sufficient to allow the construction of a curve from which the melting point of any compound of the series may be easily read off.

From a study of a number of such curves it would appear that the lines for straight-chain paraffins and their simple derivatives, such as the alcohols, have the same, or very nearly the same slope; hence a common value of B may be given which defines a family of lines. This value of B is 0.0040 and the family of lines may be represented by the equation

$$\log M = A + 0.0040\ T \tag{11}$$

For such a family, data for a single member of a given series will serve to determine A and fix the line for that series. With branched chain and cyclic compounds the slopes are in general different. In many cases the slope has a negative sign; this is true of the series given in Fig. 1, since the "constant" lines have a negative slope and the slope of Equation 10 is the same as for the "constant" lines.

It should be mentioned in conclusion that Equation 10 applies only to true homologs; a series such as the normal paraffins has one curve, the secondary paraffins another. Complete failure results if an attempt is made to include isomers of the ortho–meta–para type in one curve.

Summary

A relation between the melting points and molecular weights of organic homologs has been derived. It is particularly useful in a critical examination of melting point data.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, McGILL UNIVERSITY]

THE ADSORPTION OF WATER BY WOOD

BY LLOYD M. PIDGEON AND O. MAASS

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Variation in the amount of adsorbed water in wood has a definite effect on many of its physical properties, such as swelling, strength, etc. In spite of the practical importance of these properties few determinations have been made of the adsorption of water by wood and cellulose throughout an extended range of vapor pressure and temperature. Even fewer determinations have been conducted by methods free from inherent error.

In this paper a method is detailed whereby the adsorption of water by various samples of coniferous woods and pure cellulose has been examined throughout the complete range of vapor pressures and between the temperatures of 12 and 42°. The corresponding adsorption isothermals are of particular interest from the point of view of the modern theory of gel structure.

While a considerable number of investigations on the fiber saturation point of wood have been made, the complete adsorption has rarely been produced. Tiemann,[1] Myer and Rees,[2] Dunlap[3] and Stamm[4] have determined saturation points by various methods, the method of Stamm being capable of considerable accuracy. Extensive work on cotton cellulose is due to Urquhart and Williams,[5] who have produced complete adsorption isotherms over a large range of temperature. Several investigators have noticed a hysteresis effect between the gain and loss of water. In general it has been the practice to report the two values of adsorption for each vapor pressure, though certain investigators have assumed a mean value as the true equilibrium point.

Little of the work which has been done is entirely free from objection. In even the most careful determinations of the adsorption by cotton cellulose the amount of adsorption was measured indirectly. In the case of wood, by the use of large samples the rate of establishment of equilibrium was often confused with the rate of diffusion into the interior of the block; also, the presence of air with a partial vapor pressure of water greatly inhibited the adsorption. A second objection was the possibility of liquid condensation on the sample at pressures near the saturation point. Thus by a combination of these factors McKenzie[6] was able to report a saturation value of 43.2% after seventy-nine days with "adsorption" still slowly taking place.

As will be seen in the following, the time to equilibrium has been reduced to a reasonable duration by removing all gases other than water vapor from the apparatus, and by the use of small samples weighing no more than 0.15 g. Also it has been possible to obtain a direct measurement of the amount of adsorption free from error due to liquid condensation.

Experimental

In principle the apparatus employed was simply a spring balance suspended in an evacuated chamber. The required vapor pressure of water was obtained either by maintaining a known temperature in a body of water in communication with the apparatus or by direct measurement with a manometer. The amount of adsorption at any vapor pressure was obtained directly from the weight of the sample.

The apparatus is shown in Fig. 1. The spirals were mounted in triplicate in special chambers (C, D, E) furnished with ground-glass joints. The spirals were suspended from glass hooks sealed just above the ground joint. Connecting these tubes to the

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[1] Tiemann, U. S. Dept. Agr. Forest Service Bull., **70**, 82 (1906); Forest Service Circ. 108 (1907).

[2] Myer and Rees, New York State College of Forestry, Tech. Bull. 26, No. 19 (1926).

[3] Hawley and Wise, "The Chemistry of Wood," p. 286, data of M. E. Dunlap, U. S. Forest Products Laboratory (1929).

[4] Stamm, *Ind. Eng. Chem. Anal. Ed.*, **1**, 94 (1929).

[5] Urquhart and Williams, *Shirley Inst. Mem.*, **49**, 197, 307 (1924).

[6] Hawley and Wise, "The Chemistry of Wood," McKenzie, unpublished report U. S. Forest Products Lab.

pumping system was a phosphorus pentoxide tube (G). To supply water vapor to the apparatus a tube was placed at (B) filled with water which had been carefully freed from all dissolved gases by freezing and evacuating several times. The stopcocks connecting these parts of the apparatus were of large bore to reduce to a minimum the time required to establish a constant vapor pressure throughout the apparatus. The tubes containing the spirals were immersed in a glass-sided thermostat fitted with a thermoregulator giving temperature control to ±0.01°. By means of a cooling coil a temperature range of from 10 to 42° was obtainable.

Deflections of the spiral were measured by means of a cathetometer accurate to 0.05 mm. Before each reading of the deflected end of the spiral the position of the fixed end was taken as a reference point. In this way it was possible to obviate any error due to displacement of cathetometer or apparatus between readings.

