase in the average particle size, followed by the inevitable decrease in the ability to absorb water vapor.

The amount of water sorbed, at zero humidity as given by the extrapolation of the sorption curve from 60% relative humidity down, might be considered as indicating the amount of water more definitely held and having a stoichiometric relation to the adsorbing surface.

In order to discuss sorption from the point of view of its fundamental nature, it is necessary to take into account the fundamental structure of cellulose. such as it occurs in nature, in cotton fibres. (See paper by Clark (12).) According to this the cellulose is a hexose, the next stage being two of these hexoses which appear to be more closely allied to one another as a glucoside. These glucosides form chains which theoretically may be of indefinite length. Actually, these chains are found to have an average cell length and to be bundled together to compose a unit crystal of cellulose

which is called a micelle. The dimensions of these micelles have been determined by x-ray analysis and by other means. They may be looked upon as forming parallelopipeds which are, on the average 500Å.U.)ong and 50Å .U. in cross section. From the x-ray analysis it is found that there are, on the average, 85 chains each containing 100 hexose units, so that there are 8500 units in one micelle.

If now adsorption is considered to take place only on the surface of these micelles, that is, if the water does not penetrate into the micelle itself, then two types of adsorption may be discussed. In the first place, if the adsorbent is one having specific secondary valences such as water<sup>as</sup>(an account of its oxygen atom) then such an absorption curve(as obtained with water) might well be explained. Because in that case all points of the surface of the micelle would not have equal adsorbing powers. In the second place, where pronounced secondary valences do not exist in the adsorbent, the surface alone would govern the amount of adsorption.

Taking up the case of the water adsorption first of all, the difference in the adsorption may be traced to the different latent valences of different points of the micelle surface. The eight corner hexoses of

the micelle must possess the greatest latent valence, next come the hexose groups around the edges of the ends of the micelle-48 in number. Then come the ends of the chains 120 in number, then possibly the four longitudinal edges containing 384 hexose groups and finally, the surfaces along the sides with 2350 hexose groups. If now we first consider one molecule of water adsorbed per hexose group existing at the surface, the percentage of water adsorbed on the eight corners corresponds to 0.01%, on the end edges 0.05%, on the ends 0.15%, along the remaining edges 0.45%, and on the remaining sides 2.7%. Those familiar with the theory of adsorption put forward by Langmuir and extended by H.S. Taylor will realize the hypothesis about to be discussed.

The water at the corners of the micelle 0.01% will be the most difficult to drive off and then will follow the other adsorbent portions of the surface in the order mentioned. The greatest difference occurring, probably, between the first four types that were mentioned and the last. If the first four are added together it will be seen that this corresponds to about 0.75% of water which is of the order of magnitude of the water adsorbed at zero vapor pressure, from

extrapolation of the experimental values. After this adsorption there follows the much more loosely held water on the surfaces other than the end. Here it is not unlikely that a value up to six molecules of water per unit of hexose will be reached. This would be what might be termed the saturation value, that is when the whole surface of the micelle is covered with a layer of water one molecule thick. This would correspond to some 20% of water adsorption. As is seen, these values are in agreement with the observed absorption curve, within the limits within which the calculation is justified. That the curve is a continuous one, and not broken at definite points, is to be expected. After all, the dimensions of the micelle, are from their nature only able to give average values, so that doubtless micelles, of smaller and greater dimensions exist, these gradations giving rise to the continuity found in the absorption curve. The so-called saturation value, found experimentally by several investigators of a higher percentage than mentioned above, may have to do with a filling up of the capillaries between the micelles, and from that point of view there is no limit to the amount of water which may continue to be sorbed.



From the point of view of the above hypothesis, the nature of the hysteresis may be explained.

Once those portions of the surface (edges and ends of the chains) are saturated, the remainder of the surface has not nearly the same affinity for the water. On the other hand, the surfaces of the various micelles must have a considerable affinity for one another, the partial valences coming into play there, being the origin of the strength of the fibre which the cells form. Consequently there is competition between the saturation of the secondary valence by cellulose surface for cellulose surface, and cellulose surface for water molecules. Originally the cellulose surfaces being together, a certain amount of energy is required to displace them before the water will take their place, either partially or completely. Consequently, the amount of adsorption with continued increase in concentration of water vapor lags behind a value which would be obtained were the micelle surfaces not acting upon one another. On desorption, that is with decreased concentration of water vapor, this hindrance has been removed, and the water adsorption has a greater value.

