

Specific Heat of Wool in the Temperature Range -50 to 100°C .

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Synopsis

The specific heat of wool containing 2.6, 2.9, and 8.9 g. of water per 100 g. of dry wool has been measured over the temperature range -50 to 100°C . All of the wool samples showed an approximately linear increase of c_p with temperature, but small increments appeared at -30 , 20 , 50 , and 70°C . With increasing water content at any one temperature the specific heat increased. The specific heat of the sorbed water seemed to be more nearly like that of ice than of liquid water; if the sorbed water is assumed to have the specific heat of ice at all compositions and temperatures, an apparent specific heat of the wool can be calculated. With increasing water content the apparent specific heat of the wool approaches that of the synthetic polymer, nylon 6.

Introduction

The only available data on the specific heat of wool appear to be those reported by Dietz¹ in 1912. He found a value of 0.325 cal./deg.-g. and remarked that the effect of temperature was negligible between 0 and 100°C ., while the effect of absorbed water was given by the additive formula.

In this paper we present results of a study of the specific heat of a wool sample at two different water contents, over the temperature range -50 to 100°C . The conclusions of Dietz are found to be invalid.

Materials and Methods

The wool used was from a Corriedale fleece (designated SW1). It was cleaned by repeated washing at room temperature in petroleum ether and distilled water. In order to give better packing in the calorimeter the fibers were cut into short lengths; the distribution of length was very wide, with an average of about 1 mm. The disulfide bonds in wool are relatively labile, and as a check on damage due to cutting analyses for $-\text{SS}-$ and $-\text{SH}$ were done: there was certainly no loss of $-\text{SS}-$ or increase of $-\text{SH}$.

The calorimetric techniques were the same as those employed by Wilkin-son and Dole.²

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Details of the treatment of the wool sample after it was loaded into the calorimeter are given in the next section. After the specific heat measurements were complete the wool was recovered, brought to saturation water content, and then dried to constant weight (76.3 g.) at 100°C.

Results

Run 1. The calorimeter containing the wool sample was evacuated for about 60 hr. filled with helium to a pressure of 20 cm. Hg, sealed and weighed. After appropriate corrections for buoyancy the weight of wool plus absorbed water was found to be 78.5 g., thus the water content was 2.2 g. or 2.8%. The specific heat of the sample was now measured by heating in approximately 5°C. steps with the results shown in Figure 1.

The general trend of the data is well represented by a straight line over the whole range from -58 to 90°C., but the scatter of experimental points is unusually great in the ranges 5-15°C., 35-50°C., 60-90°C., indicating the possibility of minor structural transitions in these regions.

Run 2. The calorimeter was now allowed to cool to 27°C., and again heated in steps to 93°C. The solid circles in Figure 2 show that the results of the first run indicated by the straight line were fairly well reproduced up to 65°C., but then the specific heat increased sharply.

Run 3. After a check that showed no change in weight, the calorimeter seal was opened and the wool exposed to a high relative humidity (~100%) at low air pressure. The polypeptide chains in wool have a considerably enhanced freedom to rearrange at high water content, and the purpose of this step was to see if the original specific heat curve could be restored

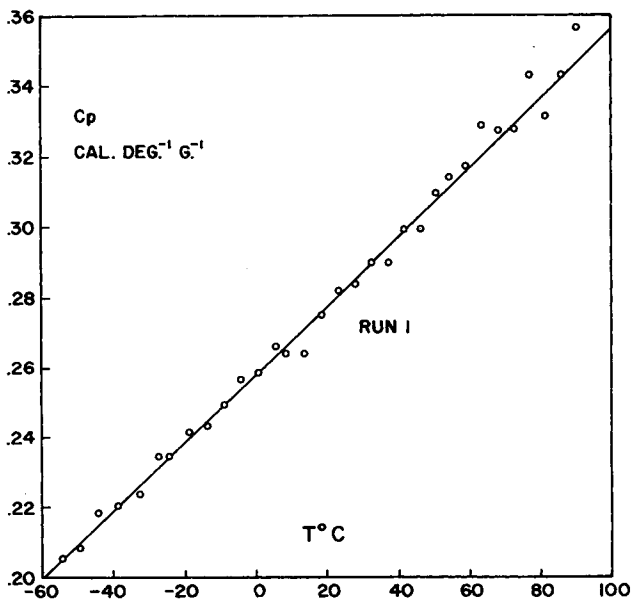


Fig. 1. Specific heat of wool containing 2.8% water.

