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Specific Heats of Collagen and Leather

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Determinations of the specific heats of collagen, vegetable-tanned leather, chrome-retanned leather, chrome leather, and these materials containing varying percentages of moisture were made at 25° C. The same determinations were also made on dry chestnut and quebracho tanning extracts and on a stuffing grease and an animal oil. The results obtained with the collagen and leather containing various percentages of moisture show abrupt breaks in the curves, which indicate phase changes. These changes are explained on the basis of changes in the vibrational activity of the polar groups in the collagen molecule.

Lubricating materials, added to leather, increase the specific heat. This affects the comfort of the leather adversely during cold weather.

1. Introduction

In connection with the heats of wetting of collagen and leather [1],[1] interest arose with regard to the specific heats of these materials. For highly accurate calorimetric measurements, a knowledge of the specific heats of all components is necessary.

Although specific heat is a fundamental physical property, little information with regard to its values for leather or collagen is available in the literature. An examination of the literature located only one study of the specific heat of leather. A. Cheshire and N. L. Holmes [2] give a value of 0.263 cal/g for dry leather and 0.321 cal/g for leather containing 16.28-percent of water. The Handbook of Chemistry and Physics [3] gives a value of 0.36 cal/g/deg C for the specific heat of dry leather.

An important study related to leather was made by Hampton and Mennie [4]. They determined the specific heats of gelatin gels over a temperature range of 25° C to −180° C, in an effort to obtain some information on bound water. They found that the specific heats of water and dry gel were not additive, and their studies yielded no reliable information on the percentage of so-called bound water in these materials.

Specific heat is an important factor in determining the comfort of wearing materials. Although not as important as the rate of conduction of heat, the amount of heat required to maintain temperature equilibrium will depend upon the heat capacity of the materials worn. This is especially noticeable in cold weather when shoes are changed.

A study of the property of specific heat is most important in the elucidation of some of the fundamental properties of a material. A determination of the specific heat of leather containing varying amounts of moisture may yield information with regard to the manner in which the two components combine. The comparison of the specific heat of collagen with that of leather may yield similar information with regard to the tanning agent and collagen.

In the present study, the specific heats of collagen and three different tannages of leather were determined at 25° C. Determinations of specific heats were made on the dry material and on the materials containing various percentages of water ranging from 0 to 17 percent. Specific heats were also determined for two types of tanning agents and for oils and greases used to lubricate leather.

2. Apparatus and Procedure

The calorimeter used in this work was the same as the one used in a study of the heats of wetting of collagen and leather [1]. This calorimeter was originally developed by Newman and Wells [5] to study the heats of hydration of cements.

An attempt was made, in the initial experiments, to make the determinations by suspending the materials in carbon tetrachloride. Carbon tetrachloride was used as the suspending liquid and heat transfer medium because it has a low specific heat (approximately 0.2 cal/g/deg C) and because it is a nonpolar liquid, which should not react with leather or collagen. A liquid of low specific heat was desired, so that the accuracy of the measurement would be improved by having a greater percentage of the total heat absorbed by the sample under test.

However, the determination of specific heats by suspending the specimens directly in the liquid medium used for thermal transmission was found to be unsatisfactory. The apparent specific heats obtained in this way were quite variable and sometimes negative, which is impossible. The medium apparently reacted with the materials to take up energy, or a slow solution process occurred.

In order to obtain reliable data, it was necessary to place the test specimens in a container where no direct contact was made with the heat-conducting medium. The specimens were placed in small copper tubes 11 cm in length and 1 cm in diameter. About 2.5 g of sample was contained by each tube. A series of ten tubes was used for a determination on each sample, making a total specimen size of about 25 g. The ten tubes were wired together to form a raft, and then submerged in the heat-conducting

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[1] Figures in brackets indicate the literature references at the end of this paper.

medium of carbon tetrachloride. This procedure proved to be very satisfactory. The small diameter of the tubes, and the intimate contact will all the tubes by the medium, gave rapid thermal equilibrium.

