THE HEAT CONTENT OF WATER SORBED ON CELLULOSE.

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A

THESIS

by

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Submitted to the Faculty of
Graduate Studies and Research
of McGill University, in
partial fulfilment of the
requirements for the degree of
Doctor of Philosophy.

McGill University,
Montreal, Canada.

April, 1938.

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A. SCOPE OF THE INVESTIGATION.

The research work to be described in the following pages of this thesis deals with a further investigation of the properties of cellulose and especially the cellulose - water system. While the organic structure of cellulose is important, this physico-chemical investigation deals with the physical structure of cellulose and the influence of water upon it. When it is considered how much of the nature of cellulose is bound up in its fibrous structure, its tensile strength, and the swelling behavior that it exhibits, it is seen how inadequate are formulae which explain only its chemical reactions and leave its physical properties untouched.

From an academic standpoint the interest is that concerned with the properties of a swelling gel that is, with the chemistry and physics of surfaces involving the interplay of surface forces, cohesion, of structural units, adhesion to foreign materials, adsorption, swelling, and the like.

Cellulose is the chief product of vegetable life and forms so large and important a part of all plant structures that its formation in the vegetable world is said to be synonymous with growth. Because of its physical properties and its relative inertness towards the attack of chemicals cellulose is of enormous commercial importance forming, as it does, the basis of the paper making and textile industries, and being used in modified forms in the manufacture of high explosives, artificial silk, and celluloid products. A knowledge of the surface chemistry and physics of cellulosic materials has been invaluable in the past for the development of new cellulose products and undoubtedly any further knowledge will aid in the improvement and profitable commercialization of older products as well as help in the formulation of new products of commercial value.

The precise problem was to determine the specific heat of cellulose and particularly the specific heat of water adsorbed on the cellulose. As it was thought that it would be necessary to measure the specific heats of small amounts of adsorbed water as well as large amounts of adsorbed water a difficult problem was presented from an experimental point of view. While in the first year's work data were accumulated by an established procedure which were sufficiently accurate to obtain the specific heat of the bone-dry cellulose material, an entirely new procedure had to be designed to carry out measurements in order to estimate the specific heats of small amounts of water with the desired accuracy. One of the most important features of the work to be described is that such a method has been devised, which will make it possible to determine with considerable accuracy the specific heat of 2% of water adsorbed on a colloidal material. In the light of this portion of the work it is incumbent to review, in the latter part of this introduction, the previous developments in calorimetry which led to the entirely new method to be described.

The specific heats of standard cellulose and mercerized cellulose were obtained over the temperature range - 80° to + 25°C and are compared to the specific heats of other carbohydrates. The specific heats of 5.9 and 12% of adsorbed water were determined for the temperature range - 80° to +25°C although the accuracy of these measurements is not particularly great. And finally, the specific heats of 2, 4 and 8% of absorbed water were obtained by means of the new experimental tecnique over the temperature range - 35° to + 25°C. with a high degree of accuracy.

This is the first time that the specific heats of dry cellulose have been obtained accurately over a large temperature range and the first time that an attempt has been made to determine the specific heats of adsorbed water.

The latter is of importance as the following investigations on the physical properties of adsorbed water have been made with a view towards ascertaining how the properties of the absorbed water vary with the extent to which the water has been adsorbed: adsorption isothermals, heats of adsorption, dielectric constants, and heat conductivities.

It is necessary to introduce the subject by giving a somewhat more detailed account of the structure of cellulose. It is also of value to discuss the hypothesis of the colloidal structure of cellulose which has been advanced to account for the results on measurements of the properties of the cellulose-water system.

B. STRUCTURE OF CELLULOSE AND THE SYSTEM CELLULOSE-WATER.

While the problem of establishing a better understanding of the mechanism of water adsorption and of the physical structure of cellulose has been attacked from many angles, this is the first attempt from the standpoint of the heat capacity of adsorbed water and should present admirable possibilities along these lines. For the most part, X-ray data and double refraction investigations have contributed the greatest amount of information with regard to the ultimate crystalline structure of cellulose fibres. Microscopical observations have yielded much information on the microstructure of the fibres and the nature of the structural units. Strength measurements, diffusion measurements, capillary studies, conductivity measurements and many others of a very diversified nature have been undertaken by numerous experimenters and all have yielded valuable information which could be correlated to give a more complete idea of the nature of cellulose. Perhaps the most fruitful field of research is the study of the cellulose-water system from all possible angles. Studies on the adsorption and desorption isothermals, the dielectric constants of adsorbed water, the density of adsorbed water, heats of wetting at various stages of water adsorption, swelling properties, freezing measurements on bound water, have all been directed towards the determination of the quantitative interrelationship of the various colloidal properties in order to make possible a more intimate understanding of the physical nature of cellulose.

The chemical structure of cellulose has been the object of many investigations and it has been definitely established to have an empirical formula of $C_6H_{10}O_5$. It can be hydrolyzed almost completely to glucose, showing that it is made up of anhydroglucose units. The structural glucose units contain amylene oxide rings, while the linkage between glucose units is through carbon atoms 1 and 4. Alternate rings in a chain are rotated through 180° about the chain axis while the length of the chain in native cellulose varies between the limits of 100 and 3000 glucose units. This is the so-called molecular chain of cellulose but cannot rightfully be called the cellulose molecule since these chains undoubtedly are not of one definite equal size, as are true molecules. Individual chains have not been isolated from cellulose, but their presence in very dilute solutions of cellulose esters has been strongly indicated (1, 2). Haworth (3) has reviewed the development of the structural organic chemistry of cellulose and the summation of all the evidence so far leads to the above chemical structure of the cellulose molecule; that is, consisting of glucose anhydrid units linked, by primary valences, into long chains.

As far back as 1858 Nägeli (4) advanced the idea of a finely organized structure for natural fibrous materials.

From double refraction, swelling and mechanical properties he concluded that fibrous materials had a basic structural unit consisting of submicroscopic, water insoluble, birefringent crystallites which he called micelles. Nägeli believed that imbibed liquids entered the intermicellar spaces, separated the micelles, and reduced the cohesion of the swollen body. He also believed that the ultimate dispersion unit was the micelle and not the molecule, which conception is recognized as the groundwork of the modern idea of the cellulose structure. Today, it is generally believed by most investigators that cellulose is made up of long primary valence chains butthere is a difference of opinion as to the grouping of these chains. Meyer and Mark (5) believed the micelles to be definite bundles of primary valence chains; Astbury (6) and Neale (7) believe that the micelles are chance groupings of similarly oriented primary valence chains with part of the chains extending from one group to another, while Staudinger (8) believes that the micelles are single-chain macromolecules.

At the time when the controversy as to whether the cellulose "molecule" was a small discrete unit or a long chain structure was at its height, the first adequate picture of the molecular chain structure was provided by the application of the tecnique of X-ray analysis to cellulose. Such analyses which originated withSponsler and Dore (9) provided the impetus which resulted in the more correct and perfect elucidation of the true "molecular" structure that has since been worked out by Meyer and Mark (10), by Astbury (11) and others. Cellulose from all sources was found to consist of definitely arranged crystallites with a unit cell, containing four glucose residues, belonging to the monoclinic system. This unit cell was the smallest repeating group in the crystal structure when it is considered that the glucose units are united by primary valence forces to form long chains which are arranged spirally about the longitudinal axis in such a way that a half turn in the screw axis occurs for each unit, cell height. Such periodicity gives rise to the observed submolecular unit, which will not be a physical or chemical entity but merely a geometrical unit.

The X-ray pattern found for cellulose lies part way between the Laue type which is produced by a single crystal and the Debye-Scherrer type which is produced by numerous crystals having all possible orientations. This is to be expected since the cellulose fibre is not a single crystal but a bundle of crystallites. From the breadth of the X-ray diffraction pattern it is possible to calculate the size of the crystallites in the solid crystal lattice. Such a calculation indicates that the cellulose crystallite is made up of chains about 100 glucose units long with about 60 of these valence chains held together laterally in a bundle. The forces which align the primary valence chains into these crystalline aggregates are thought to be the secondary valences or polar forces of the hydroxyl groups which lie along the sides of the chains. The fibres of cellulose are composed of groups of crystallites or micelles twisted together in the form of a spiral.

The X-ray crystal lattice of cellulose was found to remain unchanged after swelling in water by Katz (12). He explained this by assuming that the swelling is between the structural units, micelles, rather than within them; that is, intermicellar rather than intramicellar. Swelling in alkali of sufficient concentration changed the X-ray lattice although on washing out the alkali, the original diagram reappeared, and was superimposed on a retained new diagram. The actual changes in the lattice dimensions were given by Clark (13), and it may be noted that no change occurred in the direction paralled to the chains.

Various unrelated microscopic studies have recorded the breakdown of the cellulose fibre into shorter units which are however larger than micelles. They have been given such names as dermatosomes, granules, crystals, and fusiform bodies. In the fibre itself the structure may be only superficially observe but when it is subjected to mild solvent or swelling treatment, the structural units can be loosened one from another and thus made visible. Ritter (14) isolated sleevelike layers from wood by alternately swelling and shrinking and on continued treatment further separation could be obtained. Fine cellulose strands known as fibrils were next observed which could be dissected into spindle shaped units and finally into smaller units termed spherical units.

Capillary structure is a well known feature of cellulosic materials and arises either from the tabular structure of the fibres or from the interstices between the unoriented or partially oriented fibres making up the structure of materials such as paper. Permeability of the materials to liquids or gases has formed the basis of most of the studies on capillary structure. In this way the rates of flow of various liquids through specimens of the material in various directions have been measured and from the results some idea as to the direction and size of the capillaries may be obtained

Studies on the cellulose-water relationship have been carried out extensively in this laboratory and elsewhere and have yielded important results as to the physical structure of cellulose. When contact between micelles occurs, crystal forces come into play similar to those holding the chains in the micelle. These forces are due to secondary valencies and are frequently associated with the three free hydroxyl groups of the glucose unit. In the plant cellulose is produced in the presence of an excess of water and this water is presumably held on the surface of the micelles, known as the inner free surface. Since cellulose fibres are not peptized in water forming a colloidal dispersion of micelles, the naturally formed cellulose-cellulose bonds must be considered as stronger than the cellulose-water bonds. On drying, however, the removal of the adsorbed water layer releases new secondary valences and there will therefore be a tendency for new cellulose-cellulose bonds to be formed. According to Campbell (15) these bonds must be considered as under a strain since they did not form in the presence of water.

During the process of adsorption of water by dry cellulose the first bit will go to the free surface of the micelles, that is to the valence bonds which are not satisfied in any way. It must be assumed that the water can penetrate into the fibre reaching all the inner free surface but that the micelles themselves are impenetrable. When the inner free surface is saturated, subsequently adsorbed water will condense and fill the intermicellar spaces. In the presence of an excess of water the strained cellulose-cellulose bonds between the micelles will be disruped and replaced by cellulose-water bonds. This readily accounts for the increased surface of cellulose after swelling and is partially responsible for a hysteresis effect in the sorption curves.

After the first water vapor required for saturation of the inner free surface, originally present, has been adsorbed, subsequent addition of water vapor creates further surface and the lowering of the vapor pressure is greater than can be accounted for by the curvature of the liquid water in the intermicellar spaces. Furthermore, on desorption the water first removed is that in the intermicellar spaces. Water held on freshly created surface will require a lower vapor pressure to be removed before the cellulose surfaces can join up again.

When further amounts of water vapor are added it condenses in the intermicellar spaces and in the capillaries.

Therefore it appears that water is held by cellulosic materials in three distinct ways, as water of constitution, as surface-bound or surface-adsorbed water, and as capillary condensed water. The line of demarkation between these three types is by no means sharp. It is found that some of the surface-adsorbed water still remains on the cellulose even after heating to 100°C under vacuum. Similarly all the available data on sorption by cellulosic materials give smooth moisture-content - relative vapor-pressure curves with an inflection point which is generally believed to indicate the transition point between surface-adsorbed water and capillary condensed water.

It seems reasonable to suppose that the inner free surface is not uniform in relation to its adsorbing powers but that there are positions of maximum activity and a gradation down to bonds which have attractive forces of the same order of magnitude as the capillary force exerted in the finest capillary.

This hypothesis as to the structure of the cellulose-water system is essentially the same as that advanced by Urquhartas a result of investigations on the sorption equilibrium of water on cellulose (16). Pidgeon and Maass (17) and Campbell and Pidgeon (18) also made measurements of the moisture-content - relative vapor-pressure relationship of cotton and wood and found the normal sorption curves and hysteresis effect. This hysteresis effect is that a different moisture equilibrium is obtained if equilibrium is approached from a higher relative vapor-pressure than whenapproached from a lower relative vapor-pressure.

By reference to the structure of the cellulose-water system given above the hysteresis effect may be readily explained. In the original water soaked condition the free secondary valence bonds are all satisfied by the adsorbed water. On drying these bonds are freed and mutually satisfy themselves. Upon readsorption only part of these bonds are freed to form cellulose-water bonds thus giving decreased adsorption and the consequent hysteresis effect.

The heats of wetting of dry cellulose and of cellulose containing various amounts of adsorbed water have been investigated by Argue and Maass (19). A greater amount of heat was given out when water was added to cellulose containing a known amount of water left by desorption than when water was added to cellulose containing an equal amount of water which had been put on by adsorption. This result follows from the theory of the cellulose-water system outlined above. Sorption of water by cellulose involves the disruption of the cellulose-cellulose bonds which are under any strain. When water has been left on the cellulose by desorption there is a larger exposed surface than when an equal amount is put on by adsorption. Therefore, when more water is added to the cellulose containing water left by desorption, there are fewer bonds to be broken, which requires energy, and thus more heat is given out. At low concentrations of water, there is a large difference in the heats of wetting since the surface of the micelle is not saturated and the predominant factor in the formation of heat is surface adsorption. In the vicinity of 7% water content capillary condensation is the chief effect. Therefore, the greater the amount of water initially present in the cellulose fibre, the smaller are the differences in the heats of wetting of samples containing adsorbed and desorbed moisture.

Filby and Maass (20) have measured the specific volume of cellulose and the density of adsorbed water over the range zero to 20% adsorption. They considered the first water to be adsorbed as entering into chemical combination with the cellulose because the total volume resulting was less than the volume of the cellulose and the water originally. The density of this water was found to be over 2. Subsequently adsorbed water first caused an increase in cellulose surface, with further contraction in the volume of the two components, and then a filling up of the so-called capillary spaces in which the water retained its liquid properties and the density became unity again.

Filby and Maass (21) have also determined the sorption and desorption isothermals and found the normal hysteresis effect. The vapor pressure of the first portion of adsorbed water was very low and rose rapidly with subsequent additions of water until the vapor pressure approached that of free water at about the fibre saturation point. Again there is apparently a difference between the initial sorbed water and that added later.

Measurements on the dielectric constant of water adsorbed on cellulose by Argue and Maass (22) present further evidence in support of this viewpoint. The dielectric constant of the water first adsorbed was 12, and increased with further additions until the normal value of 79 was reached in the neighborhood of the fibre saturation point. The phenomenon may be explained by assuming that the water molecules which form the first adsorbed layer on the cellulose micelle are strongly held to the surface and will rotate through only a very limited range. The dielectric constant of these adsorbed water molecules would be low. The molecules in a second adsorbed layer would be more free to rotate and would thus exhibit a higher dielectric constant. Thus the dielectric constant would rise as further additions were made until finally, when the adsorbed molecules are no longer under the influence of the surface, the dielectric constant reaches a maximum value equal to that of liquid water.

Findlay (23) has measured the thermal conductivity of cellulose and cellulose containing various amounts of adsorbed water. The change in thermal conductivity of cellulose with increasing water content was found to be very small and the change that did occur was linear with respect to humidity changes. These measurements were made up to 70% relative humidity which corresponds to 9% adsorbed water. From his results Findlay postulates that heat flow across a cellulose sheet consists mostly of a flow across the fibres, into an air space and across it to the next fibre. Resistance is offered to the flow by the thermal resistivity of the fibre, that of the interface and that of the air space, the resistánce of the air space being much greater than that of the fibres. Sorption of water takes place in a unimolecular layer on the fibres and in the intermicellar spaces, which does not greatly affect the conductivity of the system because the main resistance to heat flow lies in the air spaces which are still present. The interface resistances will not be greatly changed by the amount of water adsorbed. The state of the adsorbed water could not be calculated because the measurements were not of sufficient sensitivity.

Apart from the last measurements on heat conductivity unusual properties are found for the water first adsorbed on the cellulose sustem. The density is greater than that of water in the bulk; the vapor pressure is small compared to the vapor pressure of liquid water; the heat of adsorption is considerably greater than that of the heat of condensation of water vapor; the dielectric constant is much less than normal. These facts indicate that the initial portions of water adsorbed on the surface of a cellulose fibre are held very strongly and may even be held in the form of a surface compound.

With the results of these previous investigations before us it was thought that a study of the heat capacity of water adsorbed on cellulose would make possible a more intimate understanding of the physical nature of cellulose and the cellulose-water system. Therefore, in what follows is described the first attempt at the measurement of the specific heats of water adsorbed on cellulosic materials.

Before going on to a description of the experimental tecnique it is pertinent, as was mentioned earlier, to trace the developments in calorimetry which led to the method of measuring heat capacities of small amounts of adsorbed water at low temperatures.

ADIABATIC CALORIMETRY.

The measurement of quantities of heat by any method has been styled calorimetry and it constitutes one of the most difficult branches of exact measurements owing to the fact that a perfect non-conductor of heat does not exist. The common methods of measuring quantities of heat are by utilizing the different effects of heat on materials and may be conveniently summarized under the headings:

1. The Method of Mixing.
2. The Method of Cooling.
3. Methods based on Change of State or Latent Heat Calorimetry.
4. Electrical Methods.

The methods based on Change of State such as the use of the Bunsen ice calorimeter and the Joly steam calorimeter were very important at the time of their inception more than half a century ago because they did not require an accurate measurement of small temperature changes of the calorimetric fluid, and taking into consideration the state of thermometry at that time this fact was unquestionably of real advantage. Further, the temperature of the surroundings can have but little effect upon the indications of the calorimeter since the initial and final temperatures are the same. In recent years calorimetric thermometers have been so highly developed that the measurements of small temperature changes presents no serious difficulty and the tecnique of temperthe use of electrical heating, so that the inherent difficulties associated with this method of calorimetry more than counterbalance the advantages it offers: consequently it is very little used at the present day.

For the determination of the mean specific heat of a substance over a range of temperature or for the determination of the heat of combustion the Method of Mixtures is a convenient one to employ and is probably the best known of all calorimetric methods. The principle of this method is to impart the quantity of heat to be measured to a known mass of water contained in a vessel of known thermal capacity, and to observe the rise of temperature produced. This method is the simplest of calorimetric methods, but is not the most accurate. Heat is lost in transferring the hot object to the calorimeter, and although it can be minimized by arranging that the transfer take place rapidly or in vacuo, it cannot be eliminated or even accurately allowed for.