Both in mercerized cotton and in wood, x-ray analysis has shown the existence of the unit cellulose cell. The micelles however, are smaller thus

presenting a much larger surface for adsorption. The same type of curve and hysteresis is, therefore, to be expected, and the amount of adsorption, in a way, can be used for estimating the relative surfaces. From that point of view the micelles in wood probably, present the largest surface. The relation between the water adsorbed on the ends of the micelles and along the edges, to the further surface adsorption, must have definite relationships, from geometrical considerations. One of the important conclusions of the work described, is the realization that this point is worth consideration, by an extended investigation over the low relative humidity range, attention being paid to the obtaining of the greatest possible precision. But already, from these results it is seen that an increase in the total absorption is accompanied by an increase in the adsorption on the selective part of the surface, where the water is most firmly held. In the case of wood this value is 1.40% as compared to 0.90% for cotton cellulose, and Dr. Campbell obtained about 2% with an unbleached Kraft pulp, with the corresponding increase in the total absorption.

The hypothesis put forward above is of a highly speculative character and may not be in agreement

with all the facts. It may serve a useful purpose though, in stimulating further experimentation along certain lines. For instance it may just be possible that the difference between the various forms of cellulose may be brought down to a question of a limiting number of carbon chains going to form the bundle in one micelle. Work is being carried out in connection with sodium hydroxide adsorption which may prove to be of interest in this regard.

The sorption of hydrochloric acid appears to be in the nature of an adsorption on the surface which everywhere, has equal potentialities of adsorption. There does not exist the same affinity between the hydrochloric acid and the micelle surface that seems to exist in the case of the water adsorption. As was pointed out before, the presence of the water seems to increase the available surface and this can be reconciled with the ideas put forward above. There is an indication of a residual adsorption at zero vapor pressure, this is rather against the hypothesis as indicating a selective surface adsorption. However, this residual adsorption is not the same as the extrapolated value discussed in the water adsorption, but is more in the nature of a permanent adsorption which a continued evacuation at low

temperature will not remove. It is probable that it is directly connected with a chemical change which has taken place in the cellulose. That the hydrochloric acid does not hydrolyze the cellulose is indicated by its unchanged sorption of water vapor on the removal of the hydrochloric acid. The nature of this permanent adsorption must, of course, be investigated still further.

## References.

- (1) Pidgeon and Maass. J.A.C.S. 52. 1053. (1930).
- (2) Pidgeon and Maass. Can. Jour.Res. 2. 318. (1930)
- (3) Tieman, U.S. Dept. Agr. Forest Service Bull.  
70, 82, (1906)
- (4) Myer and Rees, New York State College of Forestry,  
Tech. Bull. 26, No. 19. (1926).
- (5) Hawley and Wise, "The Chemistry of Wood", page 286,  
data of Dunlap, U.S. Forest Products Lab. (1929).
- (6) Stamm, Ind. Eng. Chem. Anal. Ed. 1, 94. (1929).
- (7) Urquhart and Williams, Shirely Institute Memoirs  
3, 197. (1924).
- (8) McBain and Bakr, J.A.C.S. 48, 694 (1926).
- (9) Hawley and Wise, "The Chemistry of Wood", McKenzie  
unpublished report, U.S. Forest Products Lab.
- (10) John and Wise, Paper Industry, 10, 248 (1928).
- (11) McBain, Lucas and Chapman, J.A.C.S. 52, 2668 (1930).
- (12) Clark, Ind. Eng. Chem. 22, 474. (1930).
- (13) Sheppard and Newsome, Jour.Phys.Chem. 33, 1817 (1929).
- (14) Kruschner, T.A.P.P.I. 11, 1, 100. (1928).