Determinations were made at 25° C on each sample at various concentrations of moisture. The copper tubes were filled with the leathers or collagen conditioned at 50-percent relative humidity and 73° F. After the specific heat was determined on each specimen, the caps on the tubes were removed, the tubes and contents were placed in a desiccator, and part of the moisture was removed by means of a vacuum pump. After pumping for several hours, the tubes were removed from the desiccator, the caps were replaced, the tubes and contents were weighed, and the specific heat was determined. This procedure was continued until there was no further loss in weight on evacuation. Six to eight determinations on each specimen with varying amounts of moisture were made in this way. Finally the specimen was completely dried by heating in an oven at 100° C for 24 hr and a specific heat determination made.

Determinations in the calorimeter were made in pairs. The runs were started slightly below 25° C. After thermal equilibrium was reached, heat was added by passing a measured current from a battery through a coil having a known resistance. The temperature rise in a definite time was determined, and when thermal equilibrium was again reached, the procedure was repeated. This gave two determinations of the heat capacity of the system for each run, one slightly below 25° C, the other slightly above 25° C. If the two determinations did not check within 0.5 percent, the run was repeated. The average of the two determinations was used to calculate the specific heat.

The average deviation from the mean of a single determination of specific heat was about 3 percent. This is equivalent to a standard deviation of ±0.01 in the specific heat.

3. Results

The results of determinations of specific heats of collagen, chrome-retanned leather, vegetable-tanned leather, and chrome-tanned leather are given in table 1. These results include measurements made on the materials containing varying percentages of moisture, and also determinations on the materials dried by heating for 24 hr. at 100° C. Chemical analyses of the collagen and leathers are given in table 2.

In order to obtain some information on the specific heats of materials used in leathermaking, determinations were made on chestnut and quebracho tanning extracts. These materials were dried at 100° C for 24 hr before the determinations were made. Measurements were also made of the specific heats of stuffing grease and of animal oil (neat's foot). The stuffing grease was obtained by extracting it from a sample of chrome-retanned upper leather. The values obtained for the specific heats of the tanning materials and the lubricating materials are given in table 3.

TABLE 1. *Specific heats of collagen and leather samples at 25° C*

Collagen		Chrome-retanned leather		Vegetable-tanned leather		Chrome-tanned leather	
Moisture content	Specific heat	Moisture content	Specific heat	Moisture content	Specific heat	Moisture content	Specific heat
%	*cal/g/deg C*	%	*cal/g/deg C*	%	*cal/g/deg C*	%	*cal/g/deg C*
0	0. 3723	0	0. 3404	0	0. 3334	0	0. 3045
1. 02	. 3490	1. 52	. 3287	1. 15	. 3202	1. 98	. 2918
1. 96	. 3659	2. 12	. 3266	1. 32	. 3274	3. 69	. 3631
4. 56	. 4014	4. 23	. 3448	2. 59	. 3280	7. 59	. 3576
6. 49	. 4061	7. 23	. 3458	3. 85	. 3844	9. 39	. 3737
17. 03	. 4280	9. 23	. 3474	6. 20	. 3730	11. 07	. 3893
-----	-----	11. 29	. 3606	7. 83	. 3835	13. 46	. 3841
-----	-----	-----	-----	9. 31	. 3844	14. 96	. 4098
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TABLE 2. *Chemical analysis of the leathers (moisture- and grease-free bases)*

Leathers	Hide substance	Ash	Cr_2O_3	Vegetable tannin by difference
	%	%	%	%
Collagen	100. 7	----	------	------
Vegetable-tanned leather	52. 06	0. 24	------	47. 70
Chrome-retanned leather	59. 87	2. 20	1. 80	[a]34. 82
Chrome-tanned leather	88. 85	----	4. 25	------

[a] Calculated by using the conversion factor 2.73 to convert Cr_2O_3 to the basic chromium sulfate tanning agent and the value for the difference between percentage ash and percentage Cr_2O_3 [12].