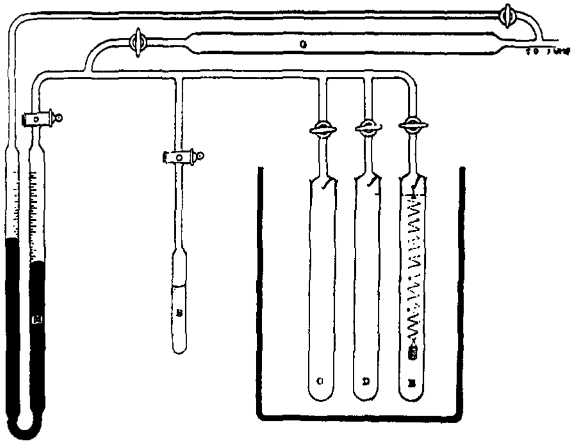

Fig. 1.—Adsorption apparatus.

Spirals were constructed of quartz after the manner of McBain and Bakr[7] by drawing fibers from a rod of silica and winding them on a carbon rod by softening the appropriate point with a small flame. The spirals employed in this investigation were considerably finer than those previously described and the most convenient flame for bending them proved to be a small gas jet without internal air supply. This flame is sufficiently hot to soften the fiber without danger of fusing it off, a frequent eventuality if any type of blast is employed.

The balance was calibrated throughout the working range by noting the deflections caused by known weights. The curve obtained by plotting deflection against corresponding weight was in all cases a straight line generally passing through the origin. The three spirals which were employed indicated a deflection of 1 mm. when supporting weights of 0.0023, 0.0022 and 0.0033 g., respectively. Thus, with the cathetometer employed, a weight of 0.0001 g. could be detected, and the total weight of a sample weighing 0.1 g. could be determined accurately to 0.1%. Since the maximum differences noted in this investigation were from 20 to 30% of the total weight, the theoretical accuracy was within 0.5% of the differences noted.

The pumping system consisted of a mercury vapor condensation pump backed by a Töpler pump. A McLeod gage was used to indicate the pressure.

To measure the aqueous vapor pressure a manometer was employed filled with

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[7] McBain and Bakr, THIS JOURNAL, **48**, 694 (1926).

"Cenco" pump oil. This oil has a negligible vapor pressure and gives a deflection some fourteen times that of mercury. In a later form of the apparatus the manometer was immersed in the thermostat so that all the connecting tubing was maintained at a constant temperature. In this apparatus the oil manometer was replaced by a short mercury manometer, the loss in sensitivity being compensated for by reading the levels with the cathetometer.

SAMPLES.—Only coniferous woods have been examined, and in particular: spruce (*Picea canadensis*), both green wood and dry wood; pine (*Pinus banxiana*), green wood; purified cotton cellulose. In the case of the wood samples a standard thickness was chosen of 1.5 mm. in the longitudinal direction. In such a sample every fiber is cut through at least once, so that all of the fiber cavities are exposed and the rate of adsorption will be unaffected by the rate of diffusion through the wood structure. Finely ground wood meal has been examined and found to give exactly the same rate and final value, giving experimental confirmation to this idea.

Experimental Procedure

Two general methods were followed. 1. **Indirect Measurement of Vapor Pressure.**—To perform an experiment the samples were suspended from the spirals and the ground joints lubricated and set in place. The pumping system was then actuated for twelve hours, at the end of which time the pressure had fallen to 0.0003 mm. of mercury and the sample had reached a constant dry weight (see later). The deflection of the spirals was then noted and the weight of the sample calculated. The tube (B) was then immersed in a flask maintained at any desired temperature, the corresponding vapor pressure of which was obtained from tables. Readings of deflection were taken until the sample had reached a constant weight. At pressures considerably below the saturation pressure this constant weight is attained in less than half an hour (see Fig. 3), though two hours was allowed to elapse to ensure complete establishment of equilibrium. The final deflection of the sample gave its weight, from which the amount of adsorption could be calculated knowing the dry weight. The temperature of tube (B) was then raised and the adsorption measured at the correspondingly higher vapor pressure. In this way the range of vapor pressures from zero to the saturation value may be investigated. This method is particularly applicable to the measurement of rates of adsorption, as several samples may be examined concurrently under identical conditions of pressure and temperature.

2. **Direct Measurement of Vapor Pressure.**—The sample is dried as in Method 1, after which a small amount of water vapor is added by momentarily opening the tap to tube (B). The pressure will be indicated on the oil manometer, which will fall from its initial value as water is adsorbed by the wood. The attainment of equilibrium is indicated by a constant pressure on the manometer. At this point the weight of the sample is found as before and the corresponding vapor pressure read directly on the manometer. A much longer time is required by this method as the pressure falls off as adsorption increases, while in the first method the pressure is maintained by the water tube, which acts as an inexhaustible reservoir. While theoretically there is no reason why several samples should not be in communication with the same manometer, it has been found practically that if more than one sample is examined at once, great time is required for the re-adjustment of equilibrium between the samples. This method is convenient in that it requires little personal attention.

By either of the methods outlined above it is possible to obtain desorption values, that is, values obtained by the loss of water from a more saturated condition. Also, by placing a little free water in the tubes with the samples, it is possible to remove the air by pumping without completely drying the samples. For vapor pressures near the saturation point Method 1 is particularly valuable, as it will be seen that as long as the temperature of tube (B) is slightly below that of the thermostat, liquid condensation cannot take place on the sample. In this way it is possible to approach closely the saturation point.