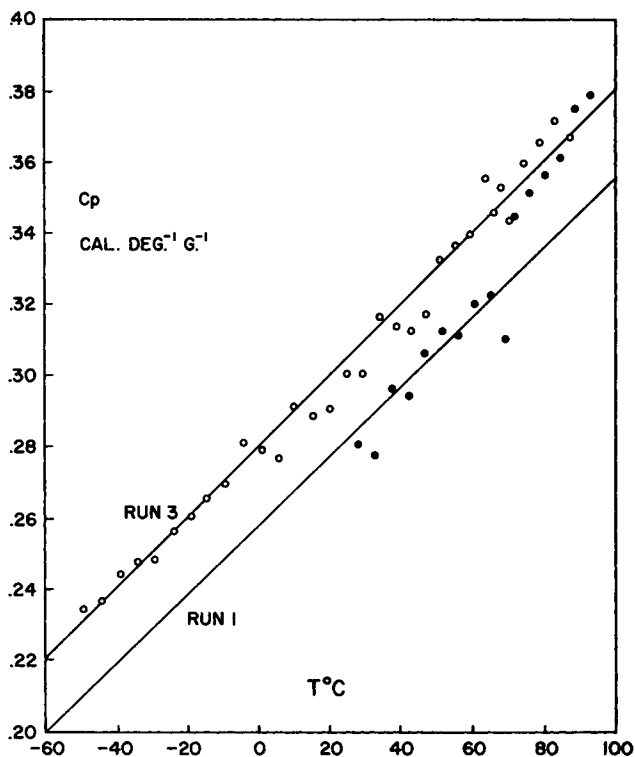


Fig. 2. Specific heat of wool: (●) wool containing 2.8% water, second series of measurements (run 2); (○) wool containing 2.55% water (run 3). Lower straight line represents results shown in Figure 1.

However, after nine days at high humidity the wool weight was only 85.2 g., i.e., a water content of 10.4% compared with the saturation uptake of approximately 26%.

The calorimeter was now evacuated for ~ 60 hr. as before, helium was introduced, and the wool plus absorbed water weight found to be 78.3 g. Specific heats were again measured over the range -50 to 90°C .; results are shown in Figure 2 (open circles).

The general trend of the data is represented by a straight line above and almost parallel to that for the first run. At temperatures higher than 70°C . results from the second and third runs are in reasonable agreement, indicating irreversibility of the step in run 2. There is unusual scatter of the experimental points in the ranges -5 to 20°C ., 35 – 50°C ., and 60 – 90°C .

Run 4. In preparation for a series of measurements at a higher water content the wool was exposed to high relative humidity for five days. After air was pumped out of the calorimeter and helium introduced the wool weight was 83.1 g. hence the amount of absorbed water was 6.8 g. or 8.2%.

The actually measured specific heat values are shown in Figure 3 by the open circles. However, these data are subject to the following uncertainty.

