At successive intervals of time samples were quickly removed and plunged into ice water to arrest the reaction. The refractive index was determined at 25.00 ± 0.01° with an Abbé refractometer with an estimated accuracy of ±0.0001. The refractometer was calibrated with a test-plate prior to each series of readings.

The above procedure gave satisfactory results for the rate measurements with 1-cyclohexenyl allylmalonitrile. For the rate measurements with 1-ethylpropenyl allylmalonitrile, however, somewhat erratic results were obtained and the end-product had a refractive index different from that of the desired pure product. It was suspected that a side reaction was occurring at the glass surface. Accordingly, the interior of each sample tube was flamed with a gas flame to poison any catalytic surface prior to the introduction of any compound. This procedure gave satisfactory results and was thereafter used for measuring the rates of rearrangement of both 1-ethylpropenyl allylmalonitrile and ethyl (1,3-dimethyl-1-butenyl)-allylcyanoacetate.

The per cent. rearrangement for any given time was calculated by the equation

$$\%\ \text{rearrangement} = 100\ (n - n_{\text{reactant}})/(n_{\text{product}} - n_{\text{reactant}})$$

where $n = n^{25}\text{D}$ = refractive index of reaction mixture at any given time, n_{reactant} = refractive index of pure reactant, and n_{product} = refractive index of pure product.

Summary

1. The energies and entropies of activation have been determined for the rearrangement of the allyl groups of 1-cyclohexenyl allylmalonitrile, 1-ethylpropenyl allylmalonitrile, and ethyl (1,3-dimethyl-1-butenyl)-allylcyanoacetate. The entropies of activation are, respectively, −11.7, −11.1 and −14.0 e.u. These high entropies of activation substantiate the cyclic mechanism previously advanced.

2. Approximately 60% of the differences in rearrangement rates of the series of compounds studied could be attributed to differences in energies of activation. The other 40% was due to differences in entropies of activation.

MADISON, WIS. RECEIVED MARCH 18, 1947

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

A Calorimetric Investigation of Moisture in Textile Fibers[1a]

BY FRANK C. MAGNE, H. J. PORTAS AND HELMUT WAKEHAM

The heat of fusion, or calorimetric, method for the evaluation of bound water has been applied to a wide variety of plant and animal materials with varying degrees of success in attempts to elucidate the nature of water in such substances.[2–7] Certain difficulties encountered in experimental application of the method and in interpretation of the results have led in some cases to the obvious conclusion that the method may be applied only to systems in which all the "free" water will freeze.[2,8]

In the present investigation the calorimetric method has been applied to cellulose, nylon and glass fibers.

Modern concepts of the mechanism of moisture adsorption by cellulose fibers involve three steps[9–23]: (a) the selective adsorption of water molecules by hydrogen bonding to the free hydroxyl groups in the noncrystalline or intermicellar regions; (b) the adsorption of water into the lattice of the crystalline regions in those particular cellulose structures exhibiting changes in cellular dimensions with moisture adsorption, such as regenerated or mercerized cellulose fibers; and (c) capillary condensation or "multiple-layer formation" in those spaces in the cellulose fiber which permit occupancy by additional water molecules.

Of these three classifications, the water adsorbed in the first two may be considered as "bound" with energies greater than those involved in the water-to-water hydrogen bond. Conversely the water taken up by capillary condensation might be expected to behave similarly to bulk water and to freeze under suitable conditions.

The experimental demonstration of this hypo-

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

(1a) Presented before the Division of Cellulose Chemistry at the 110th meeting of the American Chemical Society, Chicago, Illinois, September 9 to 13, 1946.

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(16) P. H. Hermans, J. J. Hermans, D. Vermaas and A. Weidinger, *Rec. trav. chim.*, **63**, 44 (1944).

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(21) F. T. Pierce, *J. Textile Inst.*, **20**, 133T (1929).

(22) A. J. Stamm and M. A. Millett, *J. Phys. Chem.*, **45**, 43 (1941).

(23) A. R. Urquhart, *J. Textile Inst.*, **20**, 125T (1929).

thesis should present independent evidence of the nature of moisture adsorption by cellulose fibers and of the number of cellulose hydroxyl groups accessible to the water molecules. One of the problems involved in the interpretation of moisture adsorption isotherms by the method of Brunauer, Emmett and Teller[11] is the difficulty in interpreting the "B" and "D" points of inflection, which, according to the theory of Assaf, Haas and Purves,[9] indicate saturation of the available primary and secondary hydroxyl groups, respectively. The calorimetric method herein described gives a clearer indication of the limit of hydroxyl adsorption and, in addition, gives some evidence concerning the nature of the capillary spaces in which the condensation of step (c) occurs.