## Appendix.

In the following compilation of experimental data, the sample weight is not specified each time. The minimum weight of sample was 0.0850 gms. and the maximum was about 0.1380 gms. On the average the weight of the samples used in this investigation was 0.1070 gms.

## (1).The Sorption of Water Vapor against Time.

## Hemlock.

Time (min).	Sapwood.	Heartwood.
2	2.89	1.71
5	3.83	2.60
10	5.13	3.75
15	5.78	4.58
20	6.16	4.77
30	6.34	5.08
40	6.44	5.21
50	6.34	5.28
55	6.34	5.40
60	6.34	5.40

## Sugar Maple.

Time(min).	Sapwood.	Heartwood.
2	2.22	2.02
5	2.73	3.20
10	3.67	4.04
15	4.01	4.76
20	4.35	4.98
25	4.61	5.11
30	4.78	5.25
40	4.69	5.38
50	4.69	5.43
60	4.69	5.52
75		5.52

## Cherry.

Time(min).	Sapwood.	Heartwood.
2	1.911	1.12
5	2.27	2.18
10	3.59	3.23
15	4.41	3.76
20	4.50	4.13
25	4.63	4.51
35	4.77	4.69
40	4.86	4.81
50	5.00	4.88
60	5.00	4.88

## (2) The Water Vapor Equilibria of Canadian Woods.

(The temperature of the thermostat is 20°C in all cases)

## Red Pine

Sapwood.	Heartwood.	Vapor Pressure.
per cent Sorption	per cent Sorption	mm. Hg.
2.21	2.16	0.79
4.00	3.19	1.97
6.38	6.20	4.57
7.94	7.73	6.51
9.65		9.14
12.95	12.17	12.67
15.96	15.14	14.39
22.38	19.48	16.32

## Red Oak.

Sapwood.	Heartwood.	Vapor Pressure.
per cent Sorption	per cent Sorption	mm..Hg.
2.19	3.84	0.79
2.88	4.39	1.97
6.11	7.01	4.57
7.82	8.63	6.51
9.77	10.52	9.14
12.78	12.14	12.67
15.62	15.25	14.39
20.38	18.98	16.32



## Ironwood.

Sapwood	Heartwood	Vapor Pressure.
per cent Sorption	per cent Sorption	mm. Hg.
2.49	2.48	0.79
3.75	4.31	1.97
7.45	7.36	4.57
8.39	8.75	6.51
11.14	11.20	9.14
13.31	13.76	12.67
17.36	16.57	14.39
21.81	21.91	16.32

## White Pine

Sapwood	Heartwood	Vapor Pressure
per cent Sorption	per cent Sorption	mm. Hg.
1.46	1.64	0.79
3.51	3.26	1.97
5.92	5.71	4.57
7.45	6.99	6.51
9.05	7.86	9.14
12.28	12.67	12.67
17.32	18.77	14.39
22.00	24.67	16.32

## Black Spruce

Sapwood.	Heartwood.	Vapor Pressure.
per cent Sorption	per cent Sorption	mm. Hg.
1.82	2.13	0.79
4.38	4.11	1.97
6.64	6.71	4.57
8.83	8.69	6.51
10.73	10.44	9.14
14.09	14.03	12.67
20.01	20.27	14.39
23.30	24.84	16.32

## White Elm.

Sapwood.	Heartwood.	Vapor Pressure.
per cent Sorption	per cent Sorption	mm. Hg.
2.20	2.75	0.79
3.17	4.55	1.97
6.08	8.03	4.57
7.92	10.53	6.51
9.60	11.51	9.14
13.65	14.82	12.67
18.06	18.66	14.39
22.02	22.68	16.52

## Soft Maple.

Sapwood	Heartwood	Vapor Pressure.
per cent Sorption	per cent Sorption	mm. Hg.
2.26	1.98	0.79
3.87	2.97	1.97
6.26	6.55	4.57
8.15	8.63	6.51
12.02	11.71	9.14
14.91	16.38	12.67
17.69	19.16	14.39
22.66	22.93	16.32

## Basswood

Sapwood	Heartwood	Vapor Pressure
per cent Sorption	per cent Sorption	mm. Hg.
1.26	1.11	0.79
2.62	3.33	1.97
5.05	4.70	4.57
6.41	7.11	6.51
7.76	9.33	9.14
11.16	13.89	12.67
	18.33	14.39
	24.22	16.32