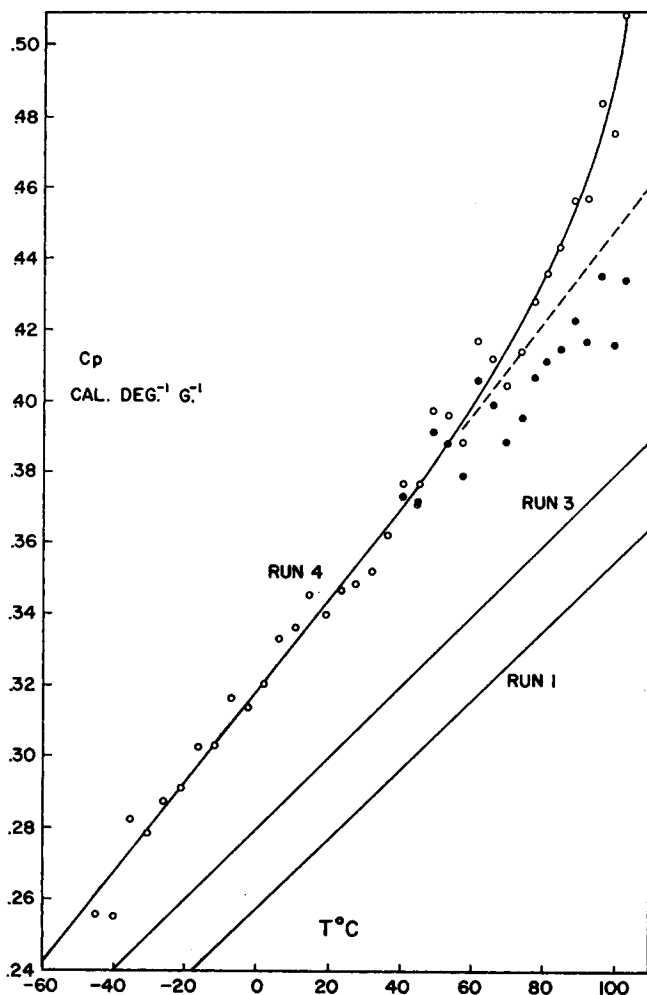


Fig. 3. Plot of (O) specific heat of wool containing 8.18% water (run 4); (●) data of run 4 corrected for heat of evaporation of water. Lower two straight lines represent data of Figures 1 and 2.

During the heating period the temperature of the calorimeter plus contents rose by an amount ΔT , usually 4–5°C. As the vapor pressure of the sorbed water in the wool rises with temperature, a certain amount of water has to evaporate from the wool to produce the required increase in vapor pressure in the calorimeter. The free volume in the calorimeter was measured to be 0.58 liter. In one experiment in which the temperature of the calorimeter rose from 100.86 to 104.49°C., it is estimated from the vapor pressure data of Wiegerink³ (which agree fairly well with values calculated from the more recent thermal measurements of Morrison and Hanlan⁴ on wool keratin) that 0.034 g. of water must have been evaporated to produce the calculated increase in vapor pressure. Taking the average differential heat

of desorption⁵ as 115 cal./g. and the heat of vaporization of water at 100° C. as 538 cal./g., the heat required to evaporate 0.034 g. of water was 22.3 cal. This is extra heat which should be subtracted from the heat added electrically to the calorimeter in order to obtain the true specific heat of the partially hydrated wool. The solid circles of Figure 3 are the specific heats so corrected. There is considerable uncertainty in this correction, because the actual changes in vapor pressure were not measured. It was assumed that the desorption vapor pressure-temperature curve of Wiege-rink³ (on clothing wool) was applicable to our case. Also the heats of desorption change with temperature and with composition.

Prior to the first run the wool samples had been at ambient conditions of relative humidity and temperature for some weeks. Under these circumstances the amount of "incorporated" water⁶ in the wool increased, "incorporated" water being defined as water which remains in wool at zero relative humidity even at temperatures in the vicinity of 100°C. During the first two specific heat runs the water content was 2.8%, and during the third, 2.6%. These quantities are within the range possible for "incorporated" water,⁶ and hence the humidity in equilibrium with the wool should have been very low at all the temperatures used during the three runs. No correction was necessary.

The corrected specific heat data of run 4 show that a linear relation between specific heat and temperature is approximately valid. Although there is considerable scatter, we may represent the specific heats of runs 1, 3, and 4 by the linear equation.

$$c_p = A + BT \quad (1)$$

where temperature is in degrees centigrade, and where the constants *A* and *B* have the values given in Table I. In the case of run 4, the constants were determined from the data over the temperature range -40 to 70°C.

TABLE I
Data for the Specific Heat of Wool

Run	H ₂ O, g./100 g. dry wool	<i>A</i> , cal./g.-deg.	<i>B</i> , cal./g.-deg. ² × 10 ⁴
1	2.9	0.258	9.8
3	2.6	0.280	10.0
4	8.9	0.319	12.8

Discussion

We first consider the relative contributions to the specific heat of the wool and water separately. If we make the unlikely assumption that the specific heat of the wool component was unaffected by the presence of the water, we can extrapolate the specific heats of runs 3 and 4 to zero water content and obtain the specific heat of dry wool. Equation (2) was obtained in this way. Equation (3) is the specific heat of the water

component of the wool in run 4 assuming the specific heat of the wool is given by eq. (2).