Experimental

Fiber Samples.—All samples were in the form of yarns or cords to facilitate handling in the small capsules used. This had the advantage of providing small channels through the material in the capsule so that conditioning could be carried out without removal from the capsule. Experience indicated that any difference which one might imagine between the moisture relationships of fibers in the form of cords and of fibers in the form of yarns was insignificant. In fact, the cords conditioned more easily and produced more consistent results than the yarns.

Sample I was a cord of Acala-1517 (a linear-fiber)[24] cotton which, although manufactured by standard textile mill processing, had not been treated chemically in any way, and was, therefore, considered to be a raw native cotton. Sample II was a yarn of Rowden (a roundish-fiber) cotton which, similar to Sample I, was in the raw state. Sample III was a cord of Wilds-13 (an elliptical-fiber) cotton which had been commercially mercerized (swollen in caustic soda) in the yarn stage before twisting. Sample IV was a high tenacity viscose rayon yarn known by the designation "Cordura" and similar to the type used in tire cord material. Sample V was a nylon cord also of the type used for tire cord.

In addition to these fibers, experiments were also performed on purified glass fibers (Sample VI) approximately 2 microns in diameter and woven into cloth to check the possibility of the influence of interfiber capillary condensation on the relative amounts of freezing and non-freezing water.

Apparatus.—In the calorimetric method, or method of mixture, a capsule or container of the material being investigated is cooled to a known temperature, then dropped into a calorimeter, and a measurement recorded of the thermal change effected on the contents.

The calorimetric apparatus employed is shown in Fig. 1. The calorimeter, A, was a 950-cc. silvered dewar flask with a removable top, T, containing 10 junctions of the copper–constantan thermel laced on a mica sheet and a glass bucket, operating at 30 strokes per minute, to provide stirring. This bucket also held the capsule after it had been admitted to the calorimeter. Dewar B established a reference temperature for the calorimeter. It contained, besides the reference junctions of the thermel, a differential thermocouple of copper–constantan, with its reference junction in the water-bath, J, kept constant to within 0.01° and jacketing both reference dewar and calorimeter. A stirrer operating at 60 r. p. m. established temperature uniformity throughout the reference dewar.

Capsule, C, was frozen in the insulated cooler, D, and its temperature prior to dropping into the calorimeter was established by means of a copper–constantan thermocouple located in the well of the capsule, with reference junction at 0°.

Microvolt readings of all thermal elements were effected by the use of a Rubicon Double Potentiometer and the null method of balance.

All thermels were calibrated according to usual thermometric practices.

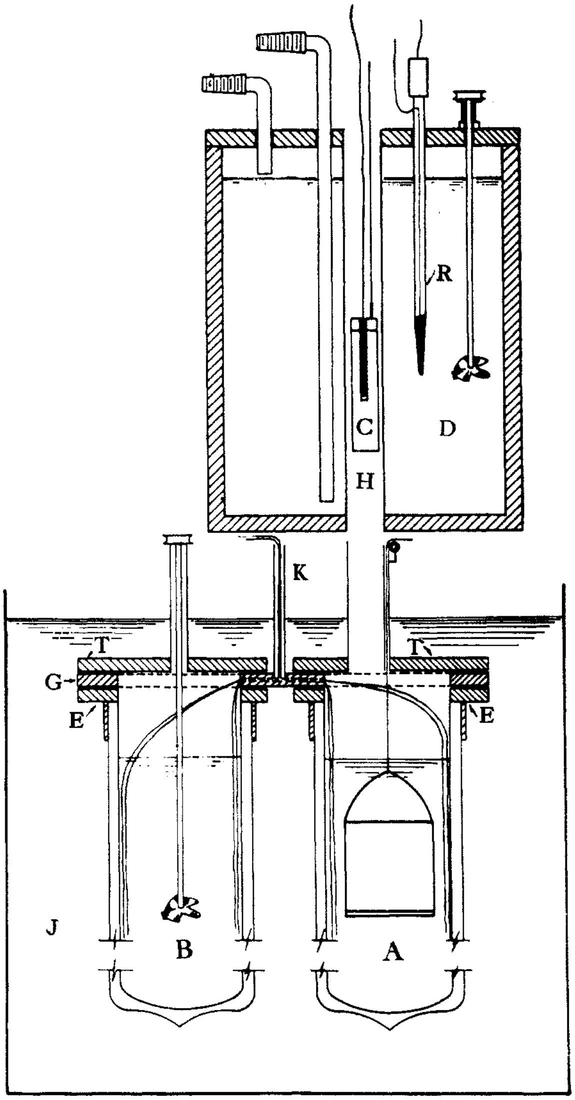

Fig. 1.—Simplified diagram of calorimeter.