Since, in practise it is impossible to secure accurately the condition that there will be no interchange of heat with other bodies, corrections must be applied and special apparatus adopted to eliminate or minimize such errors. The whole science of calorimetry consists in the invention of such apparatus and the adoption of such precautious as will lead to an accurate estimate of these corrections.

There have been several noteworthy attempts at arriving at methods for correcting for the heat loss from the calorimeter.

Rumford's procedure was to make a preliminary experiment to ascertain approximately what the rise in temperature would be and then to cool the calorimeter half this number of degrees below the temperature of the surroundings before the next experiment. On carrying out the experiment the temperature of the calorimeter would be below that of the surroundings for half the time and higher during the other half. A complete compensation is not, however, effected in this way because the rate of increase of temperature diminishes very rapidly as the heated body and the water approach thermal equilibrium.

Another method is by arithmetical calculation of the heat loss from rating periods before and after the introduction of the hot body and also after the establishment of thermal equilibrium. This method is very laborious but is far more accurate than Rumford's method.

A graphical method of determining the heat loss was developed by Rowland (24) but was applicable only to cases where the final temperature was greater than that of the air. It consisted of an ingenious method of arriving at the temperature which the body would have obtained if there had been no loss.

Hesehus (25) developed a method of avoiding the radiation correction. The principle of the method consists in maintaining the temperature of the calorimeter stationary, and the same as that of the room in which the experiment is made. This is effected by adding cold water gradually to the calorimeter, so as just to counterbalance the heating effect of the body immersed. From the quantity of cold water added the specific heat of the body immersed may be easily calculated.

The most important method of elimimating the cooling correction is the Adiabatic Method.

The first application of the adiabatic method to calorimetry was made by Person (26) in 1849. He realized that the problem of indeterminate cooling rates would be solved if the temperature of the surroundings was maintained the same as that of the calorimeter at all times. A tin calorimeter was used with a 2 cm. air gap between the calorimeter and the jacket. This space was evacuated at first but Person abandonned this procedure for several unmentioned reasons. A differential air thermometer indicated temperature differences between the inner and outer vessels and the temperature of the jacket was measured by means of a mercury thermometer. There was still a cooling correction to be applied because of the evaporation of the water from the opening at the top of the calorimeter.

This method was apparently forgotten and again suggested by Holman (27). He states that the only method which could entirely eliminate the cooling correction would be to arrange the calorimetric process so that the rate of xchange of heat would be sensibly zero or constant during he entire measurement and this could be accomplished only y keeping the jacket temperature always at the temperature f the calorimeter or at a constant difference from it. olman did not report any attempts at applying his conectures and it remained for later workers to revive the dea once more.

In 1905 the adiabatic method was again brought to the ore, independently of previous knowledge, by Richards (28). e wished to eliminate the two most serious errors in calrimetry at that time, namely, the accidental exchange of eat with the environment by radiation, convection and conuction and the thermometer lag. Richards was not satisfied ith Rumford's method of eliminating cooling corrections or ith the uncertain application of Newton's law of cooling to ystems suffering sudden changes of temperature. Richards onsidered it highly desirable to devise a method wholly liminating both irregularities and suggested that this object ight be accomplished by systematically changing the temperture of the environment of a reacting system at the same ate as the system itself changed in temperature. His original alorimeter consisted of a large platinum container fitted into deep copper cylinder so as to leave an annular space of air f only a few mm. thickness. The copper cylinder was highly olished and was sunk deeply into a bath of water the temperture of which could be maintained constant or varied at will.

The calorimeter was loosely covered by a cardboard diaphragm pierced by suitable holes. Adiabatic conditions were indicated by observing two thermometers, one inside the calorimeter and one in the bath. Using this adiabatic method Richards found that a more constant result was obtained although essentially the same average values as with previous methods.

Richards originally suggested three methods of heating the jacket in a calorimeter, running in hot water, electrical heating or making the jacket itself the scene of a chemical reaction of the same speed and intensity as within the calorimeter. The one he selected, neutralization of alkali by acid, is evidently able to give an easy and precise predetermination of the temperature change to be produced, and almost any desired degree of speed in making even large changes. Most other experimenters, however, have used one of the other two methods. Hot or cold water can easily be run into the jacket, while electric heating has some evident advantages in convenience although it is not very easily adopted to following very rapid changes in the calorimeter temperature.

In the following years many improvements and changes were made in the original adiabatic calorimeter of Richards and the method was applied to many different types of reaction such as heats of combustion (29) , heats of solution (30, 31) heats of inversion (30), heats of dilution (32) etc. (33, 34, 35, 36, 37).

In 1910, White (34) made a general survey of calorimetry up to that time and suggested several improvements to increase the accuracy. In the first place he considered it desirable that the jacket should completely surround the calorimeter and also that the calorimeter cover should be in contact with the water so that all bodies at uncertain temperatures are avoided. Evaporation of water at that time was the cause of considerable error and White realized that this factor should be made as small as possible. The real source of error at that time was in the measurement of the temperature. An increase in the temperature interval would lower this error but Newton's laws of cooling only apply for small temperature intervals.

The adiabatic method overcame one of the serious sources of error in calorimetry, namely, the distillation of water from the calorimeter. Barry (38) made very exhaustive tests on the errors in calorimetry and came to the following conclusions,

1. A closed calorimetric system must be used which allows no measurable evaporation into the insulating air gaps, and these gaps must be dry.

2. The outer environment must be thermostatically controlled whenever there are conducting parts which pass directly from the calorimeter into the surrounding air.

3. With a system of about 1000 gm. - calories capacity the air gap should be about 40 mm. wide or more.

4. Stirring can be either intermittent or continous and does not introduce any error.

5. The open calorimeter is of no use in protracted calorimetry since even with an initially dry gap, evaporation leakage is inconstant. Even with the adiabatic method, isothermal distillation took place with the resulting heating effects when the water condensed. Barry found that the water condensed on the walls of the calorimeter, which occurred on clean as well as contaminated surfaces and was probably due to the simple adsorption of moisture, an effect which cannot be eliminated nor controlled. With change of temperature its effects are greater and still more irregular, and in water - saturated gaps are complicated in the extreme. The possible extent of this adsorption process was found later by McHaffie and Lenher (39) who showed that in a water saturated space, a film of water about 100 molecules thick condensed on a plane surface of quartz or platinum. These thick films only formed when the air was near the saturation point. Barry recognized the source of the error and found that by completely closing the calorimeter the error was eliminated.

Maass and Waldbauer (40) introduced the first adiabatic calorimeter into these laboratories for the measurement of the specific heat of ice. It was necessary to determine the water equivalent of the apparatus accurately and when a Beckmann or any other thermometer is placed in the calorimeter it brings a source of uncertainty into the heat capacity of the parts. There were two alternatives, either to carry out a very elaborate electrical calibration or to move the thermometer into the outer bath and use some other means of noting the adiabaticity of the calorimeter. These authors used a thermocouple with one arm dipping into the calorimeter and the other into the outer bath and connected to a sensitive galvanometer used as a null point instrument. In its final form the apparatus consisted of an open, polished copper vessel of about 1300 cc. capacity which was supported on three ebonite legs in a submarine jacket. Adiabatic conditions were maintained by running hot or cold water into the outer jacket and stirring of the water in the calorimeter was effected by means of the up and down motion of a perforated disc. The temperature was measured by a standardized Beckmann thermometer placed in the outer bath.

This calorimeter was adapted by Chipman (41) to the measurement of the specific heats of solutions and later to the heat of solution. Because the results obtained by Chipman were not as accurate as expected Lipsett (42) came to the conclusion that the error was due to the evaporation of water from the open calorimeter as was earlier pointed out by Barry (38).

Lipsett, Johnson and Maass (43) modified the calorimeter to measure heats of solution. They designed a rotating adiabatic calorimeter which mixed the solute and solvent after the two had come to the desired temperature. The use of a thermocouple with one arm dipping into the calorimeter was impracticable so a new radiation thermel was used to indicate adiabatic conditions. The thermel consisted of pairs of copper - constantan junctions, one set being fixed against the jacket wall while the other set was supported on ebonite forks about 1 mm. from the calorimeter receiving heat by radiation. Eleven pairs of these junctions were arranged symmetrically about the calorimeter to give sufficient sensitivity. A galvanometer was used as a null point instrument. This type of radiation thermocouple was found to be very convenient and no knowledge of its specific heat was necessary. Temperature measurements were made by means of a platinum resistance thermometer with a Mueller resistance bridge. This apparatus gave very accurate results on the heat of solution and had the decided advantage that only small quantities of material were needed.

Barnes (44) replaced the thermocouple in Waldbauer's calorimeter with a radiation thermel and found it much more satisfactory for the indication of temperature differences between the calorimeter and jacket. Barnes and Maass (45) have described the improved adiabatic calorimeter used by them in the measurement of the specific heats of ice and water. Barnes (44) found that the radiation thermel could not be used with the open calorimeter and has also discussed the accuracy which can be expected from the adiabatic method. He came to the conclusion that the apparatus is as accurate as the readings of the Beckmann thermometer in the outer bath, about 2 parts in 1000. Barnes also suggests that by the use of a sensitive platinum resistance thermometer the accuracy could be greatly increased.

Brown (46) recognized that a large source of the error in the method described above lay in the uncertain amount of heat gained or lost in transferring the sample from the initial bath to the calorimeter. Therefore he devised a method of transfer through a vacuum which prevented thermal contact with any medium and therefore was accomplished without the gain or loss of heat. Operating the calorimeter in vacuum required the use of mercury as the calorimeter liquid. With this apparatus Brown was able to obtain an accuracy of 0.1 % in his measurements on the heat capacity of water and deuterium oxide. Since that time by certain improvements of tecnique it has been possible to obtain an even higher accuracy of 0.02 % with this apparatus (47).

Many types of "vacuum" calorimeters have been devised since the time of Eucken (48) who designed the first in Nernst's laboratory in 1909. A great many of these calorimeters consist of a Dewar flask immersed in a water bath with the usual methods of heating and measuring temperatures. This type of calorimeter combined with the adiabatic method has been used by many investigators (49, 50,51, 52, 53, 54).

In this laboratory Broughton (55 combined certain features of the vacuum calorimeter of Simon and Lange (49) with others of the adiabatic calorimeter developed by Lipsett, Johnson and Maass (43). This adiabatic calorimeter was of the electrical type, that is, a known amount of current was passed through a heating coil around the sample and the temperature rise was measured. Mercury was used as the calorimetric fluid but the calorimeter was not used under vacuum because the sensitivity of the thermels was lowered to too great an extent. The apparatus described in a later section of this thesis is very similar to that designed by Broughton, the main difference being the absence of a calorimetric liquid in the present calorimeter.

Perhaps the most comprehensive summary of calorimetric work in general is given by White in his book "The Modern Calorimeter" (56). He claims that the adiabatic method has been much misunderstood in calorimetry and that the errors which it is supposed to eliminate are precisely the ones it usually tends to aggravate. White suggests that writers such as T. W. Richards, who, recognizing that a continuously small thermal head lessens convection and evaporation errors, have expressed this briefly by saying that it lessens thermal leakage errors. The fallacy, then, would be in saying, that all the thermal leakage errors are lessened.

In the adiabatic method the two chief errors that are eliminated are thermal leakiness and the large and uncertain error which comes through distillation of the calorimeter water. The chief source of the eliminated error in thermal leakiness is due to the absence of convection. Therefore wide air gaps between the calorimeter and jacket may be used and also a large temperature rise which will lower the error due to the measurement of temperature. But White points out that these advantages are not exclusively the property of adiabatic calorimetry because the use of closed calorimeters eliminates the errors due to distillation and adequate control of the environment makes the calculation of thermal leakiness and the subsequent application of corrections a matter of ease. Also the use of a convection shield will give rise to the same advantage.

Therefore, to sum up, the adiabatic method renders it easier to follow abrupt changes of calorimeter temperature and is of great value in long determinations involving either large or small temperature changes where the environment must be controlled accurately. It is easy to manipulate and there are no complicated cooling corrections to apply. According to White, in general it is effective control of measurements and conditions, rather than any special "method", that is the main factor in precision calorimetry.

The method of mixtures has several obvious errors. The most serious is in the exchange of heat during the time of transfer from the initial thermostat to the calorimeter. This exchange may or may not be a constant quantity depending upon several factors, the most important being the condition of the atmosphere. Besides this error the apparatus first used in the work described in this thesis was not sufficiently sensitive to give an accurate measure of the heat capacity of small amounts of sorbed water. This was mainly due to the relatively large heat capacity of the container and the small volume of available space for the sample.

The new calorimeter described in a later section is an attempt to increase the accuracy of these measurements and incidentally removes errors due to evaporation, freedom from stirring arrangements and escape from the labor of removing, filling, weighing, and replacing for each experiment. This calorimeter is designed such that it may be used as a vacuum calorimeter but since there is such a wide air gap and because adiabatic conditions may be controlled to a high degree of accuracy it was not necessary to evacuate.

EXPERIMENTAL

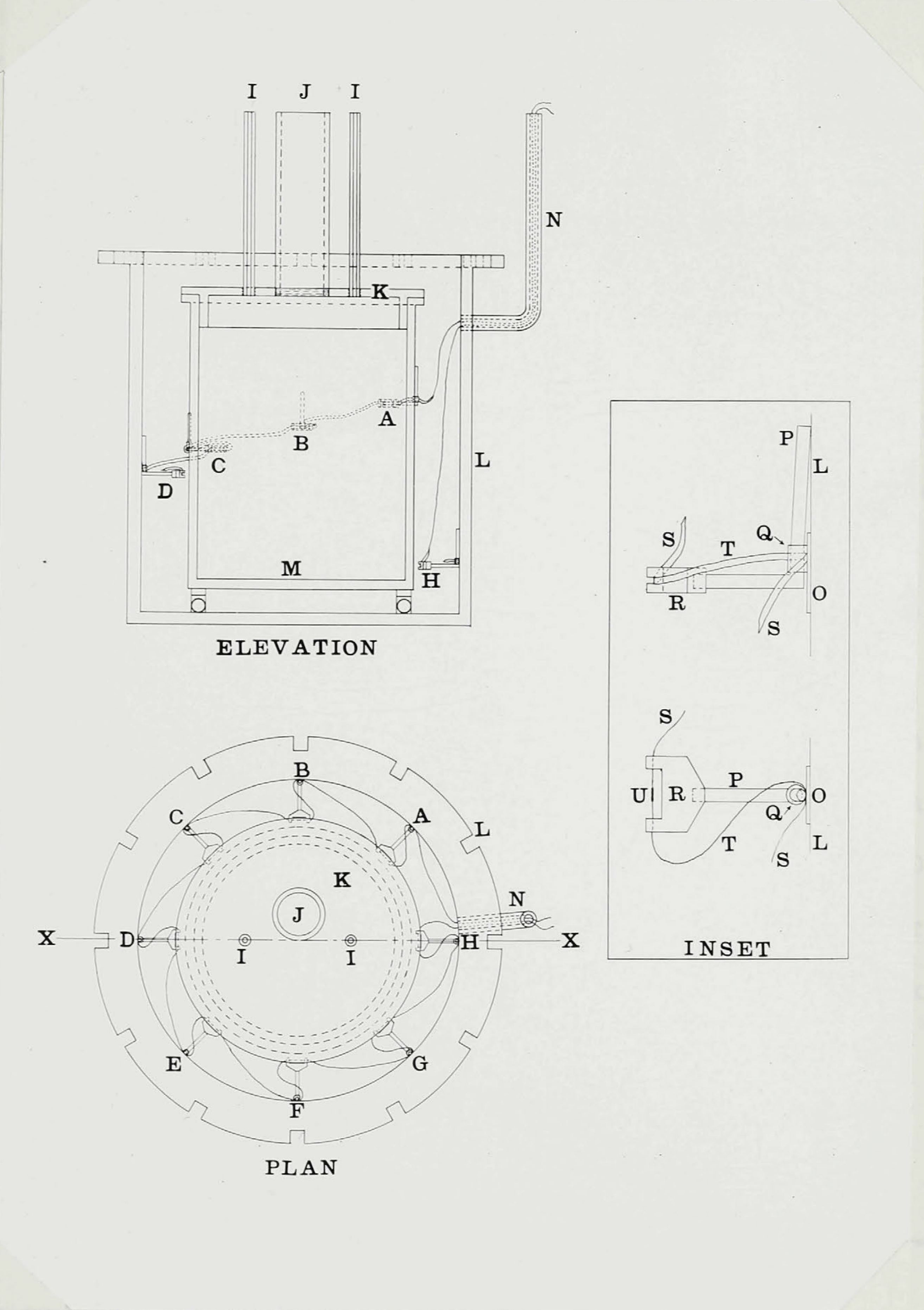
EXPERIMENTAL

A. THE ORIGINAL CALORIMETER.

1. Description of the apparatus.

The adiabatic calorimeter first employed was that designed by Barnes and Maass (45) and used by them to measure the heat capacity of ice (57). Since this apparatus has been described in detail by the authors it shall be necessary only to review certain of its distinctive features and to point out the precision with which the measurements can be made.

The calorimeter was an adiabatic one and differed essentially from all other forms of adiabatic calorimeters in that a radiation thermel was used to detect temperature differences between the inner and outer baths. The radiation thermel consisted of eight pairs of copper - constantan junctions arranged in the form of a helix around the inner calorimeter vessel in such a way that eight of the junctions made thermal contact with the inside wall of the outer jacket while the others were supported in air upon small ebonite forks at a distance of about 3mm. from the side of the inner calorimeter vessel and received heat from it by radiation. Thin strips of mica served to electrically insulate the eight junctions making thermal contact with the outer calorimeter jacket.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INSET
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D
I
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E
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PLAN

Fig. I

The diagram showing the construction of the calorimeter and the arrangement of the thermel junctions has been reproduced from the paper by Barnes and Maass (45) and is shown diagrammatically in Fig. 1. The outer jacket with the cover removed is represented by L, while M is the inner calorimeter vessel. I and I are ebonite chimneys through which pass the wires to the stirrer in the inner vessel, and J is the ebonite chimney through which the substance under investigation is introduced. A, B, C, D, E, F, G and H are the pairs of junctions of the radiation thermel.

The inset shows on a larger scale the method of supporting the thermel junctions. S indicates copper wires and T constantan. One junction U is suspended on an ebonite fork R as shown and the other passes between the light ebonite collar Q and the thin strip of mica O. The ebonite fork R is supported upon a light copper wire P which is soldered to the inner wall of the outer jacket L.

A number of distinctive features were embodied in the use of the radiation thermel. In the original form of the calorimeter the temperature differences between the inner and outer baths were indicated by a multiple junction thermocouple which was constructed in the form of an inverted U with one arm in the outer bath and the other passing through the cover of the calorimeter into the water in the inner vessel.