Specific heat assuming wool unchanged by water content:

$$c_p, \text{ dry wool (extrap.)} = 0.265 + 8.2 \times 10^{-4}T \quad (2)$$

$$c_p, \text{ H}_2\text{O (run 4)} = 0.923 + 65.5 \times 10^{-4}T \quad (3)$$

Specific heat assuming water has specific heat of ice:

$$c_p, \text{ ice} = 0.506 + 18.6 \times 10^{-4}T \quad (4)$$

$$c_p, \text{ wool (run 3)} = 0.274 + 9.77 \times 10^{-4}T \quad (5)$$

$$c_p, \text{ wool (run 4)} = 0.302 + 12.28 \times 10^{-4}T \quad (6)$$

$$c_p, \text{ dry wool (extrap.)} = 0.261 + 8.63 \times 10^{-4}T \quad (7)$$

Equations (2)–(7) are based on the assumption of additivity of specific heats, that is,

$$c_{p,\text{sample}} = Xc_{p,\text{wool}} + (1 - X)c_{p,\text{H}_2\text{O}} \quad (8)$$

where X is the weight fraction of wool in the sample. The specific heats of eqs. (2–7) should be called apparent specific heats, except those for ice which were taken from handbook data.

The apparent specific heat of water calculated from eq. (3) is plotted in Figure 4 and compared with observed values for pure liquid water and for ice. It is seen that the apparent specific heat is ridiculously large, especially at high temperatures; hence we can conclude at once that the specific heat of the wool component is affected by the presence of the water. This, of course, is not a new conclusion; all measurements of force and force relaxation in wool fibers at different water contents show the changes in hydrogen bond strength and in mobility of polypeptide chains that result from changes in quantity of absorbed water. The effect of additional water is not always to weaken the fibers. It has been shown⁷ that up to 70% R.H. (20°C.) fibers containing "incorporated" water are stiffer than in its absence. In our case, "incorporated" water should have been present in all experiments, and a weakening should have resulted from the higher water content in the wool in run 4.

A number of lines of investigation indicate that up to water contents higher than used here, most of the water exists in the form of isolated sorbed molecules. Such evidence comes from analyses of the water content versus relative humidity isotherm (see for instance, Alexander and Hudson⁸), and from thermal measurements.⁴ Furthermore, by application of Zimm's⁹ cluster integrals to Morrison and Hanlan's data, Starkweather¹⁰ calculated and graphed values of $\phi_1 G_{11}/v_1$, where ϕ_1 is the volume fraction of sorbed water, G_{11} is the cluster integral of type 1 molecules (water), and v_1 is the partial molar volume of water. By dividing by ϕ_1 we obtain the ratio G_{11}/v_1 which is a measure of the volume of the system from which sorbed molecules are excluded by one sorbed molecule. An

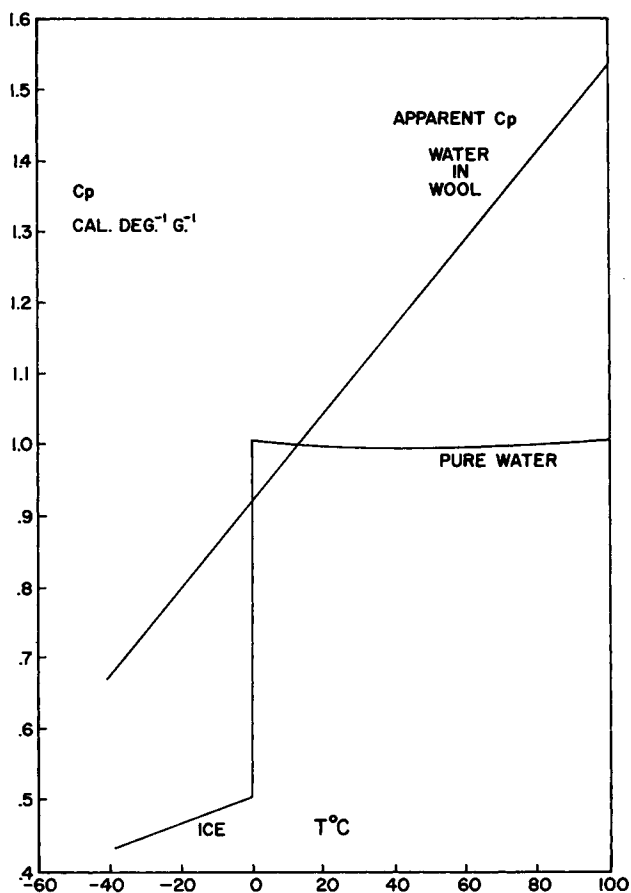


Fig. 4. Apparent specific heat of water in wool calculated assuming that the specific heat of wool is unaffected by water content and compared to the specific heat of ice and pure water.

ideal solution gives values of -1 ; i.e., each sorbed molecule excludes a volume equal to its own volume. In the case of the wool keratin system G_{11}/v_1 varied from -15 to -5 over the range of water content of interest here. This result demonstrates that there is no tendency for water to cluster at least up to $n = \text{ca. } 0.9$. Notice also that there is no break in the specific heat temperature curve of run 4 in the neighborhood of the freezing point of water.