Dry Weight of Samples.—Throughout this investigation the dry weight of wood has been taken as the weight of a sample when highly evacuated in presence of phosphorus pentoxide at ordinary temperature. It has been found that under such conditions the point of equilibrium is reached in at least twelve hours. This point is completely reproducible and may be checked several times even after the adsorption of water. Any further moisture which might be driven off by heating may be considered as chemically combined, as it is held at zero vapor pressure under the conditions of the experiment and would not appear on the isothermals.

Experimental Results

In recording the experimental results only those which are essential to illustrate the order of accuracy will be given. A large number of observations have been made but where these are identical they have been omitted.

Adsorption by Spruce Wood.—In the following table are shown the adsorption values at 23° corresponding to various vapor pressures. Each of these values was obtained by loss of water from a drier state (see later, "Hysteresis").

TABLE I

EQUILIBRIUM ADSORPTION VALUES FOR SPRUCE SAPWOOD AT 23°

V. p., mm. of mercury	1.95	4.58	9.21	10.51	12.78	15.51	17.45	20.40
Relative humidity, %	9.26	21.72	43.75	50.31	60.68	73.82	83.22	97.13
Adsorption, %	2.7	5.1	9.5	10.1	12.3	13.8	14.1	20.0

A similar set of values for both spruce heartwood and sapwood was obtained at temperatures between 12 and 42°. In order to conserve space these values are not tabulated but the results for sapwood are plotted in Fig. 2. It has been found that the final values attained by heartwood and sapwood at any given vapor pressure are approximately the same. The following typical set of values at 29° will illustrate this fact.

Heartwood	0.7	1.2	2.2	2.8	3.9	7.5	8.9
Sapwood	0.8	1.3	2.3	2.8	3.8	7.5	8.7

When plotted, these values lie on the same curve, so from the point of view of final equilibrium value the distinction between heartwood and sapwood drops out. This has been found to be the case in all of the woods examined in this investigation.

The final equilibrium is generally reached from the dry state in under half an hour in the case of moderate vapor pressures. No further change is noted from this value after the lapse of twenty-four hours. The attainment of equilibrium by desorption, or loss of water from a more saturated condition, is a more lengthy process, several hours being necessary for complete equilibrium. This is illustrated in Fig. 3, where the adsorption is plotted against time. At vapor pressures near the saturation point the time required for equilibrium in either direction is considerably greater than the values mentioned.

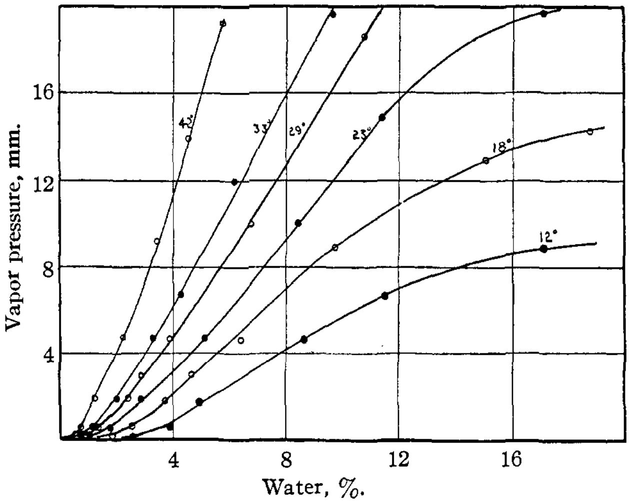

Fig. 2.—Adsorption isothermals of spruce wood.

In practically all cases a definite hysteresis effect was found. A large number of experiments have established this as a permanent effect and not simply due to incomplete equilibrium (see Fig. 3). In Fig. 4 the adsorption and desorption curves are indicated for spruce (S) and cotton cellulose (C). The hysteresis effect disappears before the origin is reached, as shown in the same figure (B), where the lower part of the curve for spruce has been plotted on a larger scale. Based on theoretical considera-

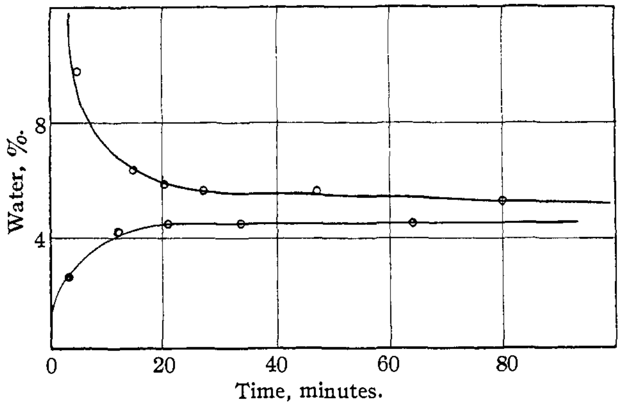

Fig. 3.—Adsorption–time curves.

tions to follow, the lower, or desorption, curve is considered to represent the true equilibrium value at any stated pressure; hence in all cases where it is not specifically stated otherwise the equilibrium adsorption value refers to the desorption value. As this desorption process is inconveniently long, a method has been developed of reaching the true value by adsorption. In a typical case, that of spruce wood at 23° and a vapor pressure of 4.58 mm. of mercury, the value reached by adsorption is 5.5%. Under the same conditions of temperature and pressure the desorption value is 6.0%, indicating the well-marked hysteresis. If, however, from a more saturated condition (*i. e.*, more than 6%) the sample is rapidly dried below the final value (to about 3%) and again exposed to a vapor pressure of 4.58 mm., the higher value of 6.0% will be rapidly reached by *adsorption*. This procedure is easily carried out in the apparatus by alternately opening the taps to the drying tube and the water tube, the latter being maintained at the required temperature. This procedure has an important bearing on the theoretical discussion to be set forth in a later section.