This arrangement introduced certain disadvantages in that contact was made between the inner liquid and the outside air through the thermocouple arm, an uncertain water equivalent was introduced and the thermocouple arm filled valuable space. The use of radiation thermels obviated these innaccuracies and moreover the designers (45)found that it was about twice as sensitive as the ordinary thermocouple arrangement. Furthermore the inner vessel could now be closed in such a way that the water was not in contactwith the outside air so that errors due to evaporation etc. were also eliminated.

The water in the outer bath of the calorimeter was stirred by means of four stirrers driven by an electric motor, each stirrer having two propellors. Stirring of the water in the inner calorimeter vessel was effected by means of two circular pieces of lead suspended horizontally one above the other and at a distance of about one and a half inches from each other. They were joined together by means of three pieces of heavy copper wire. The discs were suspended on two very fine copper wires which passed through the ebonite chimneys I, I. This stirrer when in operation possessed an up and down motion transmitted to it by means of a series of electrically driven pulleys and an eccentric. Large circular holes were cut in this stirrer to permit the passage of the container, in which was sealed the material under investigation, when it was introduced into the calorimeter.

The apparatus was made very sensitive to small differences of temperature between the inner and outer baths by placing the galvanometer scale about four meters away from the mirror. In this way a temperature difference between the two baths of about 0.00015°C could be detected.

Temperature equilibrium between the two baths was maintained constant over a period of time by means of jets of hot and cold water into the outer bath.

In its original form the adiabatic calorimeter as designed by Barnes and Maass (45) held about 1000 cc. of water in the inner vessel. With this calorimeter about 900 calories were needed to cause a change in temperature of 1°C. The calorimeter that was used in the present work was exactly similar to that described by Barnes and Maass except that the inner calorimeter vessel was much smaller and held about 200 cc. of water. The outer jacket was of course correspondingly smaller in diameter but the height of the calorimeter was the same as before and the number and arrangement of the thermels was exactly the same. With this calorimeter 200 calories caused a temperature change of 1°C and thus a higher degree of accuracy was possible with the smaller inner vessel since the magnitude of the temperature change is the determining factor which limits the accuracy of the heat measurements.

2. Sensitivity.

The sensitivity of the thermel - glavanometer system was tested by determinining the temperature between the inner and outer baths of the calorimeter corresponding to a definite deflection on the galvanometer scale. This was accomplished by first bringing the system to equilibrium as indicated by zero deflection of the galvanometer. Then the temperature of the outer bath was quickly raised and the deflection of the galvanometer for a given temperature difference was determined. Similarly the deflection of the galvanometer was determined when the temperature of the outer bath was lowered to a definite amount below that of the inner bath. In this way it was found that 1cm. corresponded to a temperature difference between the two baths of about 0.003°c. This indicated that a temperature difference of about 0.00015°C could be detected.

3. Standardization of the Beckmann Thermometer.

The temperature of the outer bath was determined by means of a Beckmann thermometer which had been calibrated by the Bureau of Standards at Washington and all readings were corrected by reference to the certificate supplied by them.

The thermometer was standardized by comparing it with a standard mercury thermometer at a number of different points. The corrected Beckmann readings were plotted against the standard thermometer readings and the curve obtained was extrapolated to zero reading on the Beckmann.

4. The constant temperature bath.

The material under investigation was brought to the desired initial temperature by placing it in the requisite cooling bath which consisted of a wide mouth Dewar flask. For a temperature of -78.5°C solid carbon dioxide moistened with acetone was used, while for -38.5°C and -6.25°C a bath of ether, stirred by means of a current of dry air, was used. The bath was maintained at the proper temperature to within ± 0.1°C by dropping, from time to time, small pieces of solid carbon dioxide into the ether bath.

5. The container for the cellulose.

The container employed was made from monel metal and was exactly the same as the one designed by Hampton and Mennie (58). The external dimensions were about 3 inches by 1 inch and a cross section is shown in Fig. 2.

The container was specially designed to give an air tight join between the container and cover and also to eliminate capillary spaces into which water might creep. The holes in the cover for the screws were countersunk and the heads of the screws machine-turned so that the bevelled edge fitted the countersunk hole exactly. A thin lead washer was placed between the container and the cover and thus a very efficient water-tight joint was obtained. This container therefore, was made entirely of monel metal except for the thin lead washer, having an empty weight of about 60 grams and would hold about 4 grams of cellulose.

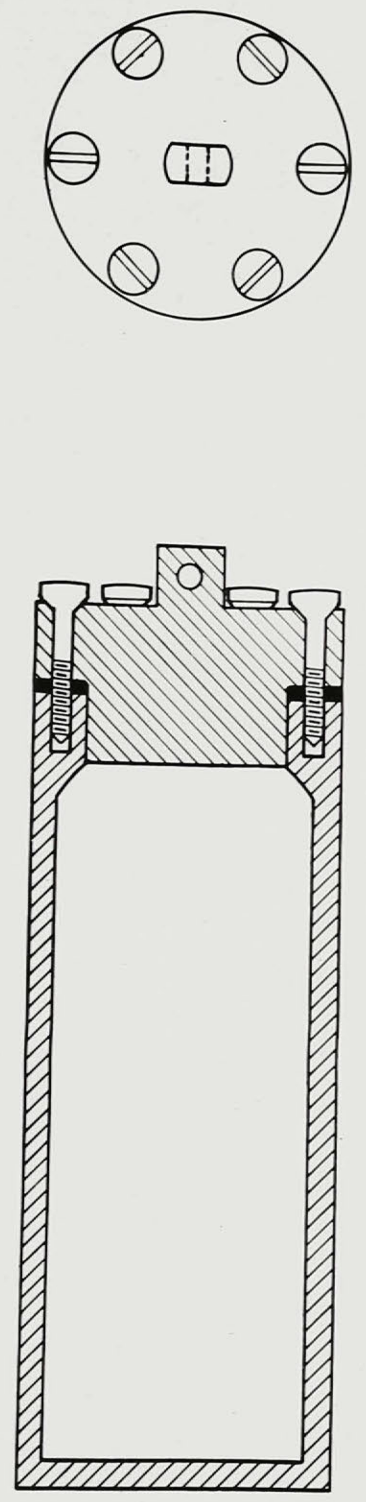


Fig. 2

6. Standard cellulose and mercerized cellulose.

The cellulose was purified in the manner developed by Argue and Maass (19) to yield a sample free from traces of impurities. Pure absorbent cotton was refluxed over a water bath with a 1% solution of NaOH for 12 hours and the liquor poured off. The sample was washed with distilled water, and the whole procedure repeated 7 times. The cellulose was then acidified with a 1% acetic acid solution, and washed free from acid with distilled water. The excess water was pressed out and the purified sample was air dried for three days. It was placed in an oven at 100°C for three days, and finally, was transferred to a storage desiccator. Cellulose prepared in this way will be called "Standard" cellulose.

The sample of mercerized cellulose was prepared by 3 hours immersion of standard cellulose in an 18% NaOH solution at 25°C.

7. Procedure

The cellulose sample was introduced into the clean, weighed monel metal container, which was then placed in an electric oven for 10 hours, the temperature being held at 100°C. Meanwhile, air, dried over concentrated sulfuric Acid and phosphorus pentoxide, was passed through the cellulose by means of an hypodermic needle reaching to the bottom of the container.

While still in the oven the cover was attached, and after cooling, the container plus the dry cellulose was weighed. It was found that this weight could be duplicated after the cellulose readsorbed water and was dried again under the above conditions. This indicated that the cellulose was rendered bone-dry by such treatment.

Water was introduced into the cellulose to the required percentage by means of steam and was accurately determined by weighing the container before and after adsorption.

The filled container was prepared for immersion in the calorimeter by suspending it from a cork by a thread of the proper length and placing it in a closely fitting, dry copper tube. Two discs, one of cardboard and the other of copper, were placed above the container inside the copper tube to prevent convection currents, and a piece of absorbent cotton was placed just below the cork to prevent moisture from creeping into the tube and condensing on the container. Adhesive tape was wrapped tightly around the cork and the top of the tube to prevent the entrance of moisture. This arrangement is shown in Fig. 3.

The tube with the container was placed in the cooling bath to bring the container to the required initial temperature. About two hours was found to be sufficient time for temperature equilibrium to be reached.

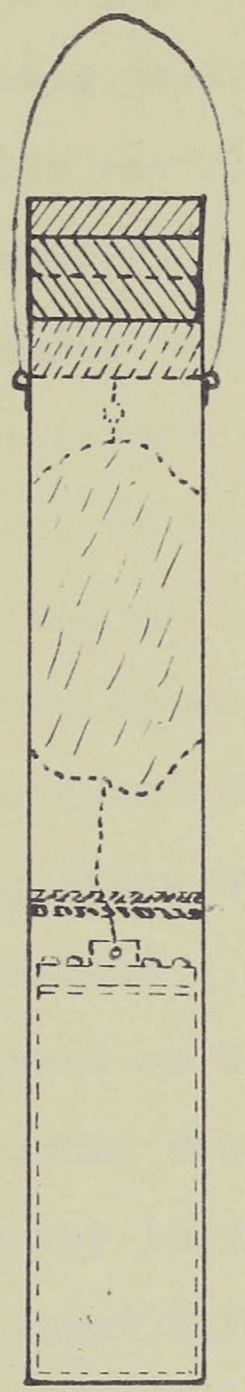


FIG. 3

In the meantime the calorimeter was assembled as shown in Fig. 1 and put into operation. About 175 grams of distilled water was introduced into the inner vessel from a weight pipette and the cover attached. The cover to the outer jacket was put in position and screwed down, vaseline making a water tight join at the flange. The chimney J (Fig. 1) was closed with a rubber stopper. The outer bath was next filled with water and both sets of stirrers were set in operation. The two baths were brought to thermal equilibrium at the proper temperature, the deflection of the galvanometer being kept to zero by running in either hot or cold water from small jets. It was found that a constant stream of warm water was necessary since evaporation from the surface of the outer bath caused a lowering of the temperature. The temperatures registered on the Beckmann thermometer in the outer bath were recorded every five minutes for 15 to 20 minutes to determine the initial temperature.

The container was next lifted out of the copper tube and lowered into the calorimeter. The transfer took from two to three seconds, and the time at which it was effected was noted exactly. The fall in temperature was followed by running ice-cold water into the outer bath, and keeping the two baths in thermal equilibrium as closely as possible.

Again the temperature was recorded until a uniform change was observed to determine the final temperature.

At the end of a run the container was removed from the calorimeter, dried and placed in a desiccator over calcium chloride. From time to time the weight of the container was checked to make sure that water was not creeping in.

From the results that are presented in a later section it seemed apparent that there was an error inherent in this procedure. Since the cellulose containing the sorbed water was cooled down very rapidly when the container was plunged into the cold thermostat it was thought that it would be possible for water to distil from the cellulose to the container wall. This would occur if the temperature difference between the cellulose and the wall were appreciable for any length of time and would explain the anomalous results referred to above.

To see if there was a temperature difference between the centre of the cellulose and the container wall, one junction of a thermocouple was embedded in the cellulose and the other was fastened to the container wall (electrically insulated by a thin piece of mica) and the leads connected through a variable resistance to a sensitive galvanometer. The container was suspended from a cork and placed in the jacket as before. The container and jacket were then plunged into the carbon dioxide - acetone bath at - 78.5°C and the deflections of the galvanometer were noted at definite time intervals. The results are shown in Fig. 4.

Duplicate runs gave identical curves. It is evident that for about eight minutes after immersion there was an appreciable temperature difference between the cellulose and the container wall, the maximum being 65°C. Therefore it would be possible for water to distil from the cellulose and condense on the container wall.

Using values of the percent relative vapor pressure in a cellulose - water system obtained by Filby and Maass (21) for cellulose containing 7% water, the allowable temperature difference under which no distillation would occur was calculated. This temperature difference was found to be a maximum of 4°C.

The container and jacket were then put in an ether bath and the temperature was lowered at such a rate that the difference in temperature between the cellulose and the container wall was always less than 4°C. It was found that the temperature could be lowered at 2°C per minute under these conditions. Various experiments were made to determine the values of the heat capacity of the sorbed water when initially cooled slowly and when cooled rapidly. The results are shown in Table 1.

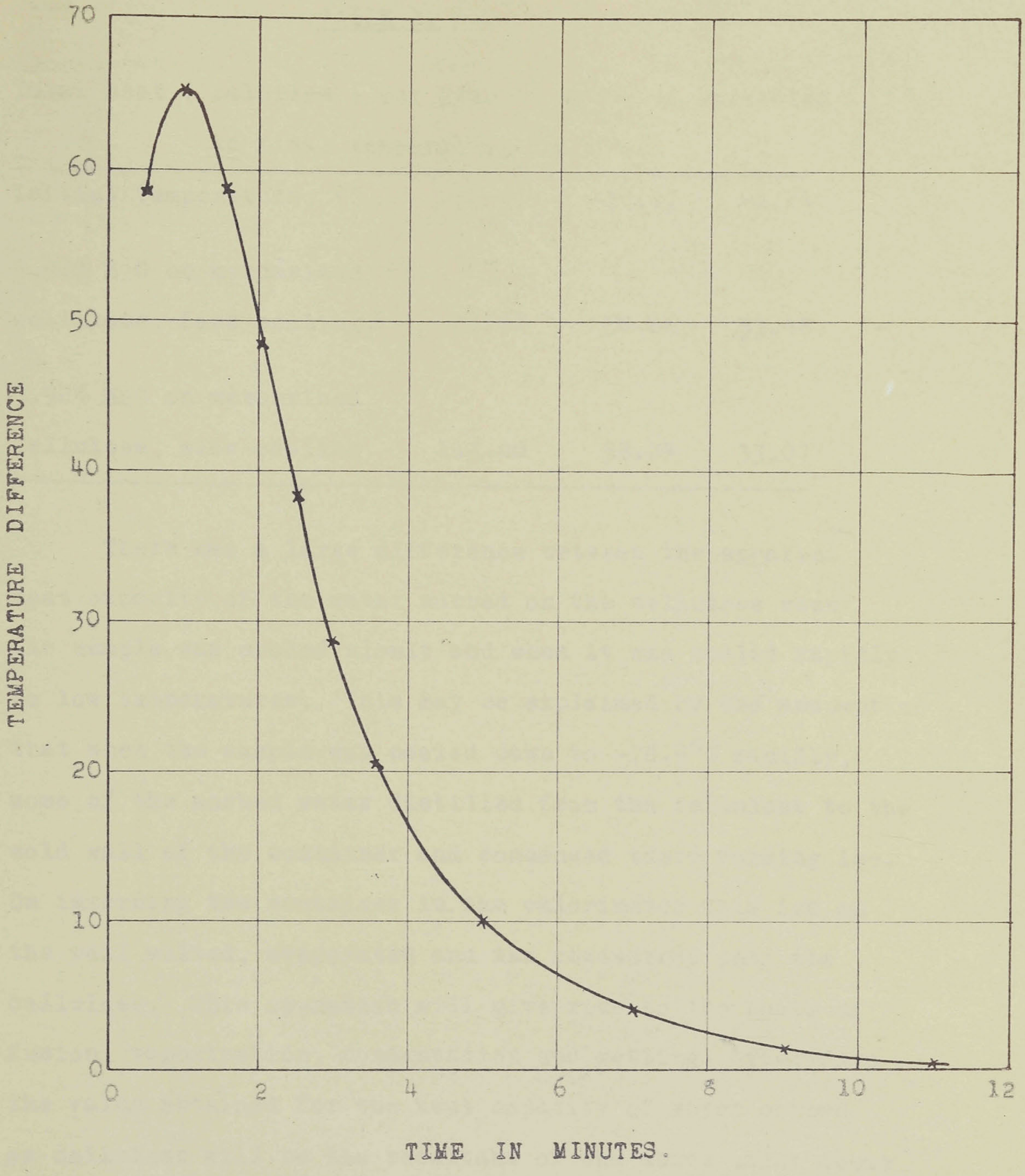

TEMPERATURE DIFFERENCE
70
60
50
40
30
20
10
0
0
2
4
6
8
10
12
TIME IN MINUTES.

FIG. 4

TABLE 1.

Total heat (calories) per gram of material corrected to final temperature 25.00°C.

Initial Temperature, °C.	-78.51	-38.47	-6.24
5.92% H_2O on mercerized cellulose, fast cooling.	81.62	52.64	33.48
5.92% H_2O on mercerized cellulose, slow cooling	113.60	58.24	33.07

There was a large difference between the apparent heat capacity of the water sorbed on the cellulose when the sample was cooled slowly and when it was cooled rapidly to low temperatures. This may be explained by the assumption that when the sample was cooled down to -78.5°C rapidly, some of the sorbed water distilled from the cellulose to the cold wall of the container and condensed there forming ice. On immersing the container in the calorimeter this ice on the wall melted, evaporated and was readsorbed onto the cellulose. This operation will give rise to the heats of fusion, vaporization, condensation and wetting. Therefore the value obtained for the heat capacity of water sorbed on cellulose will be the resultant of the above under these conditions.

If we consider 5.95% water sorbed on cellulose and assumed that all the water distils from the cellulose to the wall on immersion in the cooling bath and is then readsorbed onto the cellulose when lowered into the calorimeter it may be calculated that there will be liberated 50 calories of heat per gram of water. The amount of heat required for the melting of one gram of ice is the latent heat of fusion which is 79.4 cals. From Table II of the paper by Argue and Maass (19) it is apparent that the heat liberated when one gram of water is sorbed on 16.7 grams of cellulose, which gives 6% water, is 129.5 cals. Therefore, since the heats of evaporation and condensation will be equal and opposite and thus cancel, the overall heat change due to distillation will be liberation of 129.5 - 79.4 = 50 cals. for 1 gram of water.

From Table 1 it is evident that approximately 32 calories, which is the difference between fast and slow cooling at - 78,5 °C, are liberated due to factors introduced by the distillation of the water to the wall and readsorption. Thus 50 ÷ 32 or 64% of the water on the cellulose would have distilled. This is not unreasonable and indicates that rapid cooling to -78.5°C with a sample originally containing 5.95% water causes distillation and leaves 2.2% water remaining on the cellulose.

Therefore it would appear that with this calorimeter, involving the transfer of the sample from the initial bath to the calorimeter, the results obtained at low temperatures will not represent the heat capacity of water sorbed on cellulose alone but will be a composite of the heat capacity of the sorbed water, the heat fusion, the heat of condensation, and the heat of wetting.

It may be pointed out that the results on the heat capacity of dry cellulose, dry mercerized cellulose and the heat capacity of sorbed water at the higher temperatures are not affected by this factor. Also the error introduced shall be appreciable only for those samples containing a high percentage of moisture.

Therefore this calorimeter may be used to measure the heat capacity of water sorbed on cellulose if the proper precautions are taken but even then it is not of sufficient accuracy to deal with samples of very low water content.

This effect will not appear in the results obtained with the new calorimeter which will be discussed in a later section.

8. <u>The water equivalent of the calorimeter</u>.