The nuclear magnetic resonance line widths for water in nearly dry wool and in wool at 8.2% water content were approximately 1 and 0.3 gauss, respectively, at 20°C.¹¹ The line width for water was only 0.018 gauss. Thus, the water proton mobility in wool at these levels of uptake is much less than in liquid water, and suggests another limiting case in the treatment of the specific heat data which is to assume that the sorbed water has the specific heat of ice and then to calculate the apparent specific heat of the

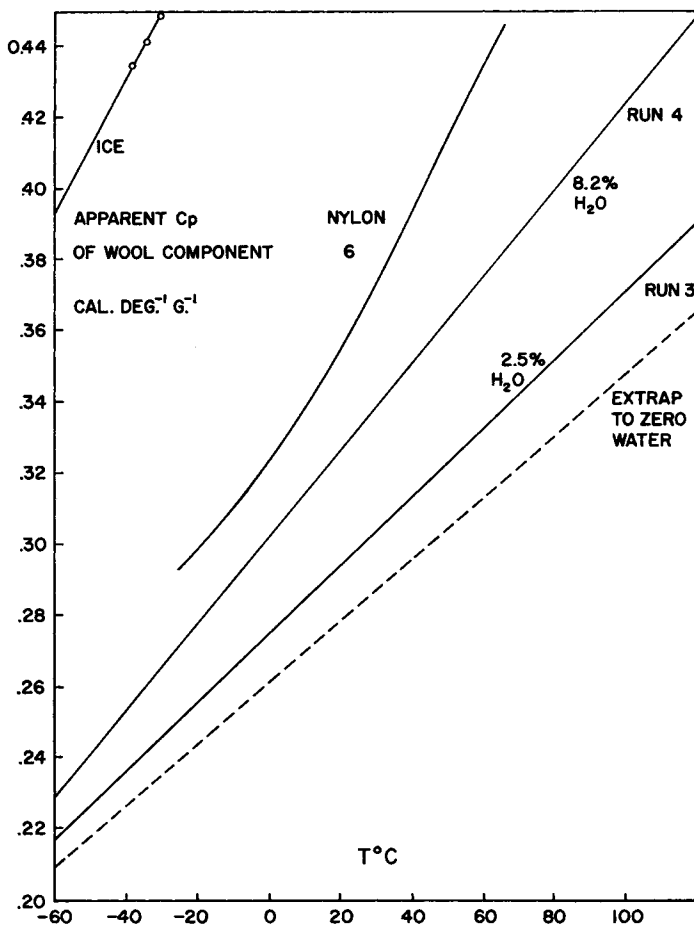


Fig. 5. Apparent specific heat of wool in 8.2, 2.5, and 0% water systems calculated assuming that the absorbed water has the specific heat of ice. Specific heats of "pre-melt annealed" nylon 6 fibers and ice also shown for comparison.

wool component. Equations (5), (6), and (7) represent the calculated specific heat of the wool component for the systems with 2.53, 8.17, and 0% water, respectively. These results are plotted in Figure 5 along with data for ice, and nylon 6¹² for comparison. Nylon 6 has almost the same number of peptide groups per 100 g., as wool. Figure 5 shows how the presence of the water "opens up" the wool structure and makes possible additional molecular motions in the solid. It may be incorrect to extrapolate the data from 8.2 and 2.5% water to 0% as done in Figure 5, because the effect of "incorporated" water on c_p may be quite different from that of the water sorbed between 2.5 and 8.2%. It would be interesting to obtain more specific heat data on wool containing water percentages below 2.5% and between 2.5 and 8.2%.