## Balsam

Sapwood	Heartwood	Vapor Pressure
per cent Sorption	per cent Sorption	mm. Hg.
2.08	3.01	0.79
3.12	4.17	1.97
6.36	6.96	4.57
8.21	9.28	6.51
10.28	10.79	9.14
14.22	15.42	12.67
18.26	18.91	14.39
22.10	22.50	16.32

## White Spruce

Sapwood	Heartwood	Vapor Pressure
per cent Sorption	per cent Sorption	mm. Hg.
2.74	2.31	0.79
4.11	4.18	1.97
7.37	7.40	4.57
8.95	9.25	6.51
11.48	11.88	9.14
15.91	15.74	12.67
20.23	20.37	14.39
24.44	24.76	16.32

## White Birch

Sapwood	Heartwood	Vapor Pressure
per cent Sorption	per cent Sorption	mm. Hg.
1.51	1.99	0.79
3.02	3.04	1.97
5.91	6.30	4.57
7.63	7.85	6.51
10.49	10.79	9.14
17.54	18.65	12.67
20.52	21.57	14.39
24.84	25.82	16.32

## Yellow Birch

Sapwood	Heartwood	Vapor Pressure
per cent Sorption	per cent Sorption	mm. Hg.
1.31	2.19	0.79
3.01	3.18	1.97
5.48	6.53	4.57
6.86	8.23	6.51
9.61	10.39	9.14
17.34	17.40	12.67
19.65	20.49	14.39
22.63	23.76	16.32

## Aspen

Sapwood	Heartwood	Vapor Pressure
per cent Sorption	per cent Sorption	mm. Hg.
1.51	2.74	0.79
2.95	4.14	1.97
6.06	6.59	4.57
6.85	7.91	6.51
10.04	11.52	9.14
14.20	13.86	12.67
19.94	20.42	14.39
24.57	27.42	16.32

## Larch

Sapwood	Heartwood	Vapor Pressure
per cent Sorption	per cent Sorption	mm. Hg.
4.47	2.91	0.79
5.96	4.88	1.97
7.62	8.44	4.57
9.26	9.85	6.51
12.71	14.18	9.14
16.27	17.90	12.67
21.31	21.58	14.39
24.35	26.38	16.32

## Eastern Hemlock

Sapwood 1929.	Sapwood 1931.	Vapor Pressure.
p.c. Sorption	p.c. Sorption	mm. Hg.
2.95	2.86	0.79
4.22	4.92	1.97
7.50	7.50	4.57
9.96	9.56	6.51
12.06	13.03	9.14
15.10	17.26	12.67
19.23	21.01	14.39
23.11	24.29	16.32

Heartwood.'29.	Heartwood.'31.	Vapor Pressure.
p.c. Sorption	p.c. Sorption	mm. Hg.
2.21	2.79	0.79
3.75	4.07	1.97
7.06	6.47	4.57
9.02	8.84	6.51
11.48	11.83	9.14
15.32	17.62	12.67
20.17	20.92	14.39
23.31	23.44	16.32

## Black Cherry

Sapwood.'29.	Sapwood.'31.	Vapor Pressure.
p.c. Sorption	p.c. Sorption	mm. Hg.
2.09	2.34	0.79
3.94	4.02	1.97
6.46	6.93	4.57
8.97	8.77	6.51
11.49	12.11	9.14
15.85	16.93	12.67
20.05	21.06	14.39
24.31	25.45	16.32

Heartwood.'29.	Heartwood.'31.	Vapor Pressure.
p.c. Sorption	p.c. Sorption	mm. Hg.
2.06	2.51	0.79
3.57	4.13	1.97
6.81	6.83	4.57
8.87	8.83	6.51
11.47	10.97	9.14
16.14	17.02	12.67
20.98	19.69	14.39
25.62	25.37	16.32