TABLE 3. *Specific heats of leathermaking materials at 25° C*

Material	Specific heat
	cal/g/deg C
Chestnut tannin extract (powder) dry	0. 2889
Quebracho tannin extract (solid) dry	. 3152
Stufing mixture (extracted from upper leather)	. 5162
Animal oil	. 5191

4. Discussion

The variation of the specific heat with moisture content for collagen, chrome-retanned leather, vegetable-tanned leather, and chrome-tanned leather is shown in figure 1. As the moisture content of the sample increases from 0 to 1 or 2 percent, the specific heat passes through a minimum. This behavior occurs with all of the samples. After the minimum, there is a sharp increase in the specific heat as the moisture content increases. After the sharp rise, the curves reach a plateau where the specific heat is nearly constant until the moisture content reaches about 9 percent. Beyond this point, the specific heat increases further with increase in moisture content. The plateau region occurs for each of the three leathers. For collagen, the number of determinations in this area was insufficient to establish the exact shape of the curve.

Breaks in the curves showing the increase in a physical property with moisture content are not unexpected. However, studies on moisture adsorption [6], heats of wetting [1], and dielectric constants

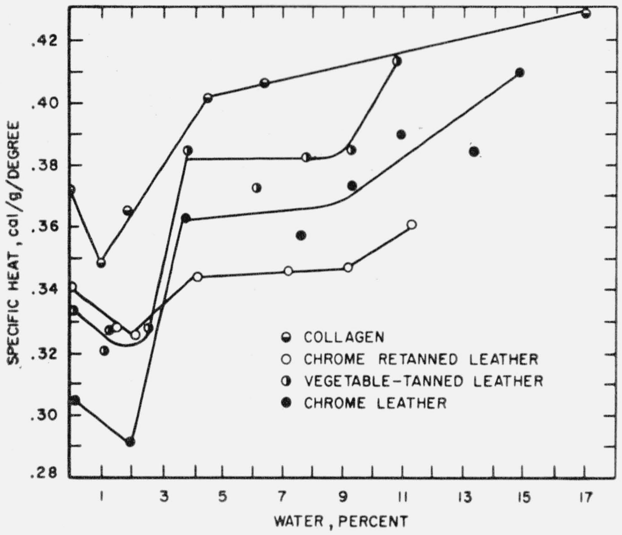

Figure 1. *Variation of the specific heat with the percentage of water in the materials.*

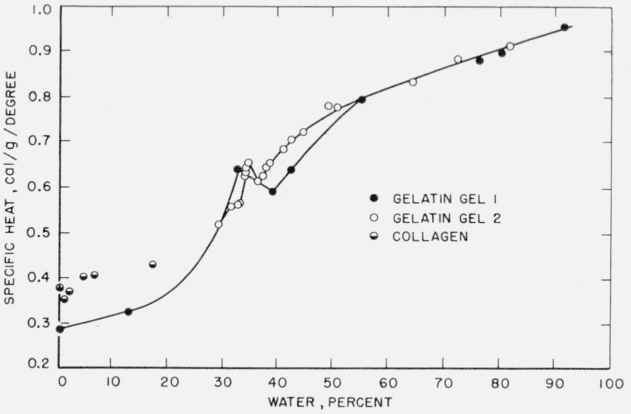

Figure 2. *Variation of the specific heats of collagen and of gelatin with the percentage of water in the samples.*

Data for gelatin from Hampton and Mennie.

[7, 8] have failed to reveal any abrupt changes with increase in moisture content. The sorption of moisture by a protein is undoubtedly similar to the formation of hydrates in inorganic compounds. The sorption of moisture over a wide range of relative humidities would be expected to form a series of hydrates. This series of hydrates should correspond to different compounds having different properties. From studies of the moisture relations of leather and other proteins by the above-mentioned procedures, it has been found that the energy of combination of moisture decreases as the amount of moisture is increased. The rate of decrease has, however, in all instances been characterized by a smooth curve indicating that the precision of the measurements was not great enough to detect a discontinuity which would be characteristic of a change in phase.

Studies of the heats of wetting [1] show that the greatest amount of heat is evolved in the adsorption of the initial amounts of water by the dry materials. The adsorption of this amount of moisture apparently lowers the activity of some of the atoms, decreasing the magnitude of their vibrations, so that they absorb less energy. This would produce a minimum in the specific heat. The addition of moisture, beyond about 2 percent, apparently forms additional vibrational sites, for an abrupt increase in the specific heat occurs.