Another uncertainty in the calculations of Figure 5 rests in assuming that the sorbed water has the same specific heat as ice. In their study of the

dielectric properties of the wool-water system Windle and Shaw¹³ concluded that the initially sorbed water was "irrotationally" bound. They divided the sorbed water into three classes: that sorbed in localized sites, mobile water, and water sorbed in a condition intermediate between the mobile and localized water. At the water percentages of concern here, most of the sorbed water would be of the first class, i.e., localized water. If we assume that the molar heat capacity of ice, approximately 9 cal./deg. mole at 0°C., is reduced by $3/2R$ for loss of rotational degrees of freedom on sorption by wool, the apparent specific heat curve of wool in run 4 would be raised almost up to the specific heat of nylon 6. Both wool and nylon 6 have approximately 0.88 moles of peptide groups per 100 g. but it is difficult to conclude that the specific heats should be nearly identical because wool's peptide groups are close together along the backbone chain and its other carbon atoms are in side chains. Nylon 6 has no side chains. The mobility of the carbon atoms in the side chains would be expected to be greater than those in the nylon 6 chain; however, the wool chain should be stiffer than that of nylon 6 because of the double character of the N—C bond in the peptide group. Hence, these two effects tend to cancel one another. At any rate, it is interesting that the apparent specific heat of the wool component in the sample containing 8.17% water is so close to that of nylon 6 when calculated assuming a reasonable apparent specific heat for the water component.

These calculations and eqs. (5), (6), and (7) might seem to be unreasonable because of the adoption of eq. (4) for ice for the apparent specific heat of water even up to temperatures of 100°C., but it is unlikely that the specific heat of the sorbed water would change markedly at a high temperature unless there were a first- or second-order phase change for which there is no evidence.

Windle and Shaw¹³ analyzed their dielectric data assuming that the molar polarization of the wool was unaffected by the presence of the water. The calculations of this paper are illustrated in Figure 5 and, if correct, demonstrate that this assumption is probably unjustified.

If the specific heat data illustrated in Figures 1 and 2 are examined carefully, it will be seen that the specific heat seems to rise in steps at a number of temperatures. In both runs 1 and 3 these temperatures at which the major jumps occurred were approximately -30, +20, 50, and 70°C. The wool acted almost as if its structure remained constant until a certain temperature was reached when suddenly some release of structure occurred, thereby allowing the specific heat to increase about 0.01 of a specific heat unit. The jumps were greater for run 3 than for run 1, and in the case of the experiment with 8.2% water (run 4), the low temperature jumps were mostly obliterated.

Evidence has previously been given for transitions at 35¹⁴ and 60°C.¹⁵ At 60°C. in this work there is considerable scatter to the specific heat data; in run 2 a significant increase is seen in the specific heat at 70°C. This deviation from linear behavior, if real, is an indication not of a first-order

phase change (no maximum is to be seen in the specific heat-temperature curve) but of an irreversible alteration in the physical structure of the wool.

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Résumé

La chaleur spécifique de la laine contenant 2,6, 2,9 et 8,9 gr d'eau par 100 gr de laine sèche a été mesurée aux températures de -50° jusqu'à 100°C . Pour tous les échantillons de laine, c_p augmente presque linéairement avec la température, mais de faibles augmentations apparaissent à -30 , 20 , 50 et 70°C . Lorsque la teneur en eau augmente, la chaleur spécifique augmente pour chacune des températures. La chaleur spécifique de l'eau absorbée semble plutôt égale à celle de la glace, qu'à celle de l'eau liquide. Si on suppose que la chaleur spécifique de l'eau absorbée est égale à celle de la glace pour toutes les compositions et toutes les températures, on peut calculer la chaleur spécifique apparente de la laine. La chaleur spécifique apparente de la laine s'approche de celle du polymère synthétique nylon 6, lorsqu'on augmente la teneur en eau.

Zusammenfassung

Die spezifische Wärme von Wolle mit einem Gehalt von 2,6, 2,9 und 8,9 g Wasser pro 100 g Trockenwolle wurde im Temperaturbereich -50 bis 100°C gemessen. Alle Wolleproben zeigten eine angenähert lineare Zunahme von c_p mit der Temperatur, es traten aber bei -30 , 20 , 50 , und 70° kleine Inkremente auf. Mit zunehmendem Wassergehalt stieg bei jeder Temperatur die spezifische Wärme an. Die spezifische Wärme des sorbierten Wassers scheint eher der des Eises als der des flüssigen Wassers gleich zu sein; wenn man annimmt, dass das sorbierte Wasser bei allen Zusammensetzungen und Temperaturen die spezifische Wärme von Eis besitzt, kann eine scheinbare spezifische Wärme der Wolle berechnet werden. Mit zunehmendem Wassergehalt nähert sich die scheinbare spezifische Wärme derjenigen des synthetischen Polymeren Nylon 6.

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