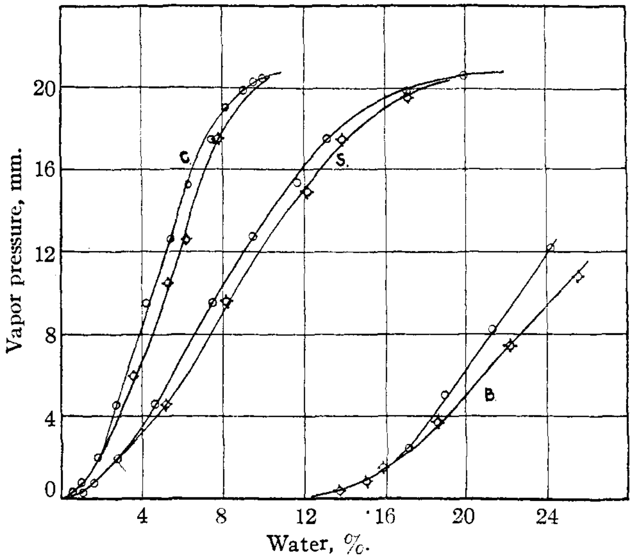

Fig. 4.—Adsorption isothermal at 23°. C, Cotton cellulose; S, spruce wood; B, S enlarged.

Effect of Drying.—While the above results were obtained with green wood, a number of measurements have been carried out on wood which has been dried in the open for some time (at least one year). A few of the results obtained are reproduced below together with comparative results for green wood.

At lower vapor pressures there is apparently no difference between the two woods, while at higher pressures the air-dried sample shows much

TABLE II

ADSORPTION VALUES FOR GREEN AND DRIED SPRUCE WOOD

Vapor pressure, mm.	4.58	9.21	12.78
Adsorption, green	5.0	9.7	11.8
Adsorption, dried	5.0	6.9	9.3

lower adsorption. This behavior may be regarded as typical in that if differences are noted they will be greatest in the region of the saturation point.

The effect of long-continued drying is to lower the value reached by adsorption. Thus in the following case of pine wood the sample was first dried, after which it was exposed to a vapor pressure of 4.58 mm. of mercury. When equilibrium had been attained, the sample was re-dried and the process repeated. The results obtained were as follows

1st adsorption, 5.2% 2nd, 5.1% 3rd, 4.8%

If, however, at any time the sample is subjected to a higher vapor pressure such as near the saturation point, the wood seems to be restored to its original adsorptive power. Thus in the following case the sample was dried and exposed to various higher pressures of water, and it is evident that the value at 4.58 mm. (33°, spruce wood) obtained between these steps shows no decrease in magnitude.

(1) 3.4% (2) 3.4% (3) 3.6% (4) 3.5%

Adsorption by Pine Wood.—In Fig. 5 the adsorption curve at 23° for pine is shown together with that of spruce. As in the case of the spruce, a definite hysteresis was noticed, and as in the previous case, the lower value is reported. Heartwood and sapwood also show little difference in adsorptive power. The fiber saturation point obtained by extrapolation of the isothermal at 23° is 31%, which may be compared with a value of 24% for spruce.

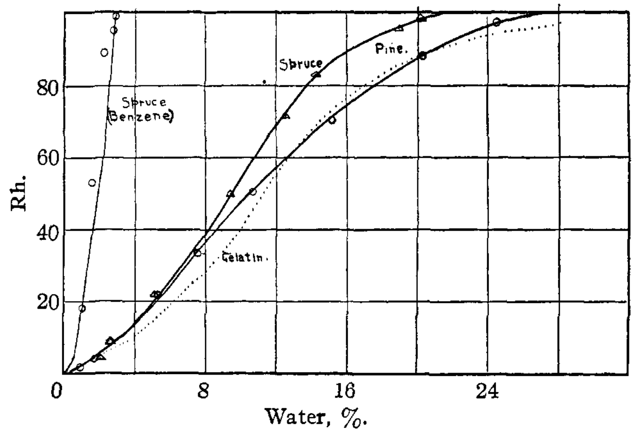

Fig. 5.—Adsorption isothermal, at 23°.

Adsorption by Cellulose.—In all cases a sample of purified cotton cellulose was examined concurrently with the wood. The values obtained are considerably lower than for wood, the saturation point obtained by extrapolation being 11%. Extracted wood cellulose, prepared by laboratory methods such as that in the analytical determination, yielded much higher values than wood, as will be seen in Table III, in which are recorded results obtained by the adsorption of water from the dry state.