## Sugar Maple

Sapwood.'29.	Sapwood.'31.	Vapor Pressure.
p.c. Sorption	p.c. Sorption	mm. Hg.
1.30	2.30	0.79
2.14	3.48	1.97
5.88	6.06	4.57
7.04	7.81	6.51
9.48	10.97	9.14
15.89	15.41	12.67
18.10	19.00	14.39
21.38	21.22	16.32

Heartwood.'29.	Heartwood.'31.	Vapor Pressure.
p.c. Sorption	p.c. Sorption	mm. Hg.
2.80	2.80	0.79
3.28	4.44	1.97
6.31	7.04	4.57
7.61	9.06	6.51
8.03	12.55	9.14
	17.20	12.67
20.75	20.92	14.39
23.08	23.95	16.32

## Spruce Sapwood

p.c. Absorption.	V.P.(mm.Hg).	p.c. Desorption.	V.P.(mm.Hg).
3.95	4.27	0.68	0.10
5.05	7.60	1.95	1.20
6.58	10.30	4.58	2.13
7.58	12.72	5.26	4.33
8.89	13.40	8.21	8.53
9.89	13.80	9.89	11.53
11.75	14.20		

## Beech

Absorption.	V.P.	Desorption.	V.P.
p.c. Sorption. (mm.Hg).		p.c. Sorption. (mm.Hg)	
0.37	0.37	1.94	0.41
1.94	1.29	2.41	0.61
3.78	2.71	3.97	1.69
4.72	4.48	5.00	2.64
6.95	8.30	7.87	5.19
11.31	12.50	10.37	7.12
19.37	17.23	18.81	15.55

## Beech Heartwood

Absorption.	V.P. (mm.Hg).	Desorption.	V.P. (mm.Hg).
%Sorpton		%Sorpton	
0.87	0.10	1.48	0.14
2.18	1.02	3.22	0.95
4.37	2.99	4.57	2.10
6.45	5.30	8.81	5.50
11.78	10.80	12.28	9.09
14.39	13.59	15.63	10.66
17.37	14.70	19.23	13.58
24.94	17.29	26.79	15.82

## Cedar Heartwood

1.53	0.41	0.24	0.00
1.93	0.68	2.06	0.14
2.06	0.75	2.66	0.54
3.02	1.97	6.03	3.12
4.48	3.56	6.79	3.60
5.32	5.22	7.34	4.55
6.65	6.38	8.84	5.29
9.19	7.88	10.65	7.13
11.01	9.70	10.76	7.91
13.32	11.85	13.68	9.84
16.21	14.39	18.77	13.10
21.07	15.01	24.57	15.95
22.51	16.55	24.69	16.36

## Cedar Sapwood

Absorption	V.P. (mm.Hg).	Desorption	V.P. (mm.Hg).
%Sorption		%Sorption	
0.91	0.27	2.05	0.41
1.94	0.88	2.51	0.68
2.63	1.49	3.65	1.29
3.42	2.24	4.34	1.83
4.34	3.60	5.48	3.12
5.36	4.83	7.31	5.02
8.22	8.55	9.58	7.20
11.30	11.41	12.55	10.70
12.31	13.24	16.65	14.32
20.66	17.03	20.52	16.90

## White Ash (sapwood)

1.88	0.52	1.88	0.33
3.40	1.91	2.11	0.46
5.28	4.20	2.58	0.72
6.69	6.04	3.43	1.25
8.45	7.95	4.86	2.10
10.44	10.58	5.40	3.42
11.96	11.82	7.39	4.53
13.61	13.47	12.09	9.33
17.37	14.92	15.26	12.02
21.83	15.90	18.31	14.92

## White Ash Heartwood.

Absorption.	V.P. (mm.Hg).	Desorption.	V.P. (mm.Hg).
%Sorption		%Sorption	
1.69	0.59	0.84	0.13
3.29	1.97	2.35	0.59
4.32	3.02	3.48	1.31
6.10	5.06	4.04	1.90
7.43	7.36	5.82	3.09
9.20	9.26	6.86	4.53
12.69	11.56	8.84	6.18
14.01	13.52	11.36	8.34
16.36	14.45	14.45	11.04
20.22	16.02	18.44	13.60
23.51	16.88	20.98	15.77

(3). The Water Vapor Equilibria of  
Extracted White Spruce

Extraction 1.