The water equivalent of all the parts and supports as well as the vessel itself and the cover was determined by calculation using certain approximations according to the procedure described by Barnes (44,45). The parts were weighed and the following specific heats were used in the calculation: copper, 0.0923 (59) ; ebonite, 0.339 (60); lead, 0.0305 (61). In this way the water equivalent of the calorimeter was found to be 16.07 cals. The weight of the lead stirrer was checked at intervals but was found to remain constant such that the above value for the water equivalent was correct in all the experiments carried out.

9. A sample calculation.

This calculation is based on the data obtained for a cellulose sample containing 6% water over the range -78.5° to $+ 25^\circ$C which is as follows:

Wt. of container = 61.4617 gm.
Wt. of cellulose = 3.9844 gm.
Wt. of water = 0.2435 gm.

Wt. of pipette + water = 289.37 gm.
Wt. of pipette = 112.95 gm.
Wt. of water = 176.42 gm.

Initial temperature = -78.51°C.

The readings on the Beckmann thermometer were as follows:

Time in minutes	Beckmann readings.
0	5.063
5	5.060
10	5.058
15	5.056
Container introduced at exactly 16 minutes.	
25	1.401
30	1.399
35	1.397
40	1.395
45	1.393
50	1.391

These readings were plotted as in Fig. 5 and the straight lines extrapolated to time at 16 minutes. This gives the initial and final temperatures for the water in the inner vessel of the calorimeter.

Initial temperature	5.056
Correction	- 0.004
Corrected temperature	5.052
Final temperature	1.405
Correction	- 0.002
Corrected temperature	1.403

Temperature difference = 5.052 - 1.403

= 3.649°C.

Zero point on Beckmann = 21.64°C.

Final temperature of calorimeter = 21.64 + 1.403

= 23.04°C.

Wt. of water in inner vessel = 176.42 Gm.

Water equivalent of calorimeter = 16.07 gm.

Hence total heat capacity to 23.04°C. = (176.42 + 16.07) x 3.649 cals.

Total heat capacity to 25.00°C. is then,

$$= \left\{(176.42 + 16.07) \times 3.649\right\} + \left\{\left[(61.4617 * 0.1) + (3.9844 \times 0.37) + (0.2435 \times 0.47)\right] \times 1.96\right\} \text{ cals.}$$

= 717.66 cals.

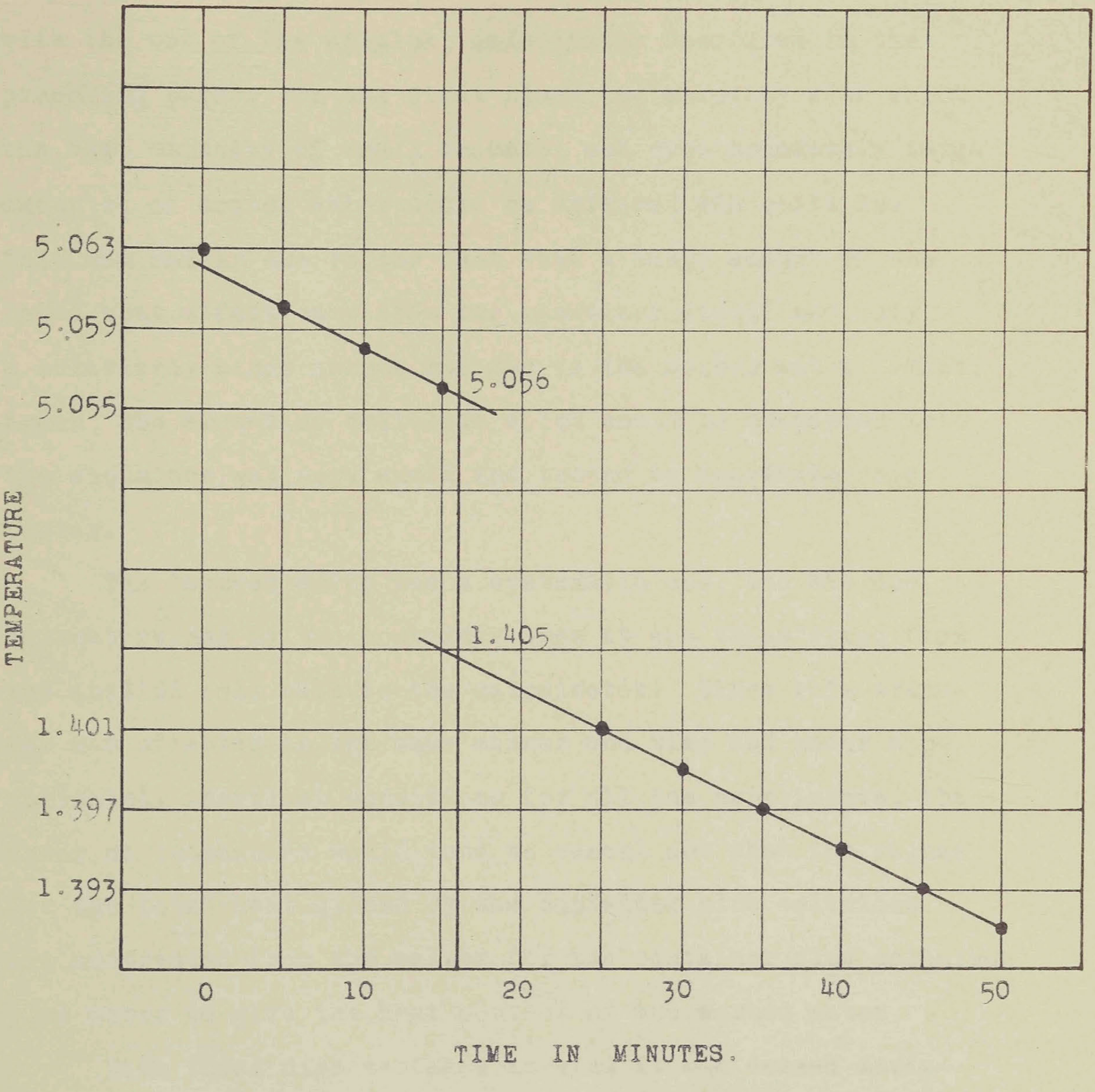

5.063
5.059
5.056
5.055
TEMPERATURE
1.405
1.401
1.397
1.393
0
10
20
30
40
50
TIME IN MINUTES.

FIG. 5

B. THE NEW CALORIMETER.

There were certain striking disadvantages coupled with the use of the original calorimeter described in the preceding pages. In the first place the accuracy with which the heat capacity of small amounts, and even moderately large amounts, of sorbed water could be obtained was quite low. This was mainly due to the fact that a large amount of the total heat effect came from the container itself and only a relatively minor amount was due to the sorbed water. Then, again, the amount of cellulose which could be compacted into the container was very small and tended to aggravate this factor.

The largest error was a systematic one, and was due to heat gained by the container when it was transferred from the initial cold bath to the calorimeter. Since this transfer was effected in the same manner and time and under approximately identical conditions for all the experiments, the error so introduced would tend to cancel out when the values for the total heat gained by the container plus cellulose are subtracted from the values for the container plus cellulose plus water to give the heat content of the sorbed water.

With these disadvantages in mind it was deemed advisable to design a new adiabatic calorimeter which would be suitable for the measurement of the heat capacity of small amounts of sorbed water at low temperatures.

1. Description of the apparatus.

The calorimeter designed for the heat measurements of water sorbed on cellulose at low temperatures was of the adiabatic-electrical type. Radiation thermels were adopted to maintain adiabatic control and it was possible to detect a difference in temperature of 0.0001°C between the inner and outer portions of the calorimeter. For the proposed work it was necessary to reduce the losses due to thermal conductance to a minimum and also to reduce the heat capacity of the calorimeter to a value such that the heat capacity of the sorbed water could be obtained with the desired accuracy. Losses due to thermal conductance were very low since the only direct connections to the inner container were the two wires conducting the current to the heating coil, and the three bakelite legs upon which it stands.

The novel feature of this calorimeter was that there was no liquid bath around the inner container, the heating coil being wound directly onto the copper container. This eliminates the errors due to evaporation of the calorimetric liquid which is large in the older types of calorimeters. Also the heat capacity of the apparatus is cut down to a much lower value.

The container, which is shown in section in Fig. 6 was made in the form of a cylinder of very thin copper, fitted with a cover which screwed on, a rubber gasket A, making a vacuum tight join. There was a small opening in the cover fitted with a screw cap B, and a vacuum tight join was obtained with a small lead disc C. This small opening was used to evacuate and dry the sample after the cover

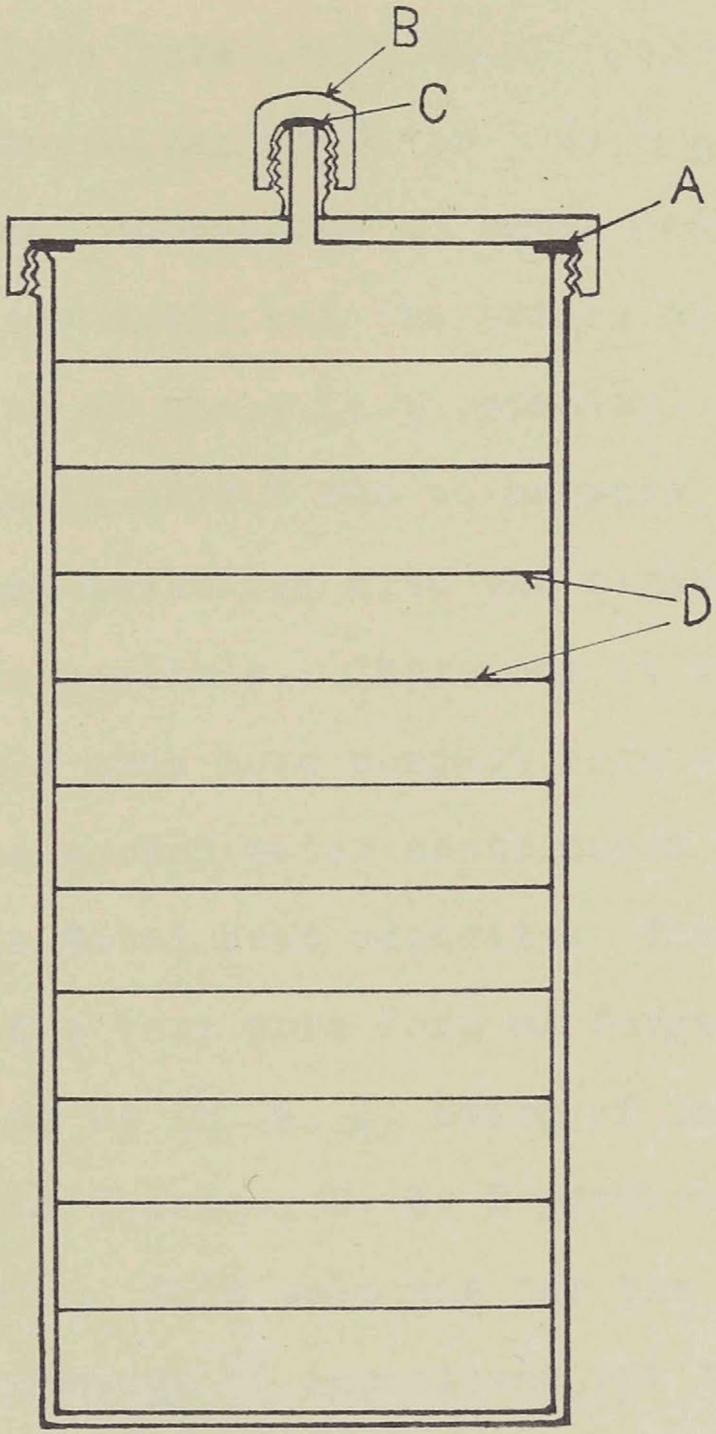


FIG. 6

was screwed down and was later used to introduce water into the sample.

The previous samples used were "standard" cellulose and mercerized cellulose in a very loose form. If these were employed only a relatively small amount could be packed into the container, that is 5 to 6 grams. This means that the heat change due to small amounts of sorbed water would be very small and the errors correspondingly large in the value of their heat capacity. In this portion of the work the main object was to measure the heat capacity of sorbed water on cellulose with the highest degree of accuracy that was possible. Therefore it was necessary to use cellulose in a much more compact form such that the cellulose and the sorbed water contributed a much larger percentage of the total heat capacity. The sample finally used consisted of a very pure form of Burgess bleached sulfite pulp supplied by Dr. A. J. Stamm of the Forest Products Laboratory, Forest Service, U. S. Department of Agriculture, Madison, Wisconsin. This pulp was for the most part cellulose with a small percentage of impurities but these would not interfere with the sorption of water and the specific heat would be practically the same as that of pure cellulose. The pulp was received in the form of a sheet, the density being about 1.57 and therefore on being cut into discs just smaller in diameter than that of the container a much greater amount could be packed into the container than was possible with the "standard" cellulose.

Ten copper discs D of 5 mils thickness were placed uniformly throughout the pulp to aid in setting up thermal equilibrium. The cover was attached and the container was given two very thin coats of bakelite varnish diluted with amylacetate which were baked on to ensure electrical insulation while still preserving good thermal contact. After the dry weight of the sulfite pulp had been determined by heating to 100°C, evacuating for 14 hours, cooling and weighing, the resistance element of #30 enamelled copper wire was wound non-inductively over the entire container in such a way as to give uniform heating throughout. The size of wire used was that obtained by calculation to give the required rate of heating. Two coats of bakelite varnish were applied to ensure insulation and a close-fitting copper cylinder fashioned from 5 mil copper sheet was placed over the coil and container to aid in the attainment of thermal uniformity.

In its final form the container weighed 101.9364 grams, of which 26.6663 grams were dried sulfite pulp. The calculated heat capacity per degree was 16.6 cals. of which half was contributed by the sulfite pulp. Actually the heat capacity per degree at about 25°C was found to be about 16.9 cals. The resistance of the heating coil was 10.45 ohms at 23.0°C.

A diagrammatic section of the calorimeter is shown in Fig. 7. The outer jacket A was made of 1/16 in. brass and was made vacuum tight by six bolts pressing the lid against a rubber gasket. The central portion was supported on three bakelite legs E which were cut to a point to minimize thermal

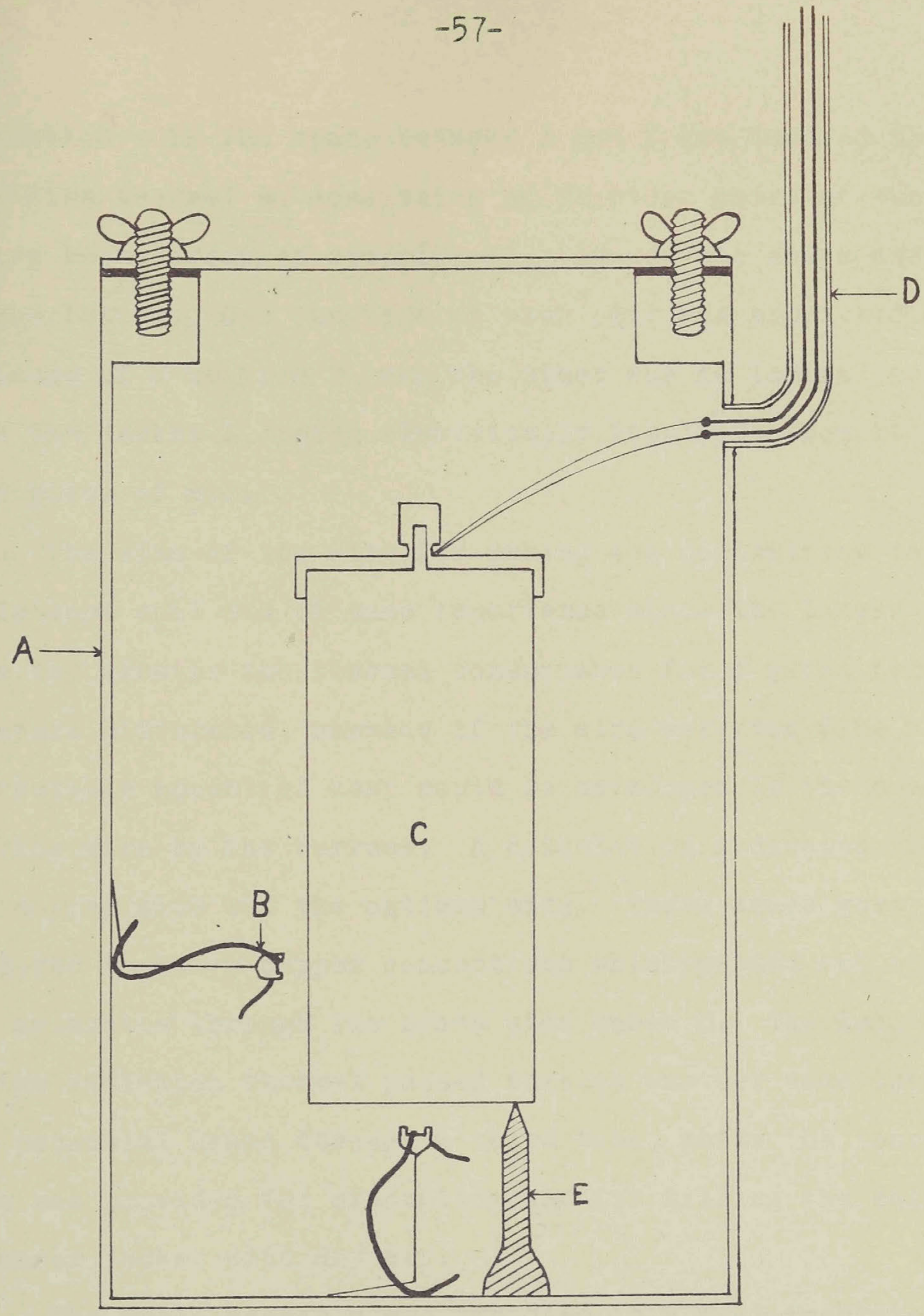


FIG. 7

conduction. In The space between A and C was mounted the radiation thermel B, consisting of thirteen pairs of junctions, twelve being arranged symmetrically around the sides and one on the bottom. One junction of each pair was supported at a distance of 2 mm from C, and the other was in thermal contact with the jacket A, being electrically insulated from it by a thin piece of mica.

The size of the wire for making the connections to the resistance coil was of some importance since the larger the size the greater the thermal conductance for a given temperature difference, whereas if the wire were too fine an appreciable amount of heat would be developed in the connecting wire by the current. A calculation indicated that #26 copper wire was the optimum size. These leads were soldered to heavy copper connections which passed out of the apparatus through the brass side tubes D. The leads to the radiation thermel passed through another side tube, the potential leads through a third tube, while the fourth tube was provided for evacuating and for filling the calorimeter jacket with dry air.

The whole assembly was immersed in a well insulated, large vacuum flask containing acetone. Acetone was used because at low temperatures water from the air would condense and form ice if it were not soluble in the liquid bath. The acetone was stirred by means of a current of dry air and the temperature measured by Beckmann thermometers. The bath was provided with electric heaters for raising the temperature, while for lowering the temperature small pieces of solid carbon dioxide were dropped in.