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(24) Linear-, elliptical- and roundish-fiber cottons are distinguished by the appearance of their cross-sections [see A. S. T. M. Standards, Part III, D414-40 T, p. 2035 (1944)]. Some unpublished experimental evidence obtained in this laboratory indicates that the moisture–cellulose relationships of the linear and roundish types of fibers may differ appreciably. A more detailed discussion of this possibility is beyond the scope of this paper.

Two approaches were employed in arriving at a calibrated value for the heat capacity of the calorimeter: (a) pure copper, whose thermal constants are well known, in a mixture method; and (b) the electrical method. Good agreement was achieved between both methods. The mean of 8 runs using a spectroscopically pure copper cylinder was 86.35 ± 1.82 calories per degree. Ten calibration values by the electrical method using an integrated current value gave a mean of 83.79 ± 2.35 calories. The average value of 85 calories per degree was chosen as the heat capacity of the calorimeter with an indicated error of about 1.5 calorie per degree.

Manipulation and Operation.—Capsules were filled with approximately 1.5 to 2.1 g. of sample. The accurately weighed capsule and contents were then placed in a vacuum container and evacuated to 10^{-3} mm. pressure until no further loss of weight was observed. The final weight of cords or yarns was then used as the dry weight in subsequent calculations.

Conditioning was carried on in the same container as drying. After the open capsule had been introduced and the entire apparatus evacuated, water was admitted by means of a stopcock in the system. Water vapor was then allowed to permeate the sample until a desired degree of conditioning was attained. Maximum conditioning secured for the cotton samples by this method was about 20 to 24% on a dry basis. Higher moisture levels were reached by direct addition of water to capsule, with subsequent pulling and releasing of vacuum in order to uniformly distribute water throughout the fibers. Experimental values of bound and free water were more consistent if the moisture content of the sample was successively reduced in each succeeding run.

Weighed and conditioned capsules were then lowered into the freezer and kept at the desired temperature for at least two hours before being run. Even after this period of cooling occasional cases of supercooling were observed especially at temperatures around −4.5°, fewer at −13°, but these could be clearly differentiated experimentally from normal runs and discarded. In some duplicate experiments the capsule was frozen at −20° and then warmed in the freezer for some time to −4.5° before dropping into the calorimeter. No detectable difference in the ratio of freezing to non-freezing water was observed in these cases, indicating that the free water was not merely water which had distilled to the inner sides of the capsule and there frozen.

A typical run consists of recording time–temperature relations between calorimeter and reference dewar, reference dewar and bath, and the capsule in the freezing chamber. After the capsule was introduced into the calorimeter at a recorded time, the time–temperature relation was again recorded, this time between calorimeter and reference dewar only. By plotting these data and extrapolating back to the time the capsule was dropped, a value for the microvolt change due to the frozen capsule and contents was determined.

Errors due to loss of water from evaporation and frequent removal of capsules were controlled by replacing the calorimeter water content at frequent intervals.

TABLE I

SPECIFIC HEATS OF DRY TEXTILE FIBERS

(Mean values between −4.5° and +28.5°)

	Sample I Acala cotton	II Rowden cotton	III Mercerized Wilds cotton	IV Cordura rayon	V Nylon	VI Glass
	0.291	0.284	0.296	0.315	0.333	0.195
	.271	.295	.281	.284	.342	.191
	.314	.290	.309	.290	.337	...
	...	...	...	.303	.342	...
	...	...	...	.318	.359	...
	...	...	...	.307	...	...
	...	...	...	.297	...	...
Average	.292	.290	.295	.302	.343	.193
	± .008	± .002	± .006	± .004	± .003	

Specific Heats of Dry Fibers.—Calculation of the amounts of freezing and non-freezing water requires knowledge of the mean specific heats of the dry textile fibers. Since reliable data on the particular fibers studied were not available in the literature, specific heat values for them were determined over the range between the freezing and the calorimeter temperature. The results are shown in Table I. These values agree reasonably well with previously reported values of 0.304 and 0.283 cal./g./°C. for cotton.[25] An average value between 20 and 250° of 0.555 cal./g./°C. has been reported for nylon.[26]