TABLE III

ADSORPTION VALUES AT 23° OF SPRUCE WOOD, EXTRACTED CELLULOSE AND COTTON CELLULOSE

V. p.	Spruce	Extr. cellulose	Cotton cellulose
0.22	0.9	1.5	0.5
0.77	1.6	1.9	1.0
1.95	2.7	3.5	1.8
4.58	4.7	5.4	2.7
9.21	7.3	8.1	3.6
12.78	9.5	11.1	5.5
15.78	11.7	13.1	6.7
17.45	13.2	14.5	7.5
19.20	15.3	18.0	8.2
19.80	17.1	18.9	9.0
20.65	20.2	23.0	9.9

Rate of Adsorption.—It has been found that the time required to establish equilibrium increases with the vapor pressure, as indicated in the following table.

TABLE IV

RATE OF ADSORPTION

Temp., 33° V. p., 0.1 mm.		Temp., 33° V. p., 4.58 mm.		Temp., 23° V. p., 18.11 mm.	
Time, min.	Adsorption, %	Time, min.	Adsorption, %	Time, min.	Adsorption, %
1.0	0.1	1.5	1.25	2.0	3.7
3.5	.2	4.5	1.4	7.0	6.3
9.0	.3	8.5	2.3	15.0	8.4
Final	.3	14.5	3.0	32.0	11.1
		21.5	3.2	67.0	13.5
		Final	3.2	195.0	15.8
				300.0	16.3
				Final	16.42

Nature of Vapors.—While in the majority of cases the adsorbate has been water vapor, one experiment has been performed using benzene. The results are plotted in Fig. 5 and will be discussed subsequently.

An experiment was performed on a sample of lignin supplied by the Department of Cellulose Chemistry of this University. At 23° and a vapor pressure of 4.58 mm. of mercury, the value obtained was 2.1%, which may be compared with 4.7% for spruce wood under the same conditions.

Discussion of Results

Variation of Adsorption with Vapor Pressure.—Figure 4 (S) representing the adsorption isothermal of spruce wood at 23° may be taken as the typical curve relating adsorption to corresponding vapor pressure. This smooth s-shaped curve is at once recognizable as typical of the adsorption of a vapor which is condensable to a liquid which wets the adsorbent. Three general divisions of the curve may be indicated. The first 1–2% of water is apparently highly adsorbed, causing a lowering of vapor pressure which brings about a flattening of the curve near the origin. From an adsorption of 2 to 10% the curve follows what is practically a straight line, indicating that in this portion adsorption is proportional to pressure. As the saturation pressure is approached, the curve again flattens out, becoming asymptotic to the axis of adsorption, so that in this region a small increase in vapor pressure will cause a great increase in adsorption. The shape of the curve near saturation demonstrates the difficulty of obtaining an accurate value for the fiber saturation point by direct measurement of water content; in fact, from this standpoint, no such sharply defined point exists. These different parts of the curve have a theoretical significance which will be brought forward later.

Variation of Adsorption with Temperature.—The effect of variation in temperature on adsorption is indicated in Fig. 2. In common, with the general case, adsorption decreases with rise in temperature. On the other hand, at more elevated temperatures the vapor pressure required to produce the same relative humidity will be greater. In fact, the increase occurs in the same ratio that adsorption falls off. This may readily be seen in a qualitative way: the adsorbed water exhibits a vapor pressure which is a constant fraction of that of pure water, so that as temperature increases the vapor pressure of the adsorbed water will be proportionately the same as that of a plane water surface at the same temperature. Since the vapor pressure of adsorbed water and the amount of adsorption are in a sense inversely proportional, the amount of adsorption will decrease with rise in temperature in the same ratio as the vapor pressure of water increases. Hence it follows that if the relative humidity be kept constant, adsorption will be independent of temperature.

Practically it is found that this is not entirely the case. In Fig. 6 the isotherms of Fig. 2 have been plotted on the basis of relative humidities in place of absolute vapor pressures. It will be seen that the lower temperatures show higher adsorption.

Adsorption Isosteres.—If the vapor pressures corresponding to a given amount of adsorption are plotted against temperature, an adsorption isostere is produced. Such a curve represents the variation of vapor pressure with temperature for a given amount of adsorbed water. From what has been said above it is evident that the isostere will be an exponential curve similar to the typical vapor pressure curve. Thus if log p is plotted in place of pressure the resulting graph should be a straight line. This procedure has been followed in Fig. 7, and it is apparent that such a line is produced for isosteres representing an adsorption value above 2%. Below this value the lines become convex to the pressure axis. These curved isosteres fall in the region where, as mentioned previously, the adsorption isotherm shows a discontinuity which is probably caused by the introduction at this point of some new factor in the mechanism of adsorption. It would be expected that isosteres near the saturation point would also exhibit anomalous behavior, but a sufficient number of experimental values in this region are not available.

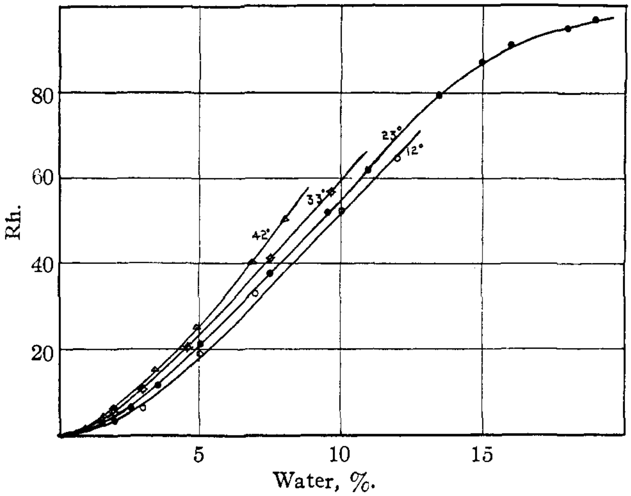

Fig. 6.—Variation of adsorption with temperature.