The electrical circuits are shown in a simplified form in Fig. 8. R is the calorimeter heater and R_1 a standardized resistance with a very low temperature coefficient of resistance. R_2 is approximately equal in resistance to R and is used to draw current prior to a run so as to bring the battery B to as constant a voltage as possible. R_3 is a variable resistance by means of which the current through the system may be varied and thus controls the rate at which the temperature rises. The voltage leads to the potentiometer P are indicated by light lines. The thermels are connected to the sensitive galvanometer G which has an optical path of about 4 meters to the scale. By measuring the voltage drops across R and R_1 and the time interval during which the current is flowing, the heat input may be calculated from

$$Q = \frac{E_1 \times E_2 \times t}{R_1 \times 4.185} \quad \text{calories}$$

where E_1 = potential drop across R_1 (Volts)

E_2 = potential drop across R (Volts)

R_1 = standard resistance (8.627ohms)

t = time in seconds.

2. Standardization of Beckmann thermometers.

Five Beckmann thermometers which were set for use at approximately - 35°, - 20°, - 5°, + 5° and + 25°C.

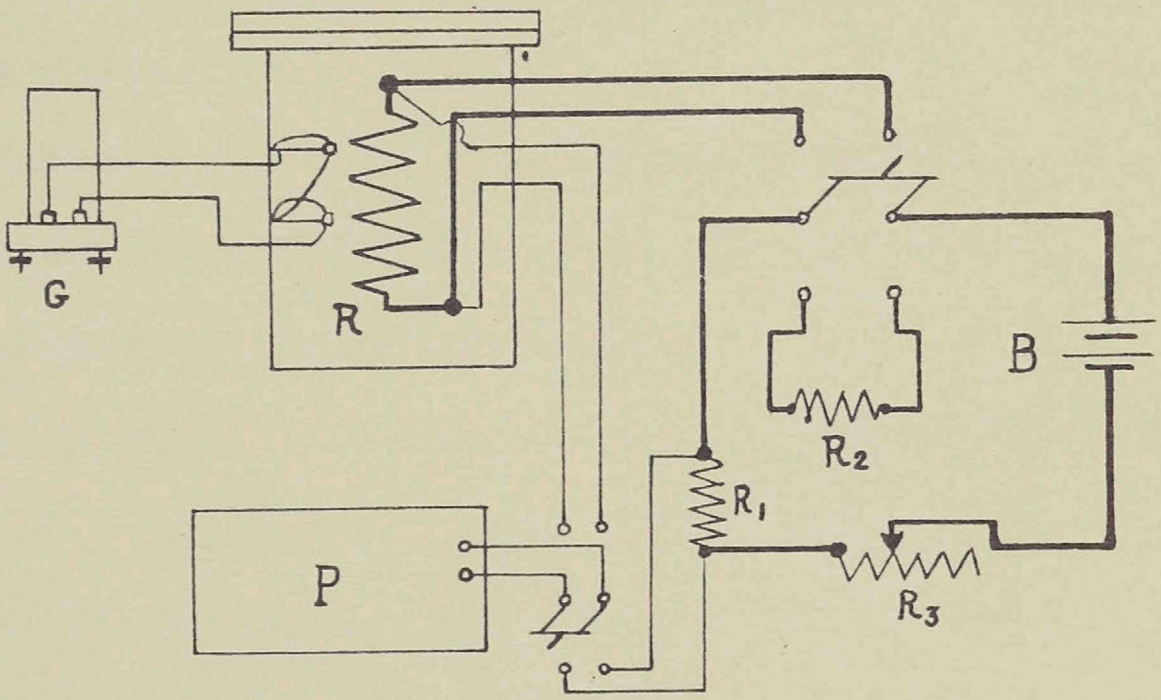


Fig. 8

were employed in conjunction with this apparatus. The zero point for each was determined by comparison with a calibrated platinum resistance thermometer. In all the experiments the thermometers were used within 0.1°C of the point at which they had been standardized and therefore there was no necessity for calibrating them over the entire scale.

It was necessary to keep ~~to~~ the Beckmann thermometers, which were set at - 35° and - 20°C, frozen in solid carbon dioxide between runs, and that set at + 5°C was kept in cold water in order to preserve the setting. The thermometer set at about - 35°C was checked at the end of a month and the zero point was found to have remained constant.

The zero points on the Beckmann thermometers were as follows:

Beckmann No.	Zero point °C.
1	- 38.090
2	+ 20.111
3	- 7.998
4	- 23.262
5	+ 1.924

3. Procedure.

The procedure followed in making a determination of the heat capacity of the container plus contents is as follows. The calorimeter bath was cooled to several degrees lower than the desired initial temperature so that the container and contents could be cooled by radiation and conduction in a reasonable time. The resistance coil around the container proved of immense value as a resistance thermometer in order to determine the temperature of the container approximately. This obviated the necessity of repeatedly bringing about thermal equilibrium by warming the outer bath to determine the temperature of the container. Also the rate at which the container cooled down could be followed when the sample contained water and thus any possibility of distillation of water from the cellulose to the cold wall could be guarded against. It was found that due to the resistance of the air gap between the jacket and the container the maximum rate of cooling of the container was about $1^{\circ}C$ per minute which was well below that causing distillation.

When the container had cooled to the desired temperature the calorimeter was warmed to the required initial temperature by adjusting the temperature of the bath and by passing current through the heating coil. The exact initial temperature was determined by maintaining adiabatic conditions and reading the temperature of the outer bath by means of the suitable Beckmann thermometer. The current was then switched on and simultaneously the heaters in the outer bath were started. Adiabatic conditions were maintained by adjusting the current flowing through the bath heaters and also by the use of a spot heater and small pieces of solid carbon dioxide. In this way it was possible to keep the temperature difference between the bath and the inner vessel to about ± 0.004°C.

When the temperature had increased to that desired the current was switched off and the exact time during which it was flowing was recorded. The final temperature was determined in the same manner as the initial temperature. During the course of the determination the voltages across the heating coil and the standard resistance were measured at intervals of 10 or 15 minutes, and the average values employed for E_1, and E_2 in the calculations.

In the initial experiments to test the new adiabatic calorimeter a single 22 ohm electric heater, sheathed in copper, was used to heat the liquid in the outer bath. It was desirable to have a heater with as small a lag as possible, therefore a 550 watt resistance coil wound on mica was acquired. After insulating with a very thin piece of mica, a sheet of 5 mil copper was wrapped about the coil and the edges were soldered. This type of heater was found to have very little lag and was admirable for the purpose for which it was designed. The current was supplied from a rheostat operating as a potentiometerin such a way that any voltage up to 110 volts could be obtained. With this arrangement, however, adiabatic conditions were very hard to control and could only be maintained to ± 0.1°C. This control was not of sufficient accuracy, therefore two smaller heaters each of 11 ohms resistance were made in a similar way to that described above. These two heaters were connected in series and were placed on opposite sides of the outer bath. Two outside resistances were put in series as well as the rheostat acting as a potentiometer. In this way the current flowing through the two heaters in the outer bath could be varied by very small amounts. Also, the larger heater was retained as a spot heater to be switched off and on as needed. Adiabatic control could now be obtained to ± 0.004°C over periods of time as long as 10 hours.

The agreement between duplicate runs was very good and will be discussed in a later section under experimental errors.

It was apparent that heat was conducted into the container along the current and potential leads thus causing a definite rise in the temperature. This was partly overcome by immersing the current leads in the outer bath for 2 feet after coming out the side arm of the jacket. The temperature rise while maintaining adiabatic conditions was found to be as follows for various temperatures:

Temperature °C.	Temperature rise of container (°C per hour)
- 35.0	0.142
- 18.3	0.104
- 9.5	0.060
+ 10.7	0.025
+ 20.0	0.012
+ 24.3	0.0

This temperature rise appeared in all the experiments to the same extent and therefore did not affect the results since they were obtained by the difference between two series of runs. The same rate of heating was used at all times so that the rise in temperature due to this leakage would be the same in all cases.

4. Introduction of water to the sulfite pulp.

After the total heat capacity of the container plus dry sulfite pulp had been determined all the electrical connections were broken at the solder joints and the calorimeter was removed from the acetone bath. The container was taken out of the outer jacket, the leads to the coil being separated at the solder joins between the #26 connecting wires and the coil proper. The container was weighed, the difference from the original weight being very small and was due to the solder left on the current leads. The small cap was unscrewed and redistilled, distilled water was introduced by means of a small capillary tube to approximately the required percentage. The cap was replaced and the exact amount was determined by weight.

To ensure an even distribution of the water throughout the pulp, the container was placed in an oven at 50°C for 10 hours. It was then removed and allowed to stand at room temperature for a period of time. This was repeated several times and finally the container was replaced in the calorimeter jacket and the apparatus was reassembled.

5. A sample calculation.

The data presented below was that obtained for one experiment using dry sulfite pulp over the temperature range - 35°C to + 25°C.

Initial temperature (Beckmann #1) = 3.100 = -35.037°C
Final temperature (Beckmann "2) = 4.246 = +24.358°C
Temperature rise = 59.395°C

Time = 19,260 seconds.
E_1 (average) = 1.2742 volts.
E_2 (average) = 1.3738 volts.
R = 8.627 ohms.

Heat capacity of calorimeter and contents per degree for the temperature range - 35.037° to + 24.358°C

$$= \frac{1.2742 \times 1.3738 \times 19260}{8.627 \times 4.185 \times 59.395}$$

= 15.722 calories

Total heat capacity from - 35.037° to + 24.358°C
= 15.722 x 59.395
=933.81 calories.

From calculations such as the above the heat capacity per degree was determined for the four temperature ranges which were approximately - 35° to + 25°C; - 20° to + 25°C; -5° to + 25°C; and+5° to + 25°C. These values (each one being the average of at least two determinations) were plotted against the mid temperatures of the corresponding temperature ranges. From the extrapolated curve obtained

In this way the heat capacity per degree was determined at - 35°, - 20°, - 5°, + 5° and + 25°C. These values were used to correct the total heat capacity as obtained above (933.81 cals.) to the total heat capacity from - 35.00°C to + 25.00°C so that the total heats may be compared for different samples over the same temperature ranges.

Heat capacity per degree at + 25.00°C = 16.933 cals.
Heat capacity per degree at - 35.00°C = 14.558 cals.

Hence total heat capacity from - 35.00°C to + 25.00°C

$$= (15.722 \times 59.398) + (16.933 \times 0.642) - (14.558 \times 0.037)$$
$$= 933.81 + 10.87 - 0.54$$
$$= 944.14 \text{ calories.}$$

Therefore, when the total heat capacity of the container plus the pulp plus a known amount of water is calculated in the same way as above, then subtraction of the two will give the heat capacity of the water for that temperature range.

6. Experimental Errors.

For the measurement of time an accurate calibrated chronometer or a stopwatch calibrated against this chronometer was used. The time interval of an experiment could be measured to at least ± 0.5 seconds or one part in 20,000 was the probable error. The combined error in e. m. f. measurements was three parts in 10,000. The initial and final temperatures could be obtained to ± 0.003°C and therefore the probable error would be one part in 20,000. Since the time interval for successive runs was very nearly the same in all cases, the error due to unequal quantities of heat entering the system along the current and potential leads would be very small and may be neglected. Errors due to imperfect adiabatic control will be small and tend to cancel out in the course of an experiment and may also be neglected. Over a 60° temperature interval (- 35°C to + 25°C) this gives a probable experimental error of 0.04 % in the heat capacity of the container plus contents. This corresponds to an error of about 0.08 % in the heat capacity of the dry sulfite pulp.

Therefore the probable error to be expected in the heat capacity of the sorbed water will be 2.5 % error for the water sorbed to the extent of 2 %, 1.3 % error for 4 % sorbed water, and 0.7 % error for 8 % sorbed water.

From the results obtained with dry sulfite pulp over the temperature range - 35° to + 25°C it was found that the heat capacity per degree for three successive experiments was 15.719, 15.722 and 15.731 cals. The average value was 15.724 cals. per degree and the mean deviation was ± 0.003 cal. This indicated that the error in this average value was 0.02 % which is in very good agreement with the value calculated above, as one would expect the actual error to be less than the calculated probable error.

RESULTS

RESULTS.

The heat capacities of dry "standard" and mercerized cellulose and of water sorbed to the extent of 5.92% and 12.0% were measured by means of the original adiabatic calorimeter involving the transfer of the sample from the initial thermostat to the calorimeter. These heat capacities were determined for three temperature ranges, viz. -78.5^{o} to $+25^{o}$C, -38.47^{o} to $+25^{o}$C, and 6.24^{o} to $+25^{o}$C.

A. STANDARD CELLULOSE.

In Table II are given the total heats of the empty container from the initial temperatures given in Column 2 to the final temperature of $+25.00^{o}$C.

The value obtained for each determination is given in Column 3, while the mean value for each temperature is shown in Column 4. In the case of the empty container, determinations were made from only two initial temperatures as the heat content varied continuously with the temperature. The container was made up of 59.121 gm. of monel metal and 3.068 gm. of lead, and allowing for the specific heat of lead, the specific heat of the monel agrees with the values obtained by Horn (62) when extrapolated to the lower temperatures.

Tables III, IV, and V, present the results obtained for the total heats of the container plus dry "standard"

TABLE II

Total heats (calories) given up by calorimeter corrected to final temperature 25.00°C.

Experiment number	Initial Temperature °C.	Total heats in calories	
		Observed	Observed Mean.
51	-78.5	602.49	
52	-78.5	601.09	601.72
53	-78.5	601.59	
	-38.5		371.0*
54	-25.4	299.07	
55	-25.4	298.73	298.66
56	-25.4	298.19	
	-6.25		183.2*

*calculated values.

cellulose, container plus cellulose plus 5.92% water, and container plus cellulose plus 12.0% water respectively. Again, Column 3 is the heat capacity of each experiment from the initial temperature given in Column 2 to the final temperature of +25.00°C, and Column 4 is the mean value of each temperature.

TABLE III

Total heats (calories) given up by the container plus dry "standard" cellulose corrected to final temperature +25.00°C.

Experiment number	Initial Temperature °C.	Total heats in calories Observed	Total heats in calories Observed Mean
3	-78.5	695.09	
5	-78.5	693.17	
6	-78.5	695.75	695.12
7	-78.5	694.90	
8	-78.5	696.67	
9	-38.47	439.56	
11	-38.47	436.52	439.87
13	-38.47	442.50	
14	-38.47	440.90	
15	-6.24	221.39	
16	-6.24	223.78	222.25
17	-6.24	221.58	
18	-6.24	222.16	

TABLE IV

Total heats (calories) given up by container + cellulose + 5.92% water corrected to final temperature +25.00°C.

Experiment number	Initial Temperature °C.	Total heats in calories Observed	Total heats in calories Observed Mean
26	-78.5	714.07	
27	-78.5	717.66	716.80
28	-78.5	718.67	
29	-38.47	450.09	
30	-38.47	451.87	452.13
31	-38.47	454.13	
32	-6.24	229.24	
33	-6.24	231.07	229.86
34	-6.24	229.27	

TABLE V

Total heats (calories) given up by container + cellulose + 12.0% water corrected to final temperature +25.00°C.

Experiment number	Initial Temperature °C.	Total heats in calories Observed	Observed Mean
41	-78.5	744.81	
42	-78.5	745.87	745.34
43	-78.5	745.09	
44	-38.47	473.98	
45	-38.47	471.63	472.36
46	-38.47	471.48	
47	-6.24	239.84	
48	-6.24	237.01	238.33
49	-6.24	238.05	

In Table VI are given the mean values of the total heats of the container and contents between the initial temperatures given in Column 1 and the final temperature summarized from Tables II - V.

TABLE VI

Total heats (calories) given up by the calorimeter corrected to final temperature +25.00°C.

Initial Temperature °C.	"Standard" cellulose	5.92% water	12.0% water	Empty Container
-78.5	695.12	716.80	745.34	601.72
-38.47	439.87	452.13	472.36	371.00*
-25.38				298.66
-6.24	222.25	229.86	238.33	183.20*

*calculated valued.

The heat content (Table VII) of the "Standard" cellulose is obtained by subtracting the heat content of the container from that of the container plus cellulose, that is, subtracting Column 5 from Column 2 of Table VI. These were recalculated on the basis of one gram of cellulose. The heat contents of the "5.92%" water and the "12.0%" water, per gram of water, given in Table VII, were obtained by subtracting the values given in Column 2 from Columns 3 and 4 (Table VI) respectively, and then recalculating on the basis of one gram of water. Similarly, the heat content of the "12.0%" minus "5.92%" water in Table VII were obtained by subtracting Column 3 from Column 4

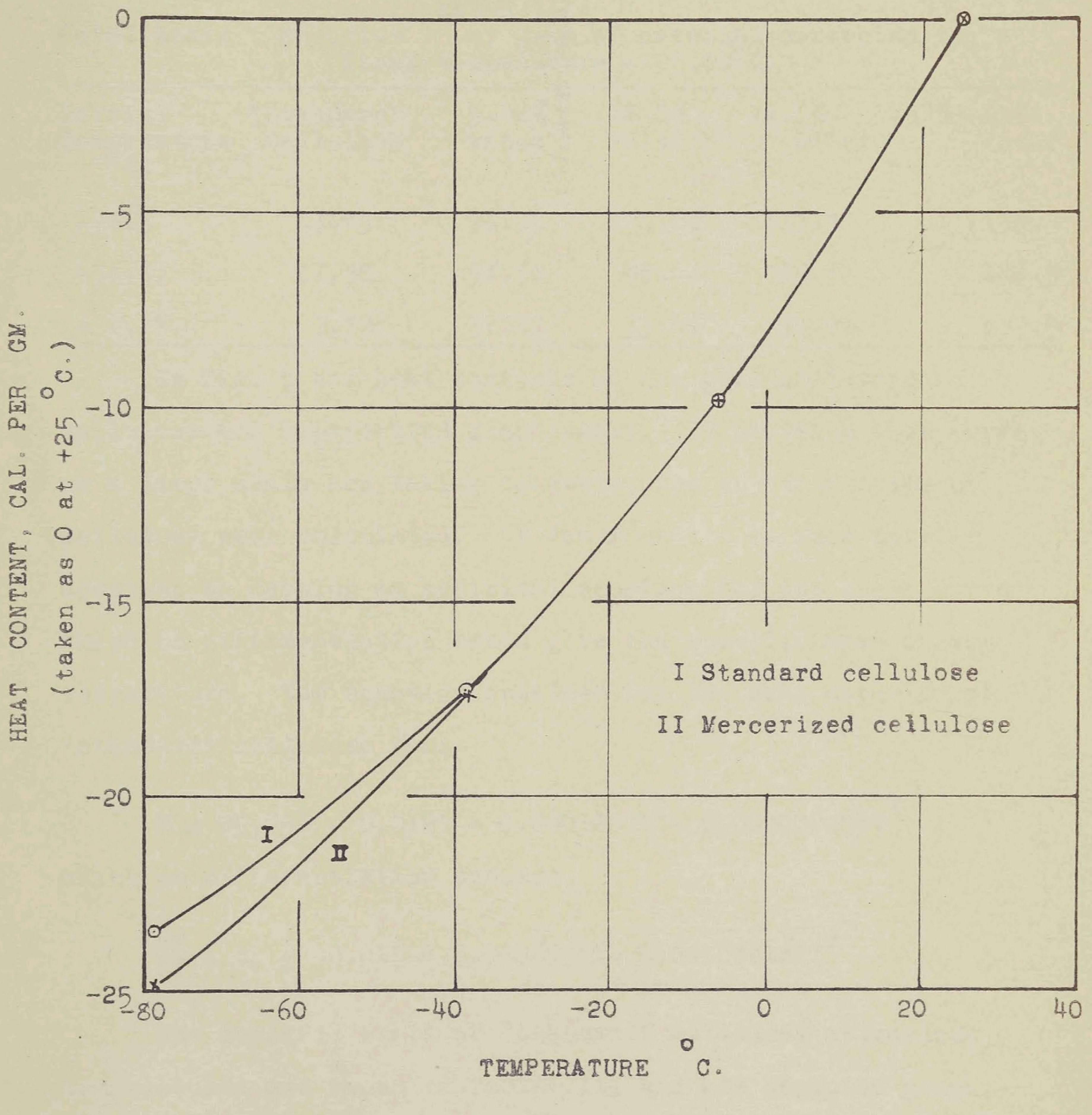

0
-5
-10
-15
-20
-25
-80
-60
-40
-20
0
20
40
HEAT CONTENT, CAL. PER GM.
(taken as 0 at +25 °C.)
TEMPERATURE °C.
I Standard cellulose
II Mercerized cellulose
I
II

FIG. 9.

of Table VI and recalculating on the basis of one gram of water. The final column in Table VII gives the total heats of one gram of free water as determined by Barnes and Maass (57)

TABLE VII

Total heats (calories) per gram of material corrected to final temperature + 25.00°C.