Sample Calculation.—Figure 2 is a typical plot of the time *vs.* microvolt relation of the calorimeter–reference differential temperature, the reference-bath differential temperature, and the capsule temperature in an actual determination of the "heat of fusion" of the water in a conditioned textile. From the respective curves extrapolated to the time at which the capsule was dropped (53.6 minutes), the following values were obtained:

Calorimeter after heat exchange (BC′, Fig. 2)	−139.0 μv.
Calorimeter before heat exchange (BC, Fig. 2)	− 51.0
Thermal change due to introduction of capsule	− 88.0 μv.
Reference dewar-bath differential (AB, Fig. 2)	− 20.9 μv.
Capsule temperature before dropping (DE, Fig. 2)	−170.7 μv.
Bath temperature, °C.	28.54°

The heat absorbed by the capsule contents is calculated in the following manner:

Initial temperature of reference, °C., 28.54 − (0.0243[a] × 20.9)	=	28.03°
Final calorimeter-reference differential, −139.0/409.95	=	0.34
Final calorimeter temperature, °C.		27.69°
Capsule temperature before dropping		−4.49
Total temperature change of capsule, °C.		32.18°
Temperature drop in calorimeter, 88.0/409.95	=	0.2147
Heat contributed by water in calorimeter, cal., 781.27 g. × 0.99748[a] cal. × 0.2147° C.	=	167.31
Heat contributed by calorimeter, 85.0 cal. × 0.2147°C.	=	18.25
Total heat exchanged, cal.		185.56
Heat absorbed by capsule, 2.2011[a] cal. × 32.18°C.	=	70.84
Heat absorbed by capsule contents, cal. (including 2.1206 g. dry cotton; 1.2043 g. water)		114.72
Heat absorbed by dry cotton 2.1206 g. × 0.292 cal. × 32.18°C.		19.93
Heat absorbed by 1.2043 g. water, cal.		94.79

[a] The physical constants used in the calculations reported were the best values taken from N. E. Dorsey, "Properties of Ordinary Water–Substance," Reinhold

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(25) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Erg. IIb, p. 1217, and Erg. IIIc, p. 2313.

(26) *Rayon Textile Monthly*, **25**, (4) 51 (1944).

Publishing Corp., New York, N. Y., 1940; Landolt–Börnstein, "Physikalisch–Chemische Tabellen," and "International Critical Tables," McGraw-Hill Co., New York, N. Y., 1929.

Only mean specific heat values determined by integration over the temperature ranges in question are used. Thus, in the sample calculation, 1.0012 cal./g./°C., is the integrated mean specific heat of liquid water between 0 and 27.69°, 1.0100 a similar value for liquid water between 0 and −4.49°, and 0.5013 is the integrated mean specific heat of ice between 0 and −4.49°.

From the quantity of heat absorbed by the water in the capsule contents, the amounts of freezing and non-freezing water were calculated by means of two simultaneous equations as follows

$a + b = 1.2043$ in which a is the non-freezing water and b is the freezing water

$$(1.0012^{a} \times 27.69)a + (1.0100^{a} \times 4.49)a + 79.71b + (1.0012^{a} \times 27.69)b + (0.5013^{a} \times 4.49)b = 94.79$$

Solving these equations for a and b yields the result

$$a = 0.4818 \text{ g. and } b = 0.7225 \text{ g.}$$

Based upon the dry weight of cotton present the weight percentages of freezing and non-freezing water are 34.1 and 22.7%, respectively.

This method of calculation is based on the assumption that all of the freezing water melts at 0°, an assumption probably not completely justified since the raw cotton contains a small amount of water-soluble impurities and since, as will be shown later, some of the capillary water is of reduced activity and probably freezes at a lower temperature. The error involved, in any case, is rather small. If, for example, we assume the extreme case in which all the freezing water melts at −4.49°, the weight percentages of freezing and non-freezing water become 33.1 and 23.7%, respectively. Errors inherent in the calorimetric measurement[27] make the quantity of heat absorbed by the water uncertain by a maximum of about one calorie. This uncertainty would change the percentage of freezing or non-freezing water in the sample calculation above by about 0.6%. The difference due to the assumption that all the freezing water melts at −4.49° instead of at 0° is, therefore, almost within the experimental error of the measurement.