Sapwood	Heartwood	Vapor Pressure
%Sorption	%Sorption	mm. Hg.
2.21	2.89	0.79
4.10	4.37	1.97
6.52	5.92	4.57
7.78	7.03	6.51
11.04	9.53	9.14
15.93	13.36	12.67
21.30	17.03	14.39
26.45	22.89	16.32

Extraction 2.

Sapwood	Heartwood	Vapor Pressure
%Sorption	%Sorption	mm. Hg.
2.85	3.15	0.79
4.79	5.12	1.97
7.28	6.87	4.57
8.79	8.74	6.51
12.01	11.50	9.14
15.41	15.09	12.67
19.17	18.90	14.39
21.60	22.52	16.32

## (4) Water Vapor Equilibria for Cotton Cellulose.

## Ordinary Cotton Cellulose.

%Absorption.	V.P. (mm.Hg).	%Desorption.	V.P. (mm.Hg).
0.84	0.13	1.59	0.27
1.79	0.34	1.78	0.41
2.63	0.68	2.44	0.96
3.48	1.73	3.57	2.24
4.14	3.36	4.89	3.38
4.99	5.34	5.73	4.69
6.68	7.92	7.24	5.60
8.93	9.69	7.71	6.32
9.87	10.35	8.65	6.66

(Saturation pressure 11.14mm. Temperature 13°C.).

## Rag Cotton

Absorption.		V.P. (mm.Hg).	Desorption		V.P. (mm. Hg).
%Sorption			%Sorption		
1.	2.		1.	2.	
0.54	0.98	0.89	1.77	1.61	1.25
1.55	1.52	1.68	2.19	2.28	1.61
3.21	3.14	6.04	3.11	2.79	3.09
4.61	4.53	8.61	3.75	3.33	4.83
6.86	7.41	12.68	5.79	5.43	8.41
9.54	9.56	14.78	8.31	8.31	12.42
13.30	11.32	15.64	11.31	11.31	14.52
16.20	16.30	16.56			

(Saturation 17.36mm. Temperature 20°C.).

Moisture Equilibria for Rag Cotton

(Results by Cyclic Process)

% Sorption	Vapor Pressure (mm. Hg).
0.96	0.79
1.91	1.97
3.83	4.57
4.90	6.51
6.42	9.14
9.29	12.67
12.11	14.39
15.61	16.32

(Results at 20°C.).

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(5). The Reversibility of Sorption following

Heat Treatments of Wood and Cotton.

(All results determined at 22°C.).

<u>%Sorption</u>				
Initial.	50°C.	75°C.	90°C.	V.P. (mm.Hg).
3.60	2.90	3.12	3.57	4.57
2.37	2.12	2.08	2.25	1.97
1.67	1.68	1.82	1.55	0.79
1.41	1.42	1.55		0.29

(Results for, cotton cellulose).



(5). Heat Treatment of Extracted White Spruce.

1	<u>% Sorption</u>				
Initial.	50°C.	75°C.	100°C.	V.P. (mm.Hg).	
5.45	7.01	9.26	6.81	4.57	
4.15	4.22	6.69	4.22	1.97	
2.72	3.31	3.74	2.72	0.79	
1.56	1.09	1.77	1.29	0.29	
Sample 2.					
			90°C.		
6.75	7.30	7.43	7.02	4.57	
4.26	4.96	5.23	4.27	1.97	
2.75	3.30	3.58	3.16	0.79	
1.17	2.06	2.34	1.72	0.29	

(All results at 22°C.).

Heat Treatment of Unextracted White Spruce.

Initial value.

	<u>% Sorption.</u>	<u>Relative vapor pressure (%).</u>
Sample 1.	Sample 2.	
5.08	4.41	18.97
3.26	2.83	7.98
2.07	1.58	3.28

Following evacuation at 50°C.

4.71	4.94	18.20
3.64	3.18	8.89
2.66	2.38	3.65
2.04	1.47	1.35

## Heat Treatment of White Spruce Heartwood.

	% Sorption	Relative vapor pressure (%)
Sample 1.	Sample 2.	