Initial Temperature °C.	"Standard" Cellulose	5.92% water	12.0% water	12.0% - 5.92% water	Free water
-78.5	23.45	91.95	105.00	117.8	138.2
-38.47	17.30	51.56	69.02	85.98	122.5
- 6.24	9.79	32.27	33.64	34.96	107.5

In Fig. 9 the heat contents of one gram of "standard" cellulose are represented graphically. By plotting this curve on a large scale and taking tangents, the specific heats of cellulose were calculated. It was found to be much more accurate to develop an empirical equation for the above curve which on differentiation would give the specific heat at any temperature. The equation obtained for the heat capacity of "standard" cellulose was:-

$$H = 29.054 - 0.019T + 0.0003489T^2 - 0.000002054T^3$$

which on differentiation becomes

$$\frac{dH}{dT} = C_v = -0.019 + 0.0006978T - 0.000006162T^2$$

The specific heats of "standard" cellulose at various temperatures are shown in Table VIII and are depicted graphically in Fig. 10.

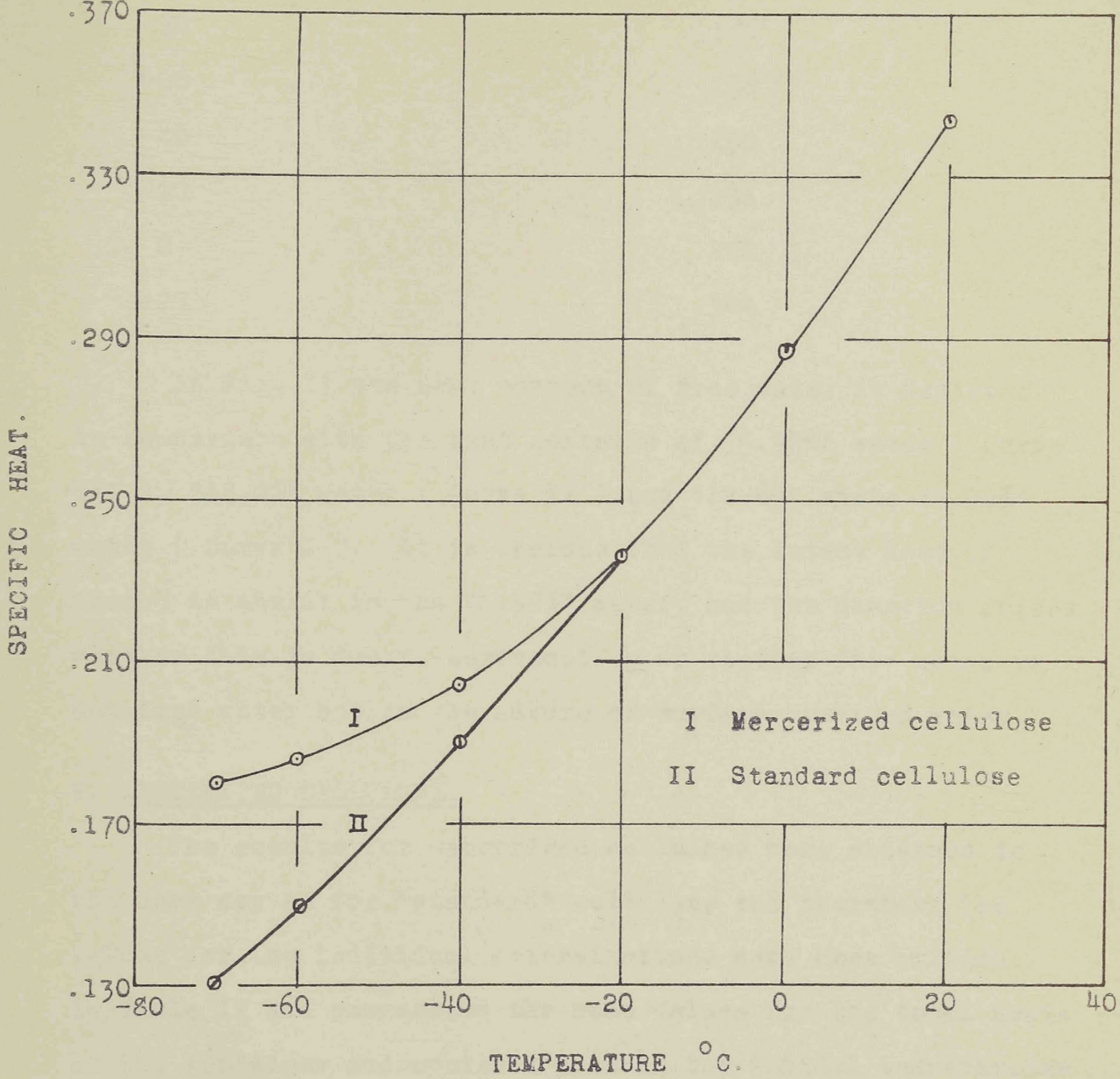

.370
.330
.290
.250
.210
.170
.130
SPECIFIC HEAT.
-80
-60
-40
-20
0
20
40
TEMPERATURE °C.
I
II
I Mercerized cellulose
II Standard cellulose

FIG. 10

TABLE VIII

Specific heat of "standard" cellulose.

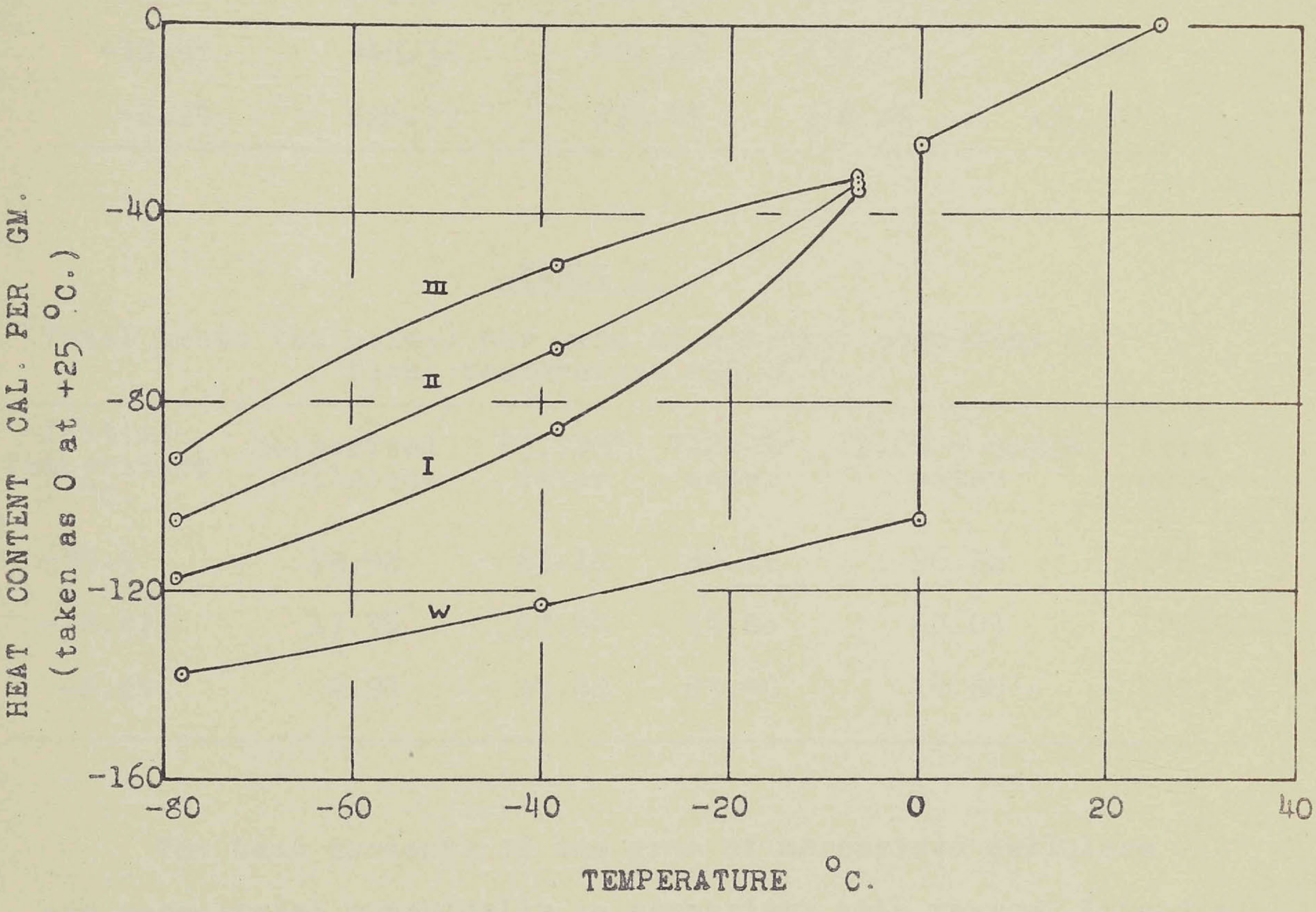
Temperature °C.	Specific heat cellulose.
-70	.130
-60	.150
-40	.190
-20	.236
0	.288
+20	.344

In Fig. II the heat content of free water is depicted in comparison with the heat contents of "5.92%" water (Curve III), "12.0%" water (Curve II) and "12.0%" minus "5.92%" water (Curve I). It is obvious that the latent heat of fusion is absent in the "5.92%" water, and the question arises whether this is due to supercooling or whether this water is not free water but in the nature of surface-combined water.

B. MERCERIZED CELLULOSE.

The results for mercerized cellulose were obtained in the same way as for "standard" cellulose and therefore the values for the individual determinations have been omitted. In Table IX are summarized the mean values for the total heats of the container and contents between the initial temperatures given in Column I and the final temperature.

Again, the heat content per gram of material was obtained as in the experiments on "standard" cellulose and are presented in Table X.



Curve W, free water; I, "12%" minus"5.92%" water;

II, "12%" water; III, "5.92%" water.

FIG. 11

TABLE IX

Total heats (calories) given up by the calorimeter corrected to final temperature +25.00°C.

Initial Temperature °C.	Mercerized cellulose	"5.92%" water	"12.0%" water	Empty container
-78.5	713.52	729.30	754.22	608.26
-38.47	448.37	461.53	476.22	375.06
-6.24	226.72	235.09	238.85	185.20

TABLE X

Total heats (calories) per gram of material corrected to final temperature +25.00°C.

Initial Temperature °C.	Mercerized cellulose	"5.92%" water	"12.0%" water	12.0% - 5.92% water	Free water
-78.5	24.92	63.12	80.19	96.76	138.2
-38.47	17.36	52.64	54.86	57.03	122.5
-6.24	9.83	33.48	23.90	14.60	107.5

The heat contents of one gram of mercerized cellulose are represented graphically in comparison with that of "standard" cellulose in Fig. 9. An empirical equation was developed for this curve also to represent the change of heat content with temperature:

$$H = 109.35 - 0.9235T + 0.003729T^2 - 0.000006247T^3$$

Differentiation of this equation gives the variation of specific heat with temperature:

$$\frac{dH}{dT} = C_v = -0.9235 + 0.007458T - 0.00001874T^2.$$

The specific heats of mercerized cellulose are shown in Table XI and are compared with the specific heats of "standard" cellulose in Fig. 10.

TABLE XI

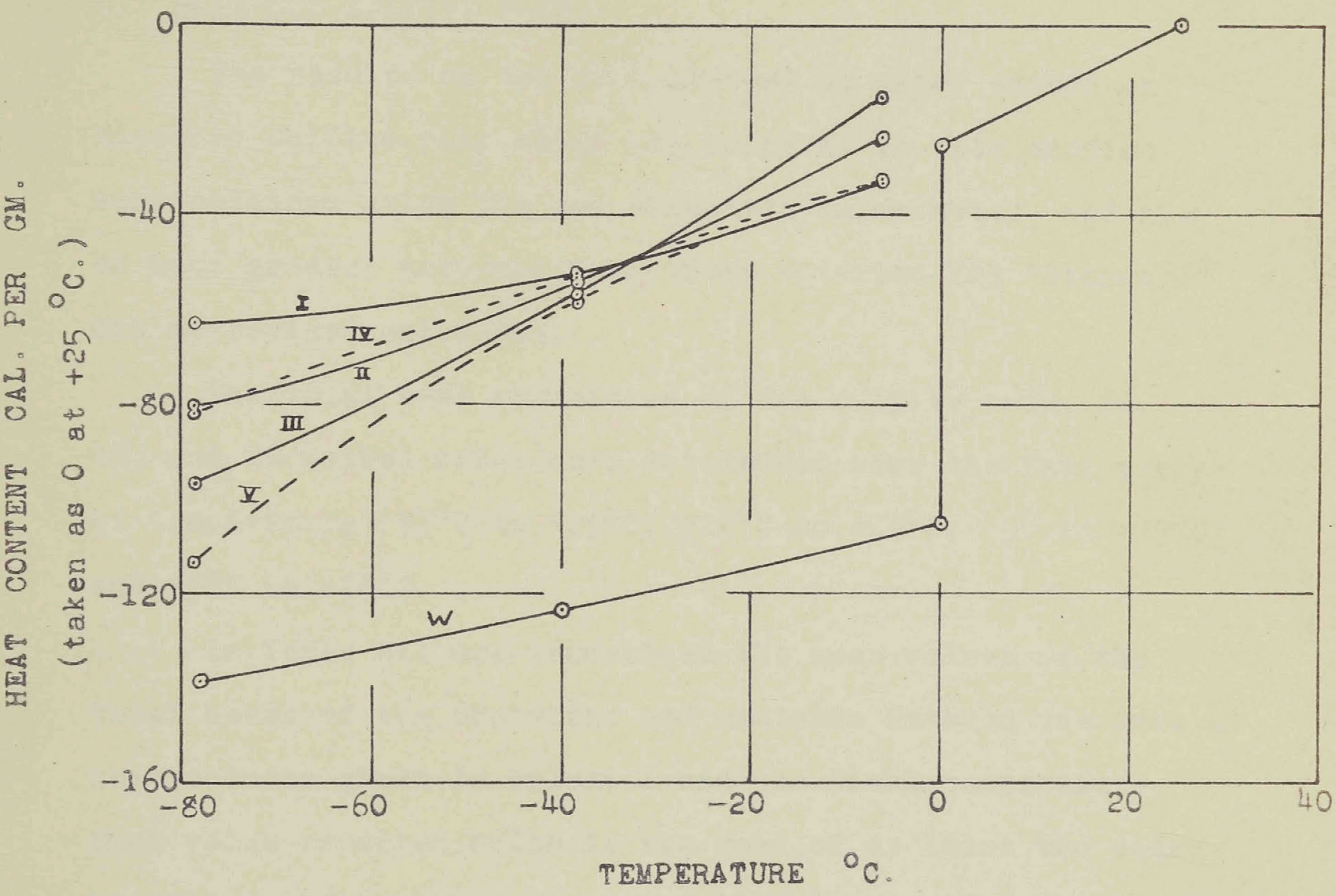
Specific Heat of "Mercerized" cellulose.

Temperature °C.	Specific Heat cellulose.
-70	0.180
-60	0.186
-40	0.204
-20	0.236
0	0.286
+20	0.345

It is apparent that at the higher temperatures the specific heats of standard and mercerized cellulose are practically the same, while at lower temperatures the specific heat of the "standard" cellulose falls off with temperature much more than that of the "mercerized" cellulose.

In Fig. 12 the heat content of free water is shown in comparison with the heat contents of "5.92%" water (Curve I), "12.0%" water (Curve II), and "12.0%" minus "5.92%" water (Curve III) for mercerized cellulose.

It seemed likely that these results were in error in so far as the heat contents of the water which is sorbed to



Curve W, free water; I, "5.92%" water; II, "12.0%" water; III, "12.0%" minus "5.92%" water; IV, "5.92%" water (redetermined value); V, "5.92%" water (slow cooling).

FIG. 12

various extents could not vary as shown in Fig. I2 unless some other factor were present. This matter was thoroughly investigated and the results obtained have been presented in the section under procedure.

C. BLEACHED SULFITE PULP.

The results on the heat content of water sorbed on bleached sulfite pulp which are reported in this section were obtained using the new adiabatic calorimeter, and are of much greater accuracy than those obtained for "standard" and mercerized cellulose.

The total heat capacities of dry sulfite pulp, 2%, 4%, and 8% sorbed water were determined over the four ranges of temperature -35°C to +25°C; -20°C to +25°C; -5° to +25°C; and +5°C to +25°C.

In Table XII are summarized the mean values of the total heats of the container and contents between the initial temperatures given in Column I and the final temperature. Each value reported below is the mean of at least two determinations which agreed to at least I part in I000.

The value of the total heat from +5.00° to +25°C for the container plus dry sulfite pulp was determined from the following equation:

$$H = 2667.3 + 1.9413T - 0.046548T^2 + 0.000033614T^3.$$

This equation represents the variation of the total heat content of container plus dry sulfite pulp with the temperature over the range -35° to +25°C. At first, the

TABLE XII

Total heats (calories) given up by the calorimeter corrected to final temperature +25.00°C.