It has been suggested [9] that the first water molecules adsorbed by a protein are taken up between two polar groups. This would definitely lower the activity of the two groups, and might correspond to the minimum for specific heat at about 2-percent moisture adsorption. In further addition of moisture, it was assumed that each group would adsorb a molecule of water. The abrupt rise in specific heat would then correspond to the point where the bridge between atoms formed by one molecule of water was broken, and the vibrational freedom of the atoms, was again increased. The plateau region in the curve from 3 to 9 percent may correspond to the adsorption of one molecule of water per polar group in the protein molecule, to complete a monomolecular layer. Pauling [9] gives data to show that approximately 9 percent of water is required for a monomolecular layer in collagen. Beyond 9 percent of moisture, the polar groups may be saturated with one water molecule per group, and possibly a second layer, with two molecules per polar group, is begun. This corresponds to the addition of more energy-adsorbing vibrational sites, and the specific heat shows a further increase.

Hampton and Mennie [4] determined the specific heats of gelatin gels containing varying percentages of water at temperatures ranging from 25° C to −180° C. Their mean results over the temperature range 0° to 25° C are shown in figure 2, together with the results obtained in the present study for collagen. The specific heat of dry collagen is higher than that of dry gelatin. When collagen is hydrolyzed to form gelatin by heating in water, a shrinkage reaction occurs with rearrangement and internal compensation of active polar groups. It is, therefore, expected that gelatin would have a more inactive structure, with fewer free polar groups to absorb vibrational energy, than collagen. For this reason the specific heat of collagen would be expected to be higher.

The results on gels by Hampton and Mennie, as shown in the curve in figure 2, show a break, which indicates a phase change at a moisture content of approximately 32 percent. There are not sufficient determinations with the gels at low concentrations to indicate whether there are any discontinuations in the curve at exactly the same points where they occur with collagen and leather. The gel-water system also does not exactly parallel the collagen or leather-water system. The former system borders on solution, whereas the latter represents a system of a solid and a vapor at low concentration.

Many attempts have been made, in studies of protein-moisture systems, to derive conclusions with regard to the amounts and properties of the so-called bound and unbound water present. This is sometimes done by subtracting the calculated value for a physical property, based on that for the dry material, from the total value for the constant when water is present, with the assumption that the difference can be attributed entirely to the water content. By the application of this procedure to the results obtained for the specific heats of collagen and leather in this study, the values shown in table 4 were obtained.

These calculated results obviously have no significance, except to show that the specific heats of the dry leather and the water present are not additive to give the specific heat of the conditioned material. A negative apparent specific heat is obtained for water when the concentration in the collagen or leather is low. At higher concentrations, the apparent specific heat of water is positive, but varies with the type of leather. The actual specific heat of water at 25° C is 0.998 cals/g/deg C.

Determinations of bound and unbound water in a protein-water system are questionable. The so-called protein-water system is probably a hydrate that behaves as a compound, differing in properties from that of either the dry protein or the pure water. As the percentage of water increases, the properties of the compound change; the activity of the water increases, but it remains restricted in mobility, as would be expected in multilayer formation. The fact that water is adsorbed by a material is sufficient basis to conclude that its mobility has been restricted. There is apparently no sharp boundary line between bound and unbound water.

Specific heats of the dry leathers are lower than that of dry collagen. In table 3, values for the specific heat of chestnut and quebracho extracts are given. The specific heat of vegetable-tanned leather is approximately midway between that of the vegetable extracts and collagen. As shown in table 2, percentage of tannin in vegetable-tanned leather is approximately 50 percent. It therefore appears that the influence of the tannin on the specific heat of the leather is additive. Chrome leather has a lower specific heat than that of the other leathers. The Handbook of Chemistry and Physics [3] gives a value of 0.200 cal/g/deg as the specific heat of $Cr_2(SO_4)_3 5H_2O$. There is, however, not sufficient chromium sulfate in chrome leather to reduce the

TABLE 4. *Calculation of apparent specific heat of water at 25° C in leather assuming that specific heat of leather is same as for dry material*