From purely theoretical reasoning Williams[8] has developed an isosteric equation of the form

$$\log a/c = B + AT$$

where c is the equilibrium concentration outside the adsorbent, a the amount of adsorption, T the absolute temperature, and A and B are functions of a but not of T. This equation has been shown to be applicable to the isostere of cotton cellulose by Urquhart and Williams (*ibid.* p. 1). The concentration, c, is replaced by pressure and the equation becomes

$$\log a/c = B' + AT$$

Since a is constant for any isostere, B' and A are also constant, so that if log p is plotted against $1/T$ the resulting graph should be a straight line. The results for spruce wood when submitted to this procedure

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[8] Williams, *Proc. Roy. Soc. London*, **96A**, 297 (1920).

give curves similar to Fig. 7, that is, a discontinuity is noticed for isosteres representing adsorptions less than 2%, while for a large part of the isotherm the results may be represented by a general equation.

Moisture Equilibria of Pine (*Pinus banxiana*).—In Fig. 5 the comparison between spruce and pine brings out the fact that while the two woods differ widely near the saturation point for a considerable distance above the origin, the two curves are identical. This is probably the typical behavior with many woods, as the lower part of the curve deals largely with true adsorption on the fundamental wood substance, which is probably similar in all species. The variation near the saturation point is probably due to differences in the larger structure of the wood, such as would exist between the different species.

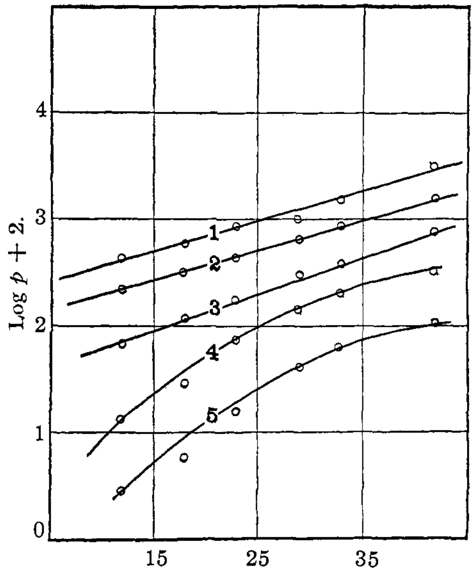

Fig. 7.—Adsorption isosteres: 1, 8%; 2, 5%; 3, 3%; 4, 2%; 5, 1%.

Moisture Equilibria of Cotton Cellulose.—The adsorption values for pure cotton cellulose are considerably lower than for wood (see Fig. 4C.). This difference is more definite than any that has been noticed between different species of wood, as the adsorption curves do not coincide over any portion of their length. Since the non-cellulose parts of wood do not show high adsorption (see lignin), this difference in adsorption is probably due to a difference in character between the cotton cellulose and the wood cellulose. Several explanations of this difference are possible. Cotton cellulose is considered to be similar to the α-cellulose of wood, *i. e.*, it is insoluble in 17.5% caustic. Hence the presence of the additional β- and γ-celluloses, which are soluble in alkali of the above concentration, may account for the higher adsorption of wood cellulose. The solubility of β- and γ-cellulose in alkali is evidence in favor of an increased affinity for water.

The difference in character between cotton cellulose and wood cellulose may be characterized by a coarser gel structure which brings about a lower adsorption. Again, it is possible that the presence of waxes in cotton may be the cause of an altered surface which has an effect on adsorption. The fact that the adsorption curves do not coincide in any part would indicate a difference in chemical attraction rather than a physical difference in structure.

General Discussion

In general a condensable vapor may be taken up by a solid by adsorption, by liquid condensation and by absorption or solution. While it is possible that all these mechanisms play a part in the adsorption of water by wood, the results of this research may be well explained by assuming a combination of adsorption and condensation based on the prevalent ideas of adsorption by gels. In Fig. 5 a comparison has been made between the adsorption isothermal of gelatin and that of wood. The similarity is at once apparent, so that with some justification cellulose may be classed with gelatin as a swelling gel.

It is generally assumed that gels possess a heterogeneous structure in which the actual particles of the gel are separated by small ultra-microscopic spaces or capillaries. No assumptions are necessary as to the shape of the particles or micelles (such as fibrillar or granular). When the dried gel is brought in contact with a condensable vapor, the great surface which is presented by its internal structure is saturated by adsorption of the vapor. As the external vapor pressure is increased, a point is reached at which liquid appears in the small capillaries, held at reduced vapor pressure by the great curvature of surface. Further adsorption of water takes place by the filling of these capillary spaces. In the case of non-swelling gels the micelles become rigid on desiccation; hence, when again brought into contact with water, they take it up only in so far as they fill the capillary spaces which remain a constant size. Thus in the case of non-swelling gels liquid is taken up at a constant vapor pressure until saturation is reached. In the case of swelling gels, on the other hand, the micelles do not lose their power of taking up liquid reversibly. That is, when liquid is again added, the micelles move apart from the packed condition which was assumed on drying and the whole gel swells. This process is characterized by an increase in the size of the intermicellular spaces which, in turn, causes an increase of vapor pressure. Thus a swelling gel takes up water with increase of vapor pressure until saturation is reached, at which point the vapor pressure will be the same as that of a plane water surface.