Initial Temperature °C.	Sulfite pulp	"2.0%" water	"4.0%" water	"8.0%" water
-35.00	944.28	974.67	1002.47	1066.53
-20.00	721.74	744.23	766.29	815.38
- 5.00	489.69	506.33	521.79	555.21
+ 5.00	330.13*	342.08	353.09	376.30

*calculated value.

values determined experimentally were plotted on a large graph and the value at +5° interpolated from the curve, but this method did not give sufficient accuracy. The value obtained by substituting for the temperature in the above equation is good to 1 part in 10,000 as indicated by the agreement between the other points which were determined both experimentally and from the equation.

The total heat contents per gram of material are given in Table XIII and were calculated from the data given in Table XII in exactly the same way as was described in the results on "standard" cellulose.

The data in Table XIII are given graphically in Fig. 13 from which it seems that there is no great difference in the heat content of the water sorbed to various extents up to 8%.

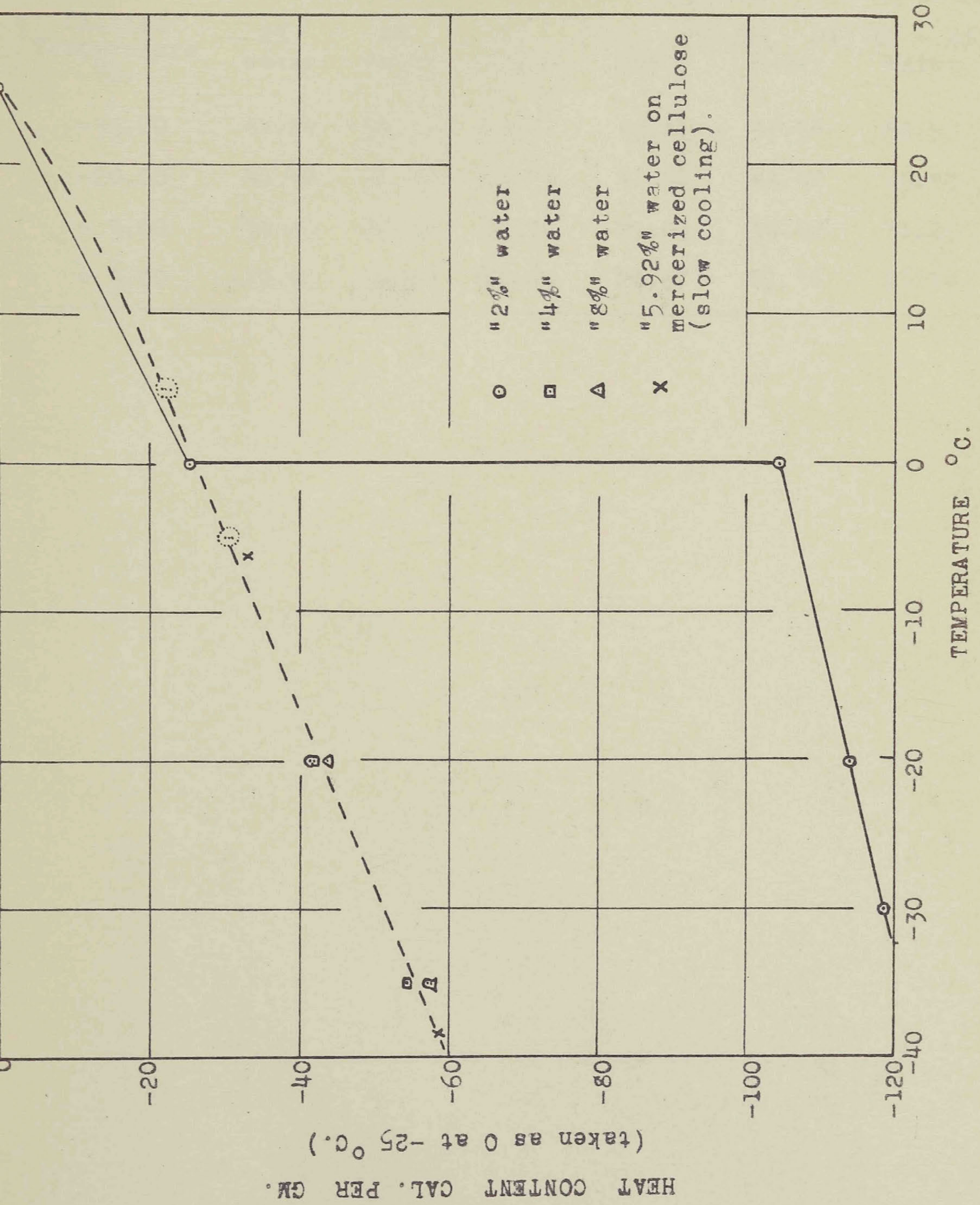

HEAT CONTENT CAL. PER GM.
(taken as 0 at -25 °C.)
-20
-40
-60
-80
-100
-120
TEMPERATURE °C.
-40
-30
-20
-10
0
10
20
30
⊙ "2%" water
⊡ "4%" water
△ "8%" water
x "5.92%" water on mercerized cellulose (slow cooling).

FIG. 13.

TABLE XIII

Total heats (calories) per gram of material corrected to final temperature +25.00°C.

Initial Temperature °C.	2% water	4% water	8% water	(4% - 2%) water	(8% - 2%) water	(8% - 4%) water
-35.00	57.24	54.72	57.32	52.21	57.34	59.90
-20.00	41.40	41.90	43.91	41.44	44.42	45.90
- 5.00	30.63	30.19	30.72	29.05	30.52	31.25
+ 5.00	22.51	21.59	21.65	20.67	21.36	21.70

DISCUSSION OF RESULTS

DISCUSSION OF RESULTS

A. SPECIFIC HEATS OF STANDARD AND MERCERIZED CELLULOSE

The results obtained on the specific heats of standard and mercerized cellulose may be summarized as in Table XIV for purposes of comparison. As a matter of interest the specific heats of dextrin and dextrose are also given. Dextrin has the same empirical composition as cellulose, while dextrose has one more molecule of water.

TABLE XIV

Specific Heats.

Temperature °C	Standard cellulose	Mercerized cellulose	Dextrin	Dextrose
-70	0.130	0.180		
-60	0.150	0.186		0.206
-40	0.190	0.204		0.230
-20	0.236	0.236		0.253
0	0.288	0.286	0.292	0.277
+20	0.344	0.345	0.311	0.300

The only values for the specific heat of cellulose that have been published are those of Padoa (63), who gives a value of).347 for the average specific heat between 0° and 80°C., and of Fleury (64) who gives a value of 0.366 at room temperature.

By reference to Fig. 10 and Table XIV it is apparent that at the higher temperatures the specific heats of standard and mercerized cellulose are practically the same. At the lower temperatures, however, the specific heat of the mercerized cellulose is higher than that of the standard cellulose.

The fact that the specific heats of standard and mercerized cellulose are so nearly the same at the higher temperatures leads to the conclusion that the heat of mercerization, as reported by Morrison (65), has a negligible temperature coefficient at the higher temperatures. But at the lower temperatures where the specific heats differ considerably, it is apparent that the heat of mercerization will in all probability have a larger temperature coefficient.

B. HEAT CAPACITY OF WATER ADSORBED ON STANDARD CELLULOSE.

In Fig. 11 the heat capacity of free water is depicted in comparison with the heat contents of the "5.92%" water (curve 111) and "12.0%" water adsorbed on standard cellulose (curve 11). Curve 1 represents what might be called the "12.0%" minus "5.92%" water. At the time when these results were obtained the following conclusions were drawn., (page 88, para. 3 to page 93, para. I).

From these curves it is obvious that the latent heat of fusion is absent in the "5.92%" water, and the question arises whether this is due to supercooling or whether this water is not free water but is in the nature of surface combined water. Curve 11 appears to be continuous with the heat content curve of free water in the liquid state and would therefore point to the existence of supercooled water. Curve 111 indicates that this is fortuitous and that the problem is not quite so simple. The two taken together may indicate that some small part of the adsorbed water has a heat capacity that is lower than that of free water, and that the remainder exists in some other form partly in the solid state, the enhanced values in this region being due to a latent heat of fusion. Curve 1 indicates that something of the kind has taken place.

At a later date in this research it was found that in all probability water distilled from the cellulose to the container wall on being plunged into the cold thermostat and when immersed in the calorimeter the net change resulted in the evolution of considerable heat which would appear in the apparent heat capacity of the sorbed water. This effect has been discussed in detail in the section under procedure. Therefore, in Fig. 11, the actual values for the heat contents of the sorbed water at the lower temperatures will in all probability be much lower than shown.

If this is the case the heat capacity of the sorbed water at the low temperature approximates that of free water and might at first sight lead to the assumption that the sorbed water is supercooled. It has been shown by various investigators (66, 67) that bound water on gelatin and egg albumin frequently shows no tendency to freeze down to - 25°C. because of the lack of nuclei to start freezing. Kistler in unpublished work (68) has recently shown that emulsions of water in oil can be supercooled to temperatures as low as - 60°C. without complete freezing. Therefore the phenomenon may be analogous to this in the case of water sorbed on cellulose and the water may not freeze because of the lack of nuclei to start the freezing. Such an explanation fits the observed facts in Fig. 11 and even more so if we consider that the values for the heat content at - 78.5°C are too high. It may be assumed that down to about - 40°C all the water is supercooled or bound to the cellulose and will not give rise to any heat of fusion, whereas at lower temperatures more and more will freeze thus giving a lower heat content until at very low temperatures the heat content of the sorbed water approaches that of free water.

It is difficult to interpret these results with respect to the ways in which water may be held on cellulosic materials. If, as has been pointed out by other investigators (19, 20, 21, 22) in this laboratory, there is a difference between the first bit of water adsorbed from that subsequently added one would expect this difference to be apparent in their specific heats. Presumably the water first adsorbed becomes surface bound water and may even be in the form of a surface compound. Since this water is so tightly bonded it is reasonable to suppose that on cooling to low temperatures there will be only a slight tendency for it to freeze. This is indicated by curve III of Fig. 11 for the "5.92%" water, there being no indication of freezing until the lowest temperature was reached. Curves 1 and 11 show that subsequently added water has a much lower heat content, which would follow if the water froze in this case. For the "12.0%" water (curve 11) the distillation of the sorbed water from the cellulose to the container wall on immersion in the cold initial thermostat would be to a much greater extent than for the "5.92%" water. This follows from the consideration that the initial sorbed water is surface bound and the water later adsorbed is capillary condensed water having a higher vapor pressure. If this were the case, the difference between the heat content of the "5.92%" water and the "12.0%" water would be much larger than is apparent from Fig. 11. The curve 11 would be displaced to a much greater extent towards the temperature axis, especially at the lower temperatures. It is also quite probable that the "12.0%" minus "5.92%" water (curve 111) will be much lower than that indicated, approximating the heat content of ice at the lower temperatures.

Therefore, it seems that the results of the heat content of sorbed water on cellulose as shown in Fig. 11 may be explained either by the assumption that supercooling is the cause of the difference between the heat contents of sorbed water, or that the water is adsorbed in the nature of a surface compound. The fact that distillation occurs does not influence the qualitative nature of the results. By taking the overall heat effect of such a process into consideration it is apparent that there will be an even greater difference between the heat capacities of the first portion of water adsorbed and that subsequently adsorbed.

C. HEAT CAPACITY OF WATER ADSORBED ON MERCERIZED CELLULOSE.

In Table X and Fig. 12 are shown the results obtained with water adsorbed on mercerized cellulose. Curves 1, 11 and 111 of Fig. 12 indicate the variation of the heat contents of "5.92%", "12.0%" and "12.0" minus "5.92%" water respectively, with the temperature. It seemed very unlikely that these heat contents of the sorbed water should vary as shown and therefore at a later date this matter was thoroughly investigated. On repeating the determination of the heat content of "5.92%" sorbed water at - 78.5°C. the value was found to be 81.62 cals. per gram rather than 63.12 cals per gram reported earlier. Using this value the heat content curve for the "5.92%" water becomes of the form indicated by curve IV (Fig. 12).

When the cellulose sample containing 5.92% of adsorbed water was cooled down slowly to the initial temperature, the values for the heat content of this sorbed water was found to be much lower than that found when the sample was cooled down rapidly (see Table 1). This was due to the distillation process already discussed, and by reference to curves IV and V of Fig. 12 it is seen that the effect is much more apparent at the lower temperatures. From the shape and position of curve V it seems that it is just a continuation of the curve for free water obtained above 0°C. This would indicate that the unexpected conclusion might be drawn that all the water adsorbed on the cellulose is in the form of free water that has been supercooled and has the specific heat of such supercooled water.

Due to the uncertainty involved in the accuracy of the results (particularly at low temperatures) the above discussion is given principally to indicate how certain ideas developed and weight is to be placed, as far as the discussion of results on the heat content of adsorbed water is concerned, on an analysis of the results obtained between - 35° and + 25°C by means of the newly devised experimental technique.

D. HEAT CAPACITY OF WATER ADSORBED ON BLEACHED SULFITE PULP.

From the results obtained for the heat capacity of water sorbed on standard and mercerized cellulose, and with the realization that the unusual behavior could possibly be traced to inaccuracies of the calorimeter and the method of mixtures, it was thought advisable to design a new adiabatic calorimeter. This was undertaken with the ultimate view of obtaining the highest accuracy possible in the measurements of the heat capacity of small amounts of sorbed water and also to eliminate any possible errors due to distillation which would conceivably take place if at any time there happened to be a sudden large temperature change. This was accomplished and the results obtained with this apparatus for 2%, 4% and 8% of adsorbed water on bleached sulfite pulp are depicted graphically in Fig. 13.

Bleached sulfite pulp was used for two important reasons. In the first place, as was pointed out in the section under

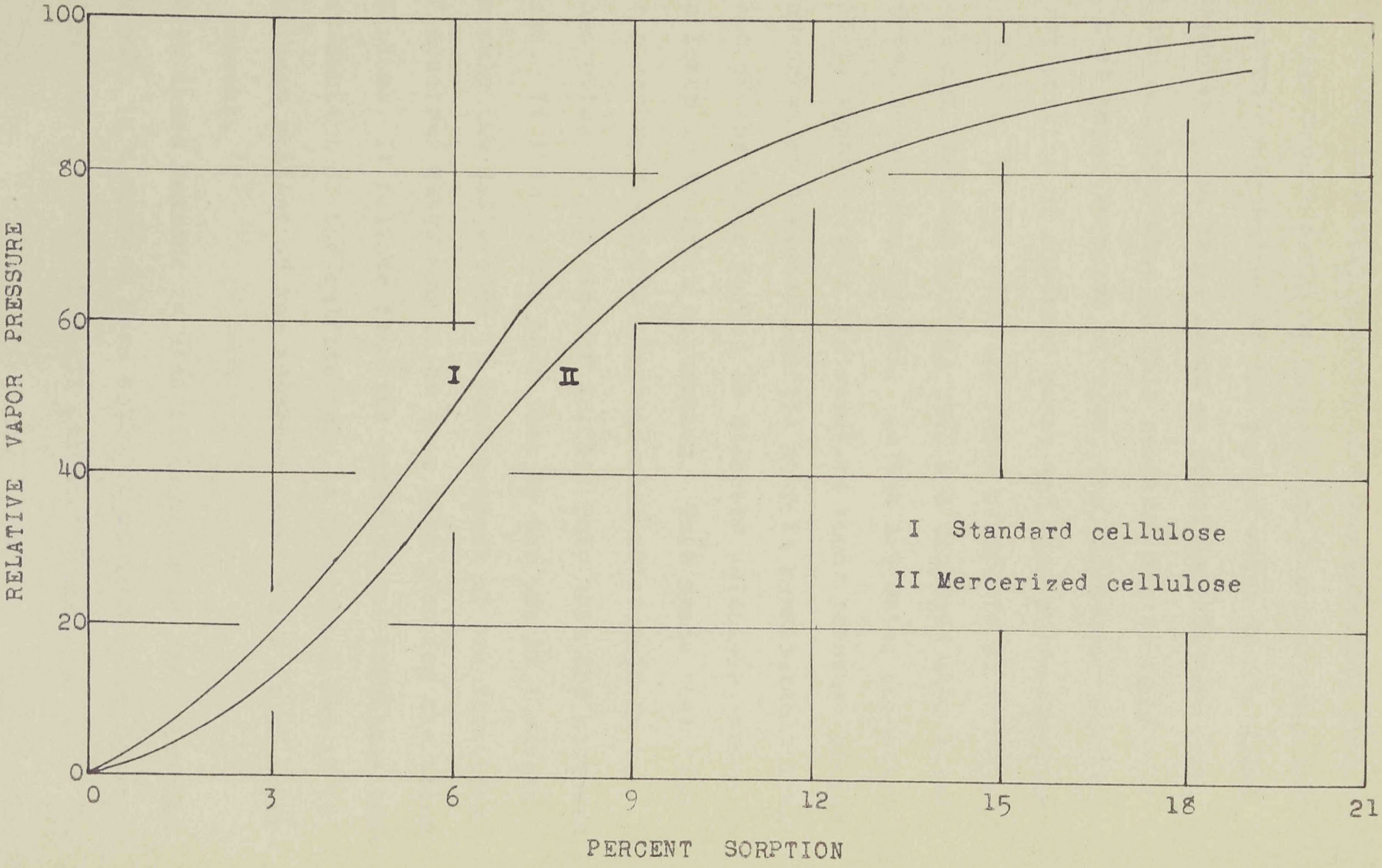

RELATIVE VAPOR PRESSURE
100
80
60
40
20
0
0
3
6
9
12
15
18
21
PERCENT SORPTION
I
II
I Standard cellulose
II Mercerized cellulose

FIG. 14.

apparatus, it was highly desirable to arrive at the heat capacity of very small amounts of adsorbed water. Therefore cellulose in a very compact form was necessary such that a large amount could be packed into the container and the relative contribution of the sorbed water to the total heat capacity would be as large as possible. Furthermore, one of the ultimate aims in this research was to determine, from a heat capacity point of view, the difference between the first portion of adsorbed water and that subsequently added. In Fig. 14 the relative vapor pressures of standard cellulose and bleached sulfite pulp are compared when water is adsorbed to various extents. At the low water concentrations it is apparent that the relative vapor pressure of the water adsorbed on bleached sulfite pulp is considerably lower than that of the water sorbed on standard cellulose, and also remains lower up to fibre saturation. This means that from a vapor pressure viewpoint there is more water held by surface adsorption in the case of sulfite pulp than for standard cellulose. If this is the case then by the use of bleached sulfite pulp the difference in heat content of the first portion of adsorbed water should be even more than for the standard cellulose. It follows from the experimental technique that the heat content of the sulfite pulp is eliminated and it is just the heat content of the adsorbed water which is of interest at present.