Following evacuation at 75°C.

5.42	4.89	19.90
3.99	3.07	9.44
2.06	1.82	3.73

Following evacuation at 100°C.

4.69	4.08	21.38
3.26	2.89	9.21
1.97		3.52
1.39		1.36

(The foregoing was repeated with new samples).

Initial.

5.93	4.81	20.63
4.08	3.69	8.28
2.46	2.57	3.48
1.56	1.57	1.28

Following evacuation at 50°C.

6.20	5.04	20.14
4.38	3.13	8.47
2.63	2.01	3.52
1.81	1.45	1.29

Following evacuation at 75°C.

4.86	4.48	17.89
3.17	3.02	8.08
2.56	1.79	3.32

## (6) Water Sorption by Sulphur Dioxide Treated Cellulose.

(Temperature of thermostat 20°C.).

% Sorption	Vapor Pressure (mm. Hg.)
0.70	0.41
0.34	0.68
1.40	0.88
2.10	1.56
3.36	3.74
4.76	7.13
7.14	12.03
7.98	13.17
8.82	13.99
10.77	15.82
11.20	16.32

(These are desorption values).

## Sorption of Sulphur Dioxide by Spruce Sapwood.

% Sorption.	Time (hours)	V.P. (cms.Hg).
4.73	1	76
13.62	10	

## Removal of the sorbed gas

5.30	1
5.07	2
3.87	24

## (7) Sorption of Ammonia by Cotton Cellulose.

% Sorption	Time (Minutes)
1.19	5
1.58	10
1.98	20
2.08	40
2.18	60
2.38	120
2.58	17 (hours).

(Gas pressure was 76 cms. of Hg).

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## The Sorption of Ammonia by Beech Sapwood.

5.19	5
5.73	10
6.23	40
6.34	80
6.54	100
6.85	120
7.37	19 (hours)

## Desorption against time.

3.58	5
2.70	10
1.24	40
1.04	80
0.96	100
0.83	15 (hours)

## (8) The Sorption of Hydrochloric Acid by Moist Cotton.

## Sorption against Time.

(Amount of absorbed water 2.92%).

<u>Time (hours).</u>	<u>% HCl Sorbed</u>
1/4	2.91
1/2	3.39
1	3.86
1 1/2	4.15
2	4.24
3	4.33
13	4.42

(Final gas pressure was 10.40 cms. Hg).

On raising the pressure of HCl to 41.50 cms. the  
following gives the sorption

1	5.46
2	5.65
6	5.93
8	5.90

## Sorption of HCl

(Water content of cotton 2.92%).

<u>% HCl.</u>	<u>% HCL.</u>	<u>% HCL.</u>	<u>V.P. (mm.Hg).</u>
	<u>(In water).</u>	<u>(By cellulose)</u>	
4.42	1.45	2.97	10.40
5.93	1.86	4.07	41.50
6.49	2.04	4.45	74.50

(Water content of cotton 4.32%).

% HCL.	% HCL.	% HCL.	V.P. (mm. Hg).
(In the water)	(By cotton).		
6.90	2.20	4.70	9.90
9.20	2.72	6.48	41.00
9.93	3.02	6.91	75.20

The Water Sorption of HCL treated moist cotton  
as contrasted to that which is untreated.

% Sorption.

Untreated.	Treated.	Relative V.P. (%)
1.00	0.60	10
1.60	1.20	20
2.40	2.25	30
3.40	3.30	40
4.35	4.30	50
5.55	5.40	60
6.35	6.60	70
7.40	8.00	80
8.45	10.00	90
11.00	12.80	100

The Sorption of HCl by Wood containing desorbed  
water vapor.

(Amount of desorbed water 7.88%).

% HCl.	% HCl.	% HCl.	V.P. (mm.Hg).
	(In water)	(By wood)	
9.85	4.01	5.84	9.30
14.17	4.99	9.18	42.60
16.08	5.50	10.58	74.13

(Amount of water present 5.40%).

8.16	2.74	5.42	9.40
12.35	3.34	9.01	39.10
14.21	3.76	10.45	71.00

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