This picture may be applied to the present case to give a theoretical explanation of the adsorption isothermal. Dry cellulose may be considered as a desiccated colloidal gel consisting of a great number of particles. These particles may be the cellulose molecules themselves or aggregates of molecules. (Herzog, by x-ray measurements, has calculated the volume of the cellulose molecule as $0.68\mu^3$. Micellular particles are generally larger than this.) The micelles are probably orientated in the cellulose fiber, as swelling is not uniform in all directions. Owing to the fineness of the particles the surface presented will be enormous. Stamm has calculated the surface per gram of wood to be 310,000 sq. cm. On this surface the vapor is first adsorbed, the pressure exerted by the water molecules being less then the saturation value by virtue of the attraction between water molecule and cellulose micelle. The amount of water required to saturate this surface will be taken up rapidly by the process of true adsorption of a gas on a solid, and for any given vapor pressure the equilibrium adsorption value may be attained in either direction, that is, there is no hysteresis effect. This is well shown, in the case of wood, by the shape of the adsorption isothermal near the origin. The first 1 to 2% of water is taken up reversibly and at a reduced vapor pressure, causing a flattening of the curve in this region.

As more water is added, eventually the opposing surfaces will unite to form a column of water in a capillary. The pressure at which this takes place will depend on the diameter, the largest capillaries being the last to fill. When this takes place, there is practically a free water surface in the gel, the vapor pressure of which is governed by the radius of curvature of the capillaries. As more water is added the capillaries fill and, as cellulose is a swelling gel, the micelles move apart, causing an increase in the radius of curvature of the water surfaces. Hence vapor pressure increases with adsorption and from the curves it will be seen that this takes place in a linear fashion.

As the vapor pressure approaches the saturation point, a very small lowering will be sufficient to cause liquid condensation. Hence it is conceivable that larger pores in the wood are becoming filled with liquid. Due to the large size of these pores a small change in vapor pressure will entail a great difference in the amount of adsorption, and the curve which expresses this will flatten out.

Further evidence in favor of this view is adduced from a consideration of the rates of adsorption at different vapor pressures (see Table IV). If dry wood adsorbs water vapor at a pressure of 0.1 mm. of mercury, the time required for the establishment of equilibrium is approximately nine minutes. This value is of an order of magnitude comparable with the usual rates of adsorption, which seldom exceed several minutes. Along the straight portion of the curve the time required to establish equilibrium is approximately twenty minutes, a value which increases at higher pressures. According to the idea submitted above, the increase in time over the case for pure adsorption will be due to the time required to fill the capillary spaces between the micelles of the wood. This time will depend on the rate of condensation and the rate at which the vapor diffuses to the condensing surface. For the upper part of the curve near the saturation point the time required is very great, the establishment of equilibrium being incomplete even after the lapse of several hours. This is again due to the time required to fill the large capillaries and the time required for gaseous diffusion. This latter factor is probably a very considerable one in this region as approximately 20 liters of vapor at the temperature and pressure of the experiment are required to saturate one gram of wood (500 volumes at N. T. P.).

Thus it will be seen that this picture of the colloidal nature of cellulose affords a plausible explanation of the observed facts. The reason why the adsorption isothermals of different woods often coincide in the lower parts of the curve is apparent. The taking up of water in this region depends on the finest part of the invisible structure of the cellulose, which is probably fundamentally the same in all species of woods. Condensation near the saturation point depends on the filling of the coarser, but still amicronic structure of the wood, which would be expected to vary widely between the different species. Hence differences in adsorptive power will be greatest in the vicinity of the saturation point.

Hysteresis.—A mechanism which offers an explanation of this phenomenon has been suggested by Zsigmondy[9] and was first applied to silicic acid gels. It is assumed that when the walls of the micelles have become thoroughly dried they are less easily wetted by the liquid. Thus, as water is again taken up, the radius of curvature of the surface is less than when water was lost, in which case the walls were already wetted by the liquid. Thus it follows that for the same content of water the radius of curvature is greater when water is lost, that is, the vapor pressure is lower. Hence wherever the adsorption or desorption of water takes place by the filling or emptying of small capillaries, a hysteresis effect will be noticed. In the present case it has been pointed out that the first water is taken up by true adsorption; hence in this region no hysteresis will exist, a fact which has been experimentally verified. For the remaining part of the curve a pronounced hysteresis exists until the saturation point is reached, at which point hysteresis presumably disappears as the radius of curvature becomes so great as to be little different from that of a plane water surface.

The natural conclusion of the above is that the true adsorption value for any given vapor pressure will be attained by loss of water since by this process the liquid makes its true angle of contact with the walls of the micelles unaffected by effects of drying.