With these reasons in mind it is apparent that bleached sulfite pulp in a compact form would be admirable for determining the heat content of small amounts of adsorbed

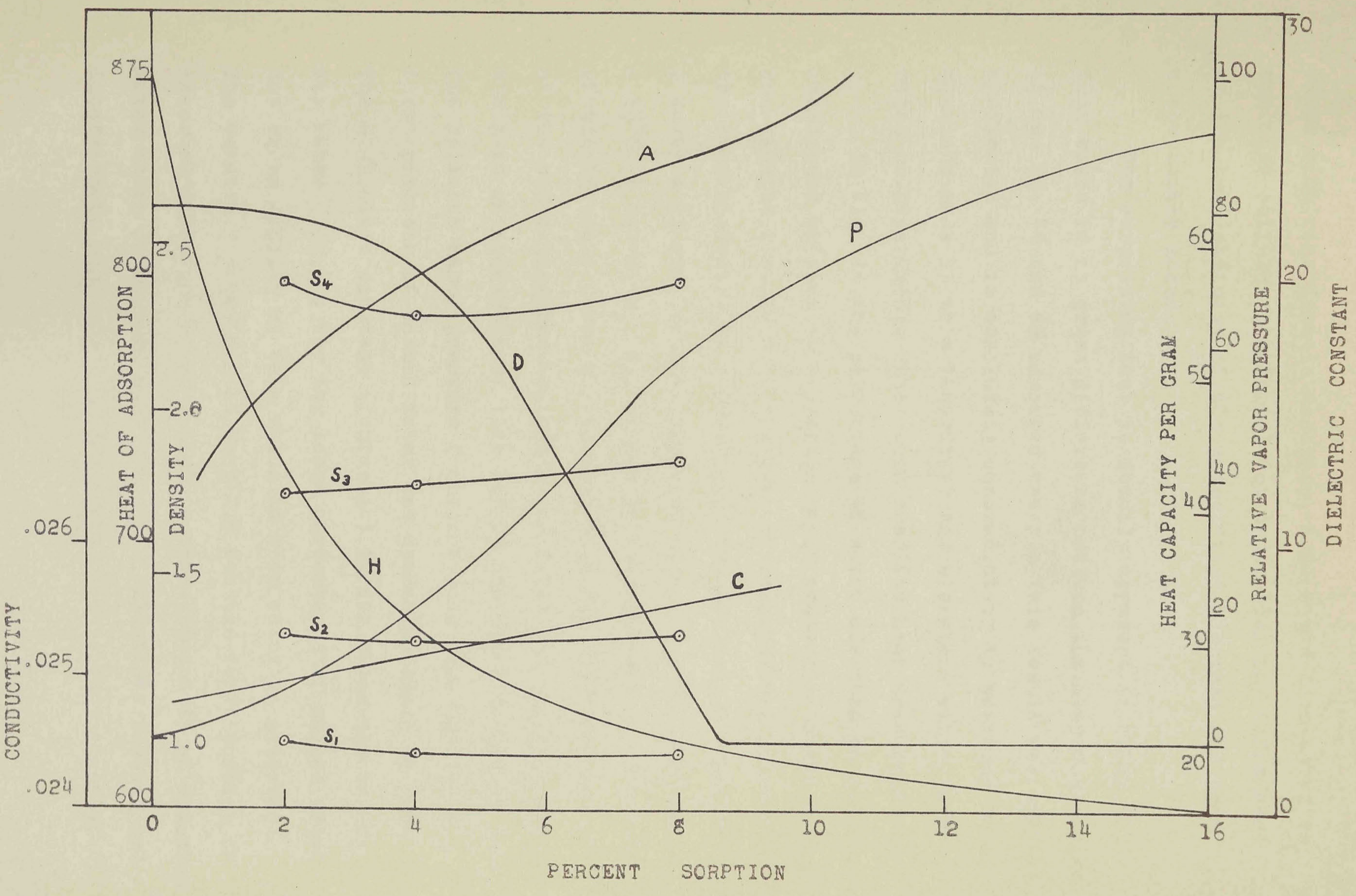

CONDUCTIVITY
.024
.025
.026
HEAT OF ADSORPTION
600
700
800
875
DENSITY
1.0
1.5
2.0
2.5
A
D
P
H
C
S_1
S_2
S_3
S_4
HEAT CAPACITY PER GRAM
20
30
40
50
60
RELATIVE VAPOR PRESSURE
0
20
40
60
80
100
DIELECTRIC CONSTANT
0
10
20
30
0
2
4
6
8
10
12
14
16
PERCENT SORPTION

FIG. 15

water with considerable accuracy, and would also serve as the best cellulosic material for indicating any difference in the heat capacity of the water first adsorbed and that subsequently added.

The surprising fact is readily apparent from Fig. 13 that there is no great difference between the heat capacities of the 2%, 4% and 8% adsorbed water. This result was totally unexpected and is absolutely contradictory to previous conclusions made in this laboratory and elsewhere which were based on experiments other than specific heat measurements.

In Fig. 15 the percentage of water adsorbed on cellulose is plotted against the relative vapor pressure (curve P), the density (curve D), the heat of adsorption (curve H), the heat conductivity (curve C), the dielectric constant (curve A), and the heat capacity at + 5°, - 5°, -20° and - 35°C. (curves s_I, s_2, s_3 and s_4 respectively). The heat of adsorption (curve H) is very high for the first portion of the water adsorbed and gradually falls off until it reaches the heat of condensation just before the fibre satuation point. The relative vapor pressure (curve P) is very low for the first portions of sorbed water and gradually rises to 100%. The dielectric constant (curve A) is far below the normal for water (78.5) for the lower percentages of sorbed water but rises rapidly to this value as more water is adsorbed. The density (curve D) is over 2.5 for the first portion of adsorbed water but falls rapidly between 3% and 8% of adsorbed water where it becomes equal to unity. All these results indicate that, initially the water adsorbed is very tightly bound and may even be in the form of a surface compound with the cellulose. As water is subsequently added the bonding becomes less secure and at approximately 8% sorption the water is probably condensing in the capillaries.

The heat conductivity measurements do not indicate a great deal of difference between the initial portions of adsorbed water and those subsequently added. However, the accuracy of these results is not particularly great and again, as Findlay (23) points out, the conductivity of cellulose may be considered as the summation of a group of conductors in series. The cellulose fibre, the air space, and the sorbed water form the conductors and the air space will be the controlling factor. Therefore, if the sorbed water does not fill the capillary spaces and cut out air gaps, then there should not be any great change in the conductivity. These measurements were pursued up to approximately 9% of adsorbed water only, and it is quite likely that the air spaces in the fibres are still present at this concentration.

Referring to Fig. 13, it may be seen that the heat contents of 2, 4 and 8% of adsorbed water lie on curves that actually indicate a higher heat content for adsorbed water above zero degrees than the heat content of free water which is indicated by curve W. It is true that the lower values might lie on an extrapolated curve for the heat content of free water, but if it were free water why are the vapor pressures low, the dielectric constants low, the density high, and the heat of adsorption very high for the first portions of adsorbed water? These facts would not follow if the water were present as free water.

In the light of these experiments on vapor pressure, dielectric constants, etc. the first portion of adsorbed water is strongly held to the cellulose surface. Such water must be partially restricted in movement and therefore the number of degrees of freedom would be diminished. This entails that the heat capacity would be lowered.

If the sorbed water is bound to the cellulose, one would expect it to have a specific heat less than 1.002, that of free water over the temperature range 0° to + 25°C. This is not the case. Since with increase in water content the proportion of free water must increase, one would expect the specific heat of the adsorbed water to increase markedly with rise in the percentage of water adsorbed. This also is not the case.

On cooling below 0°C it seems reasonable to suppose that the adsorbed water will stay adsorbed and not form ice so that no latent heats of fusion are to be expected. With increased water content and the existence of free water one would have to be prepared to expect a possible heat adsorption due to freezing although here also it probably would not occur due to the phenomenon of supercooling when water exists in a state of very fine subdivision (vide Kistler (68)). Experiments were carried out with cellulose containing up to 8% of adsorbed water between the temperatures - 35° and + 25°C and one would expect the water to be either bound or supercooled over these temperature and concentration

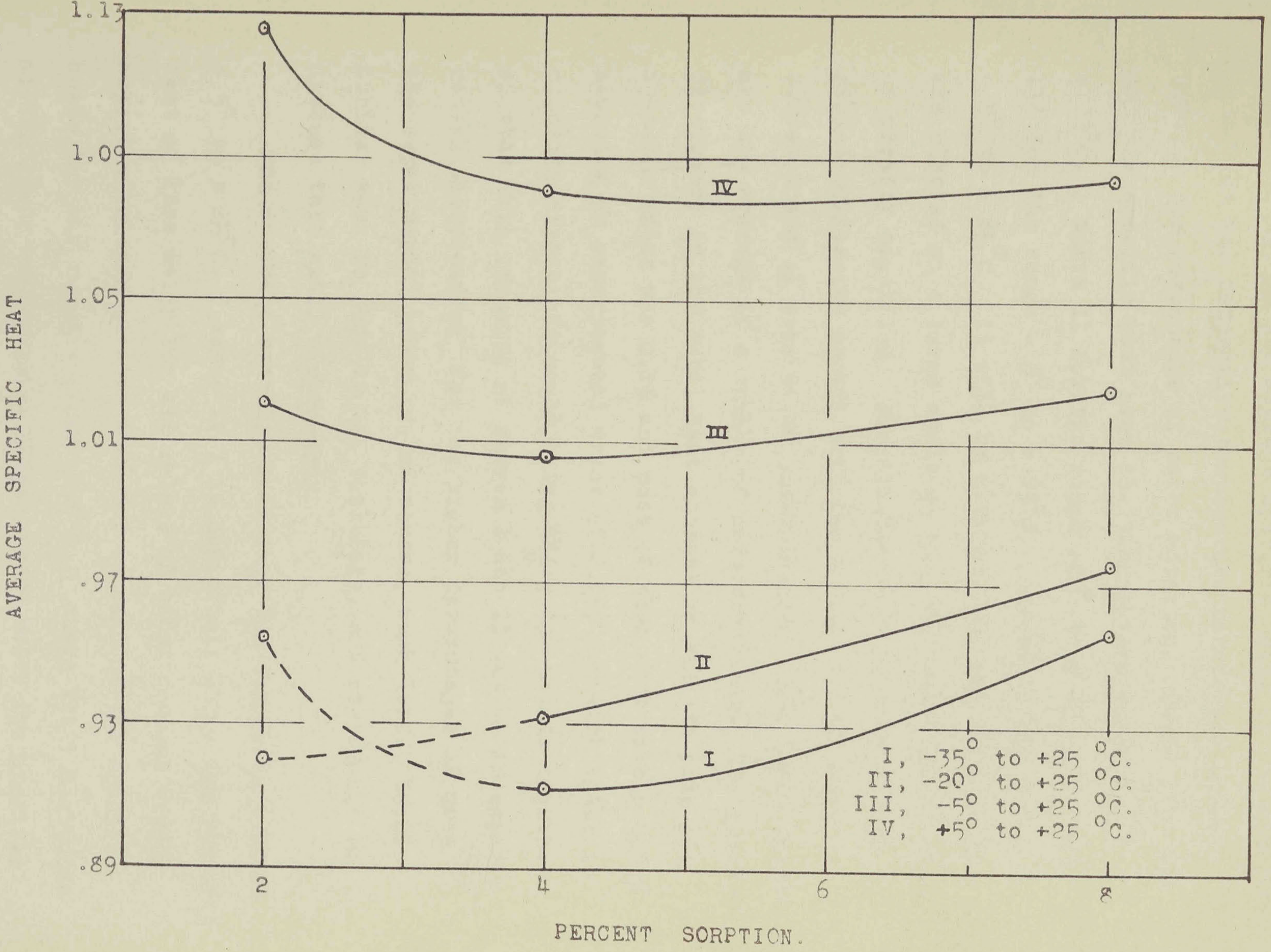

AVERAGE SPECIFIC HEAT
1.13
1.09
1.05
1.01
.97
.93
.89
2
4
6
8
PERCENT SORPTION.
IV
III
II
I
I, -35° to +25 °C.
II, -20° to +25 °C.
III, -5° to +25 °C.
IV, +5° to +25 °C.

FIG. 16

ranges and not give any latent heat of fusion.

In Fig. 16 the average specific heats of the adsorbed water for the respective temperature ranges are plotted against the percentage of water adsorbed. Curve 1 is the average specific heat over the temperature range - 35° to + 25°C. ; curve 11 for the range -20° to + 25°C. ; curve 111 for the range - 5° to + 25°C. ; curve IV for the range + 5° to + 25°C. It will be noticed that the specific heats are plotted on a large scale so that the experimental error is greatly magnified. Nevertheless all the curves show a marked uniformity except that the values for 2% water in curves 1 and 11 seem to be interchanged. Both these points are the average of a number of determinations. The greatest divergency in the total heat content of sulfite pulp and adsorbed water was 0.1% and most of them were within 0.05%. Assuming an experimental error of 0.05% for each value in opposite directions would bring these two points together so that this crossing of curves 1 and 11 may be an experimental discrepancy. For the higher percentages of water the experimental error is, of course, much less. Until further work is done it is, therefore, not profitable to discuss this small discrepancy.

The apparent specific heat over the temperature range + 5° to + 25°C. (curve IV) is definitely above the specific heat of free water for all values of water content beyond experimental error. The same may be said of the specific heats for the range + 5° to + 25°C. (curve 111) and those at the lower temperatures are not much below the specific heat of free water. This relatively high value for the specific heats occurs for the whole range of concentration from 2% to 8% of adsorbed of water. The explanation that the high value of the apparent specific heat is due to the latent heat of fusion has already been ruled out by the previous discussion and is made very obvious by the curves in Fig. 16. It may be seen that the highest values for the apparent specific heats of the adsorbed water are obtained for the temperature range + 5° to + 25°C and over this range the temperature has never been brought below the freezing point of water.

As the 2% of adsorbed water, where most of the water must be bound water, at least more so than in the higher percentages, gives the highest value for the specific heat at + 5°C. some other source of heat adsorption must be looked for than that required for heating up the cellulose and water alone. It is suggested that some change in equilibrium in the system water-cellulose must occur which brings about an absorption of heat when the system is warmed up. Such a mechanism is corroborated by other facts and it may be of considerable theoretical importance that attention has been drawn to the possibility of this mechanism.

The water that is held by cellulose at any one concentration exists in various degrees of freedom, using the term in the sense of the extent to which it is bound to the cellulose. It is suggested that a rise in temperature decreases the amount of bound water and increases the freedom of some water to the corresponding extent. The large heat of adsorption that was found by Argue and Maass (19) shows that the change from bound water to free water requires a large amount of heat. In the heat capacity measurements, the heat that was added was therefore required for two purposes, firstly for the heat capacity of the system as a whole, and secondly to supply the heat necessary to bring about a decrease in the amount of bound water with rise in temperature. If this quantity were known and subtracted, the resultant specific heats of the adsorbed water would be less, and probably conform with what one could predict from the other physical chemical measurements.

Additional evidence, that with rise in temperature the extent to which water is bound at a definite concentration decreases, is given by the following considerations. It has been found by Urquhart and Williams (16) and by Walker (69) that if the relative humidity is kept constant and the temperature is raised, the amount of adsorbed water decreases, or that for a constant amount of adsorbed water the relative humidity has to be increased with rise in temperature in order to keep the water adsorbed. In other words the vapor pressure of the water adsorbed on cellulose increases relatively, with rise in temperature, more rapidly than the vapor pressure of free water. These experimental results also show that with rise in temperature the adsorbed water becomes less bound.

A somewhat analogous case was found by Horn and Mennie (62) in the system gelatin-water. It was impossible for these investigators to carry out measurements, at that time, with gelatin containing small amounts of adsorbed water. However, heat capacity measurements carried out under their conditions seemed to indicate that there was a change in the amount of bound water with the temperature even at these concentrations, which were, actually, much higher than those used in the present investigation of the cellulose-water system.

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS.

A. CLAIMS TO ORIGINAL WORK.

The specific heat of standard cellulose and mercerized cellulose has been accurately measured over the temperature range - 70° to + 25°C.

A new calorimeter and experimental technique has been devised which is applicable to the measurement of the heat capacities of small amounts of water adsorbed on a colloidal material with a far greater accuracy than was previously possible.

The heat capacity of water adsorbed on cellulose has been measured for the first time. Measurements have been made with 2, 4, and 8% of adsorbed water over the temperature range - 35° to + 25°C with considerable accuracy.

A mechanism, that of a change in the amount of "bound" water with temperature, has been suggested to explain the high values obtained for the apparent specific heats of adsorbed water.

B. SUGGESTIONS FOR FURTHER WORK.

1. Apparatus

Although the adiabatic technique developed gave a means of measuring the heat content of adsorbed water with an accuracy unequalled before, this could be enhanced by a number of alterations in the design of the calorimeter. It is suggested that the leads from the heating coil be brought out in such a way that they can be coiled around the outer jacket of the calorimeter, thus obviating the necessity for corrections due to the leakage of heat along the wires. Furthermore, a platinum thermometer with a Mueller bridge would facilitate the operations and also make it possible to make measurements at much lower temperatures.

2. Calorimetric measurements.

It would be of interest to repeat the results obtained, with this improved apparatus and include measurements from - 80° up to + 100°C. Particularly in view of the suggested change in equilibrium with temperature of "bound" and free water, measurements at high temperatures would be of interest. Measurements should be carried out with higher concentrations of adsorbed water and it is the intention of the writer to do this with the present technique.

3. Other investigations.

From the results of the investigation described in this thesis, as brought out in the discussion, it is obvious that in order to draw further theoretical conclusions from heat capacity measurements it is essential to expand previous investigations into the properties of the cellulose-water system. The measurement of the heat capacity of water adsorbed on cellulose is not merely the simple process of measuring the temperature rise on the addition of a definite quantity of heat because, as was pointed out, there may be this change in the condition of the water adsorbed on the cellulose with rise in temperature which would involve an unknown quantity of heat which appears in the apparent heat capacity of the adsorbed water. It is suggested that adsorption isothermals be determined on a sample of the cellulose used over the temperature range in which the heat capacity measurements are made. Furthermore, measurements of the heats of wetting over as large a temperature range as is feasible should be carried out.

C. FINAL CONCLUSIONS.

Apart from the conclusions embodied in the above sections A and B, it may be worth while to stress the importance of a possible change in the condition of the water adsorbed on the cellulose with temperature. This has given a new insight into the physical-chemical nature of the system cellulose-water. It was brought out that measurements along other lines have to be carried out simultaneously in order to evaluate the true specific heat of adsorbed water, and the magnitude of the changes in the amount of bound water involved. This may, some day, prove to be of practical importance since all paper processing depends to a large extent on the addition and removal of water. Then, if this hypothesis is substantiated, it may prove to be of value in suggesting alterations in conditions, especially that of temperature, under which certain parts of the processing are carried out.

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