A larger error in the amounts of freezing and non-freezing water is undoubtedly involved in the assumption that all non-freezing water has the same heat capacity as liquid bulk water. If, as is postulated below, some of the non-freezing water is hydrogen bonded to the cellulose, such water could probably have a lower heat capacity than bulk water, possibly somewhere between the heat capacity values of liquid water and ice. C_p values for non-freezing water in hydrates (water of hydration) show considerable variation with reported extremes of 0.4 to 0.8.[28] Heat capacity of water adsorbed on cellulose, however, has been reported as slightly higher than that of bulk water.[29] An indication of the maximum magnitude of this error may be obtained by assuming that all the non-freezing water has a heat capacity approximately that of ice at 0° (0.5013 cal. per gram per degree); calculations on this basis of the example shown above yield values of 37.99 and 18.79% for freezing and non-freezing water, respectively, a reduction of 20% in the non-freezing water values. Because it is not likely that the heat capacity of the non-freezing water is as low as that of ice,[29] the actual error is quite likely less than that indicated here.

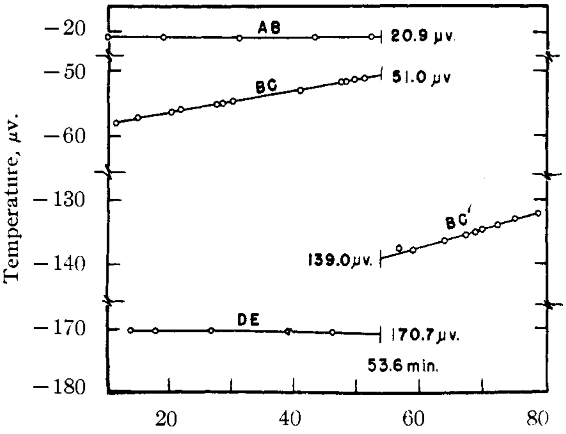

Fig. 2.—Time–temperature curves for (DE) capsule in precooler, (BC) calorimeter before dropping capsule, (BC′) calorimeter after dropping capsule, and (AB) reference Dewar-bath differential temperature.

Results

Freezing and non-freezing water values for Samples I-VI at various moisture levels are shown in Table II and are graphed in Figs. 3 and 4. In the figures the non-freezing water percentages are plotted as ordinates, the freezing water values as abscissas, the total water in the system being the sum of these two values. Precision of the results does not preclude the possibility of curves instead of straight lines as graphed in Figs. 3 and 4.

Discussion

Interpretation of the data and curves on the cellulose fibers may be made as follows: consider the case of sample I (Acala cotton). Starting with the dry cotton, the first 4.3% water adsorbed by the cellulose is all of the non-freezing type. Additional water (region AB, Fig. 3) is adsorbed under conditions which permit only part of the water to be non-freezing; approximately half of that added in this region exhibits heat of fusion when cooled to the freezing temperature of −4.5°. At moisture levels higher than that indicated by point B all additional water is of the freezing type.

The authors believe that all water adsorbed below the value of 4.3% for this cotton sample is

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(27) For a discussion of the sources of error in the "heat of fusion" method, see ref. 3.

(28) P. I. Andrianow, *Kolloid-Z.*, **78**, 107–108 (1937).

(29) Shipley, Campbell and Maass, *Canada J. Res.*, **17B**, 40–50 (1939).

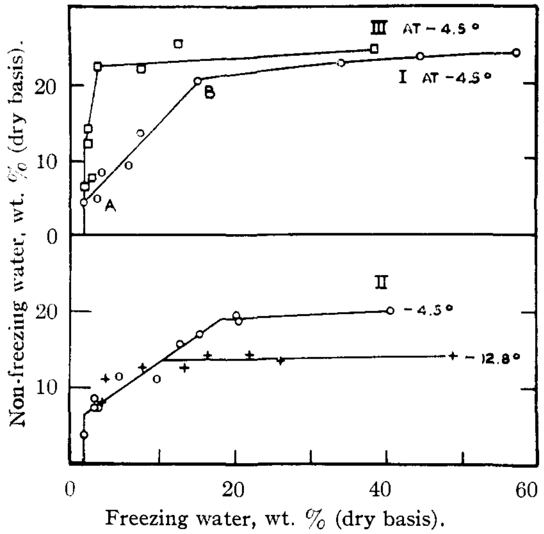

Fig. 3.—Freezing *vs.* non-freezing water values for Samples I, II and III.