A rather convincing piece of evidence in favor of this view point is afforded by the method which is mentioned above whereby it is possible to reach the *de*sorption value by *ad*sorption. If the sample is saturated at a vapor pressure which is higher than that under discussion, and then rapidly dried below this desired value, when it is again subjected to the required

[9] Zsigmondy, *Z. anorg. Chem.*, **20**, 157 (1909).

vapor pressure the desorption value will be reached by gain of water. That is, if the walls of the micelles are already wetted, no hysteresis will exist but the same value will be reached by adsorption or desorption.

Size of Intermicellular Capillaries.—If it is assumed that the pressure of the system is controlled by the curvature of water surfaces in capillaries, the pressure at any adsorption depends on the average diameter of the capillaries which are filled. Thus by the use of the formula connecting lowering of vapor pressure with curvature of surface, it should be possible to calculate the size of the capillaries. The point at which hysteresis disappears may be taken as the vapor pressure corresponding to the smallest capillary. The value for r in this region is 4.5×10^{-8} cm. Near the saturation point a value of 3.8×10^{-6} is obtained. These values are for spruce wood at 23°.

Nature of Vapor.—In the case of the adsorption of a condensable vapor the liquid of which does not wet the adsorbent, the vapor acts like a gas above its critical point, that is, no liquid condensation can take place on the adsorbent. In this case the adsorption values will be much lower and in the vicinity of the saturation point there will be no increase in adsorption. An experiment was performed using benzene vapor and wood which apparently confirms this behavior. The results are plotted in Fig. 5 and it will be seen that the curve is of a completely different form, the greatest change being in the region of the saturation point. This case is interesting as there have been few cases of adsorption of condensable non-wetting liquids.

Summary

The adsorption of water by certain coniferous woods and by cotton cellulose has been measured by a new method. The complete range of vapor pressures has been covered and adsorption isothermals produced for temperatures between 12 and 42°.

The effect of various natural factors on adsorption has been examined. Heartwood and sapwood appear to give identical values. In wood which has been dried for a long period of time the adsorption isothermals are the same at low vapor pressures but differ at the higher vapor pressures. This also applies to different species of wood.

Adsorption isosteres were shown to be represented by $\log a/c = B + AT$ for adsorptions representing more than 2%.

The form of the adsorption curve shows that wood may be classed as a swelling gel. The first part of the adsorption curve is due to surface adsorption, the rest to the filling up of the submicroscopic spaces.

The similarity in the adsorption isothermals of different species of wood in the lower parts of the curve shows that the nature and the finest part of the amicronic structure of the cellulose are fundamentally the same.

Cotton cellulose is fundamentally different from the cellulose in wood; this is brought out by the adsorption curves not coinciding over any portion of their length.

A hysteresis effect between gain and loss of water has been found, except at low vapor pressures, but the higher value attained by the loss of water is considered to represent the true equilibrium value at any vapor pressure.

By an application of modern gel theory a theoretical explanation of the observed facts is offered.

MONTREAL, CANADA

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

SALTS OF NITRILES. III. SODIUM PHENYLACETONITRILE[1]

BY MARY M. RISING AND GÉZA BRAUN

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In 1927 and 1928 Rising and Zee reported the preparation, isolation and properties of the sodium salt of phenylacetonitrile, $[C_6H_5CHCN]Na$, and of α-phenylbutyronitrile,[2] $[C_6H_5C(C_2H_5)CN]Na$. Early in 1929 a further paper was published by Rising, Muskat and Lowe on the potassium salt of phenylacetonitrile.[3] In these papers certain conclusions are stated, based upon the behavior of the salts. (1) The salts exhibit tautomerism of the carbide–nitride type, analogous to the well-known tautomerism of the salts of acetoacetic ester

$$[C_6H_5CH{=}C{=}N^-]Na^+ \rightleftharpoons [C_6H_5C^-HCN]Na^+ \qquad (1)$$

$$[C_6H_5C(C_2H_5){=}C{=}N^-]Na^+ \rightleftharpoons [C_6H_5C^-(C_2H_5)CN]Na^+ \qquad (2)$$

(2) Each salt reacts in a nitride form. The evidence for this conclusion is presented in the papers named. (3) Each salt reacts also in a carbide form. The evidence for this conclusion is presented in the papers mentioned.

Because of the difficulties met by a number of workers who have tried to repeat Zee's work,[4] a thorough reinvestigation of the problem was undertaken by the present authors.[5] Sodium phenylacetonitrile was

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[1] The work here reported was completed by April 15, 1929, but publication was postponed out of courtesy to Professor F. W. Upson and his collaborators until they should have reported upon their recently resumed work on the same problem, upon which they have published nothing since 1922 [Upson and Thompson, THIS JOURNAL, **44,** 181 (1922)]. See also THIS JOURNAL, **51,** 263 (1929). These authors have just announced by an abstract a paper on the subject to be presented at the Minneapolis meeting of the Society and we feel free, therefore, to report our findings.

[2] Rising and Zee, (a) *ibid.*, **49,** 541 (1927); (b) **50,** 1699 (1928).

[3] Rising, Muskat and Lowe, *ibid.*, **51,** 262 (1929).

[4] See footnote, Ref. 2 b, p. 1699.

[5] I wish to express here my sincere appreciation of the fine technique of my collaborator, Dr. Géza Braun, International Research Fellow of Budapest, at the University of Chicago, 1926–1928. M. M. RISING.