No.	Material (conditioned)	Material (dry)	Water	Heat absorbed by dry material	Specific heat	Heat absorbed by conditioned material	Heat absorbed by water	Apparent specific heat of water
Collagen								
	g	*g*	*g*	*cal/deg* C	*cal/g/deg* C	*cal/deg* C	*cal/deg* C	*cal/g/deg* C
1	27.6561	23.6313	4.0248	8.7979	0.3723	11.8368	3.0389	0.7550
2	25.1661	23.6313	1.5348	8.7979	.3723	10.2199	1.4220	.9265
3	24.7080	23.6313	1.0767	8.7979	.3723	9.9178	1.1199	1.0401
4	24.0947	23.6313	0.4634	8.7979	.3723	8.8163	0.0184	0.0397
5	23.8733	23.6313	.2420	8.7979	.3723	8.3318	−.4661	−1.9260
6	23.6313	23.6313	0	8.7979	.3723	8.7979	0	0
Chrome-retanned leather								
1	25.7699	23.1547	2.6152	7.8819	0.3404	9.2926	1.4107	0.5394
2	25.2911	23.1547	2.1364	7.8819	.3404	8.7861	0.9042	.4232
3	24.8295	23.1547	1.6748	7.8819	.3404	8.5860	.7041	.4204
4	24.1352	23.1547	0.9805	7.8819	.3404	8.3218	.4399	.4486
5	23.6451	23.1547	.4904	7.8819	.3404	7.7215	−.1604	−.3271
6	23.5058	23.1547	.3511	7.8819	.3404	7.7264	−.1555	−.4429
7	23.1547	23.1547	0	7.8819	.3404	7.8819	0	0
Vegetable-tanned leather								
1	26.9572	24.3265	2.6307	8.1103	0.3334	11.1302	3.0199	1.1479
2	26.5916	24.3265	2.2651	8.1103	.3334	10.2212	2.1109	0.9319
3	26.2307	24.3265	1.9042	8.1103	.3334	10.0596	1.9493	1.0237
4	25.8336	24.3265	1.5071	8.1103	.3334	9.6354	1.5251	1.0119
5	25.2632	24.3265	0.9367	8.1103	.3334	9.7112	1.6009	1.7091
6	24.8566	24.3265	.6301	8.1103	.3334	8.1861	0.0758	.1203
7	24.6467	24.3265	.3202	8.1103	.3334	8.0699	−.0404	−.1262
8	24.6065	24.3265	.2800	8.1103	.3334	7.8780	−.2323	−.2986
9	24.3265	24.3265	0	8.1103	.3334	8.1103	0	0
Chrome-tanned leather								
1	27.5517	23.9660	3.5857	7.2973	0.3045	11.2918	3.9945	1.1140
2	27.1922	23.9660	3.2262	7.2973	.3045	10.4434	3.1461	0.9752
3	26.6188	23.9660	2.6528	7.2973	.3045	10.3626	3.0653	1.1555
4	26.2176	23.9660	2.2516	7.2973	.3045	9.7970	2.4997	1.1102
5	25.7848	23.9660	1.8188	7.2973	.3045	9.2213	1.9240	1.0578
6	24.8509	23.9660	0.8849	7.2973	.3045	9.0244	1.7271	1.9517
7	24.4395	23.9660	.4735	7.2973	.3045	7.1306	−0.1667	−0.3521
8	23.9660	23.9660	0	7.2973	.3045	7.2973	0	0

specific heat to the value found, if the values are assumed to be additive. It is probable that the chromium sulfate reduces the vibrational activity by forming cross links in the collagen molecule. The formation of cross links is in accordance with the most widely accepted theory of chrome tanning [10].

The comparatively high specific heats of the lubricating materials (table 3) used in leather, diminish the comfort of the leather in cold weather by accelerating the removal of heat from the body. Greases and oils are not firmly adsorbed by the leather. They adhere to the leather by filling the pores, and form an intimate mixture. It is, therefore, expected that the specific heats of leather and the lubricating materials would be additive, and that the combination of the two would have a higher specific heat than that of leather alone. It has also been shown that both moisture and grease increase the heat conductivity of the leather [11]. The combination of these factors would, therefore, further diminish the comfort of the leather containing lubricating materials.

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