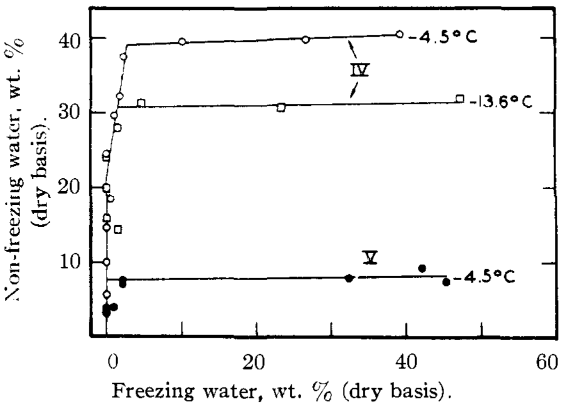

Fig. 4.—Freezing *vs.* non-freezing water values for Samples IV and V.

water hydrogen-bound to the free hydroxyl groups of the glucose units in the non-crystalline regions of the fiber. In support of this interpretation is the X-ray evidence which indicates that water does not enter the crystalline regions of native cellulose.[30] This behavior is not true of the mercerized, or regenerated cellulose crystallites which show increase in dimension of the unit cell upon the addition of moisture. Non-freezing water at higher moisture values may be considered water either adsorbed in multilayers or filling small capillary spaces, or both. In any case, its activity is lowered sufficiently so that it does not exhibit heat of fusion when cooled to the freezing temperature of the experiment. Some of the water at higher moisture values, however, does freeze, indicating that it is filling capillary spaces large enough so that its activity is still fairly high. Similar explanations might be made for the observations with samples II, III and IV, the Rowden cotton, mercerized Wilds cotton, and rayon, respectively.

TABLE II

FREEZING AND NON-FREEZING WATER CONTENT FOR TEXTILE FIBERS

(Per cent. moisture, dry basis)

Total	Freezing	Non-freezing
Sample I, Acala cotton Freezing temperature, −4.5°		
4.38	0.1	4.3
6.75	1.8	4.9
10.58	2.3	8.3
15.21	6.0	9.2
21.21	7.6	13.6
35.58	15.3	20.3
56.79	34.1	22.7
68.03	44.6	23.4
81.29	57.3	24.0
Sample II, Rowden cotton Freezing temperature, −4.5°		
3.97	0.1	3.9
8.80	1.5	7.3
9.26	1.9	7.4
10.08	1.6	8.5
16.16	4.8	11.4
21.01	9.8	11.2
28.74	12.9	15.8
32.42	15.4	17.0
39.17	20.5	18.7
39.68	20.2	19.5
60.65	40.6	20.1
Sample IV, Cordura rayon Freezing temperature, −4.5°		
5.69	0.0	5.7
9.90	.0	9.9
14.75	.0	14.7
19.24	.6	18.6
24.40	.0	24.4
30.81	1.1	29.7
34.05	1.9	32.2
39.91	2.3	37.6
49.71	10.1	39.6
66.41	26.7	39.8
79.74	39.2	40.6
Freezing temperature, −13.6°		
15.81	0.0	15.8
15.82	1.5	14.3
20.05	0.0	20.0
24.18	0.0	24.2
29.40	1.4	28.0
35.90	4.8	31.3
54.14	23.3	30.8
79.18	47.2	31.9
Sample II, Rowden cotton Freezing temperature, −12.8°		
10.38	2.3	8.1
14.21	3.0	11.2
20.77	7.9	12.8
26.19	13.5	12.7
30.66	16.5	14.2
36.49	22.0	14.5
39.43	26.1	13.4
63.23	48.9	14.3
Sample III, mercerized Wilds cotton Freezing temperature, −4.5°		
6.50	0.0	6.5
8.91	1.0	7.9
12.67	0.5	12.2
14.89	0.6	14.3
24.11	1.8	22.3
29.40	7.6	21.8
37.77	12.5	25.3
63.12	38.6	24.6
Sample V, Nylon Freezing temperature, −4.5°		
3.21	0.0	3.2
3.75	.0	3.75
5.01	1.0	4.0
9.20	2.1	7.1
9.89	2.1	7.8
40.43	32.4	8.0
51.38	42.1	9.2
52.75	45.3	7.5
Sample VI, glass fibers Freezing temperature, −4.7°		
29.88	29.5	0.4
23.95	24.0	0.0
Freezing temperature, −19.6°		
25.19	24.9	0.3
41.90	41.9	0.0

This interpretation is supported in the following considerations.

(30) Katz, *Physik. Z.*, **25**, 321 (1924); *Trans. Faraday Soc.*, **29**, 279 (1933).

1. Lowering the freezing temperature should freeze water in smaller capillaries without changing the amount of hydroxyl adsorbed water (or A-point). The system should, therefore, exhibit larger amounts of freezing water when the freezing temperature of the system at the same moisture level is decreased. This is seen to be so for the Rowden cotton (sample II) and the rayon (sample IV), which were both run at a freezing temperature of approximately −13° as well as at −4.5°. The only change which occurs is that the B intersection is moved down the line AB.

2. If one assumes that the intersection of the line AB with the *y*-axis indicates all the water bound to the hydroxyl groups of the glucose units in the non-crystalline regions of the cellulose fiber, a calculation of the "degree of crystallinity" or percentage of crystalline material in the fiber should be possible. This is accomplished by merely assigning three water molecules to each glucose unit in the non-crystalline region of the native cellulose, and in the case of regenerated or mercerized fibers, as postulated by Hermans,[17] an additional one-half water molecule in the crystalline region, and calculating the fraction of non-crystalline material required to give a moisture content indicated by point "A." The results of such a calculation, along with the "degree of crystallinity" found by Philipp, Nelson and Ziifle[31] by heterogeneous acid hydrolysis studies on similar cottons but the same mercerized cotton and viscose rayon samples are summarized in Table III. The agreement is seen to be fairly good, especially when the inaccuracies involved in determining the A point by the calorimetric method are taken into consideration.

TABLE III

CRYSTALLINE FRACTIONS OF COTTON AND RAYON SAMPLES

Sample	Bound water (Point A)	Non-crystalline fraction	Crystalline fraction (Calorimetric)	Crystalline fraction (Philipp *et al.*[31])	Non-accessible fractions by other investigations[d]	
I	4.3%	0.13	0.87	0.81	0.60[a]	0.95[b]
II	6.4	.19	.81			
III	12	.23	.77	.76	.76[c]	.85[b]
IV	19	.48	.52	.62	.25[a]	.73[b]

[a] P. H. Hermans, "Contribution to the Physics of Cellulose Fibers" Elsevier, New York, 1946, p. 71. [b] Data on cotton linters, alkali treated linters, and high-tenacity, viscose tire-cord yarn reported by C. C. Conrad and A. G. Scroggie, *Ind. Eng. Chem.*, **37**, 592 (1945). [c] Data on caustic-swollen cotton linters from A. G. Assaf, R. H. Haas and C. B. Purves, THIS JOURNAL, **66**, 66 (1944). [d] Non-crystalline and accessible cellulose are not necessarily synonymous, although the latter may be included in the former. All cellulose not in the crystalline form may be defined as non-crystalline, but it may not be equally accessible to chemical reaction by oxidizing agents.

3. These two considerations do not eliminate the possibility of part of the non-freezing water in the region AB being water involved in multilayer adsorption on the cellulose in the non-crystalline regions where the hydroxyl groups have already adsorbed one water molecule each; and, indeed, such differentiation is beyond the scope of this investigation.

There is some evidence that in systems exhibiting adsorption–desorption hysteresis, such as in that formed by water and cellulose fibers, adsorption consists of monomolecular layer formation followed by capillary condensation.[32] If, however, multilayer formation, in which the second water molecule has attached itself to the first already hydrogen-bonded to the glucose unit hydroxyls, does take place, it must occur simultaneously with capillary condensation. The experimental observations indicate that when enough water has been taken up by the system to satisfy the requirements of bound water as outlined earlier, at least part of any additional water adsorbed occupies positions where it can readily form the ice crystal lattice and exhibit heat of fusion. It seems more likely, therefore, that this will occur if fairly large aggregates of liquid water are formed, as, for example, in capillary condensation, than if the additional water is distributed in a manner similar to a second layer.

If, then, one rules out the possibility of adsorbed multilayers, the capillary radius may be approximated from the freezing point of the water in the capillary by assuming that the lowered freezing temperature is due to the reduced activity of the water in the small capillary. Integrating the Clausius–Clapeyron equation between the limits T_0 to T and p_0 to p one may obtain for the case of ΔH constant

$$\ln a = \ln \frac{p}{p_0} = -\frac{\Delta H(T_0 - T)\,{}^{32a}}{RTT_0} \qquad (1)$$

in which a is the activity of the water in the capillary referred to pure water in a plane surface at 0°, p and p_0 are the vapor pressures of both the capillary water and the water in a plane surface, ΔH the heat of fusion, T and T_0 are the absolute freezing temperatures of the water in the capillary and in a plane surface, respectively, and R is the gas constant. The relation between $\ln(p/p_0)$ and the capillary radius, r, has been shown to be

$$r = -\frac{2\gamma M}{d\,RT \ln (p/p_0)} \qquad (2)$$

for the case in which the liquid wets the capillary walls.[33,34]

In equation 2, γ, M and d are the surface tension, molecular weight and density of the liquid, respectively. Substituting the right-hand side of Eq. 1 into Eq. 2 for $\ln(p/p_0)$ one obtains the expression

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[31] H. J. Philipp, M. L. Nelson and H. M. Ziifle, "The Crystallinity of Cellulose Fibers," presented at the 109th meeting of the A. C. S. at Atlantic City, April 8-12, 1946.

[32] L. H. Cohan, THIS JOURNAL, **66**, 98 (1944).

[32a] Equation (1) as employed is in reality an approximation. Rigorously equation (1) holds only when p and p_0 refer to the same temperature, or when $T_0 - T$ approaches zero.

[33] Lord Kelvin, *Proc. Roy. Soc.* (*Edinburgh*), **7**, 63 (1870).

[34] For a discussion of the derivation of this equation see N. K. Adam, "The Physics and Chemistry of Surfaces," 3rd ed., Oxford University Press, New York, N. Y., 1941, Chapter 1; also, A. J. Stamm, *Physics*, **6**, 334 (1935).

$$r = \frac{2\gamma M T_0}{d\Delta H(T_0 - T)} \qquad (3)$$

Application of equation 3 should give some indication of the maximum capillary radii of those pore spaces containing free water which does not freeze at a given temperature. Furthermore, the volume of free water which does not freeze at moisture levels below the B-point may be interpreted as being that of the pore spaces having radii equal to or less than the value calculated by equation 3 on the assumption that the pores are filled with water.

Calculations based on the above considerations have given the results shown in Table IV. Column 3 shows estimated (by equation 3) maximum capillary radii of those pores containing water which does not freeze at -4.5 and $-13.0°$ and column 6 indicates the amount of unbound water contained in capillary spaces having radii less than the maximum value. Since some swelling of the non-crystalline regions in the fiber probably occurs when the fiber is wet, it seems possible that the volume of capillary space having certain radial dimensions in an elastic cellulose fiber varies with the moisture content of the fiber. The volumes in column 6, therefore, probably vary considerably with the condition of the fiber.

TABLE IV

ESTIMATED CAPILLARY RADII AND CAPILLARY VOLUMES IN COTTON AND RAYON SAMPLES

	Sample	Freezing temp. °C.	Max. radius of capil. filled with non-freezing water, °A.	Total non-freezing water, % (Point B)	Bound water, % (Point A)	Volume of unbound water/g. of fiber in capillaries less than max. radius (Col. 3), ml.
I	Acala cotton	− 4.5	285	20.3	4.3	0.16
II	Rowden cotton	− 4.5	285	19	6.4	.126
		−13	94	13.6	6.4	.072
III	Wilds mercerized cotton	− 4.5	285	22.3	12	.103
IV	Cordura rayon	− 4.5	285	39	19	.20
		−13	94	30.8	19	.12

4. Nylon adsorbs non-freezing water up to a total of about 8% (dry basis). All additional water freezes at $-4.5°$. This is approximately the amount of adsorbed water reported for stretched nylon at room temperature and 90 to 95% R. H.[35,36]

Bull[36] and Pauling[37] have interpreted the moisture adsorption of nylon as the attachment of one water molecule to each free polar carbonyl and imido group. Apparently this primary adsorption is the only way in which nylon can take up water, because the calorimetric data herein reported indicate no non-freezing water in addition to that taken up by primary adsorption. If water is taken up in second or higher multilayers it must be in a position to freeze and exhibit heat of fusion; if capillary water is present it must be in fairly large spaces because it freezes at $-4.5°$ or above.

5. Glass fibers exhibit practically no moisture regain, and, therefore, would not be expected to hold appreciable quantities of non-freezing water. The data in Table II confirm this expectation and also indicate that water held by interfiber capillarity is all of the freezing type.

Summary

The calorimetric technique employing the method of mixtures has been applied in a study of the nature of moisture in textile fibers. Measurements were made on native cotton, mercerized cotton, rayon, nylon and glass fibers with various moisture contents. The amounts of freezing and non-freezing water were calculated for each fiber–moisture combination measured. Interpretation of the results for cellulose fibers permits differentiation between water of primary adsorption and water adsorbed in multilayer formation or by capillary condensation. From the data obtained estimates of the degree of crystallinity and capillary volumes with certain limiting radii were made for the cotton and rayon fibers.

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(35) G. Lobasy, *Rayon Textile Monthly*, **24**, 637 (1943).

(36) H. B. Bull, THIS JOURNAL, **66**, 1499 (1944).

(37) L. Pauling, *ibid.*, **67**, 555 (1945).