THE DIELECTRIC CONSTANT OF CELLULOSE AND ADSORBED WATER VAPOUR

THE MEASUREMENT
OF
THE DIELECTRIC CONSTANT OF CELLULOSE
AND
THAT OF ADSORBED WATER VAPOUR

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.

Montreal, Canada April, 1937.

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INTRODUCTION

Introduction

The importance of a clearer insight into the cellulose-water relationship can hardly be over-emphasized. Aside from its value as a purely theoretical consideration in the realm of colloidal chemistry, a knowledge of the under-lying mechanism is greatly to be desired because the phenomena involved are fundamental to the art of paper-making. It is undoubtedly the use of cellulosic materials in the latter connection that has supplied the greatest impetus to research in this direction. It would therefore not be amiss to introduce a discussion of the cellulose-water relationship with an indication of its role in the making of paper (1) as it involves fundamental concepts of theoretical interest.

Paper is made by depositing on a screen, from a dilute water suspension, a "mat" of cellulose fibres. This mat is pressed in order to compact the mass and to remove most of the water. It is then subjected to a heat treatment that extracts all but the final traces of moisture. During the above process, the sheet acquires a structural strength which is due, to a slight extent, to the interlacing of the fibres, but mostly to the adhesion of the latter to each other. It is the physico-chemical nature of the forces bringing about this ad-

hesion that are of theoretical interest.

It might be useful for the purpose of subsequent discussion, to define "paper" as a system, deposited in sheet form, having coherence governed by forces of another order of magnitude than might be accounted for by the mere mechanical picture of the interlacing of the unit parts.

Now many other materials, such as silk, wool, hair and asbestos, form dilute suspensions in water. Sheets can likewise be made from these but such sheets do not dry to form paper. They possess only the structural strength that results from the interlacing of the fibres since adhesion of fibre to fibre is lacking.

Nor is water the only liquid in which cellulose can be suspended. Alcohols, oils and other liquids likewise possess this property. Sheets prepared from such suspensions, however, do not form paper on drying. Just as in the case of silk, wool or asbestos which has been deposited from water, such a sheet possess but little structural strength, since here also there exists no adhesion of fibre to fibre.

It is evident from the above discussion, that there is some unique property of the cellulose-water system, that

favors the formation of adhesive bonds, under the conditions that are present in the making of paper. In an attempt to discover the source of this peculiar affinity between cellulose and water, investigators have attacked the problem from numerous angles. Filby and Maass (2), Urquhart and Williams (3) and others have established the adsorption and desorption isotherms. Argue and Maass (4) have measured the heats of wetting of cellulose. Filby and Maass (5) have determined the apparent density of the adsorbed water. These investigations are only presented as examples of the methods of attack that are being employed for it would be an endless task to attempt to enumerate all of them.

Because of the high degree of accuracy that is associated with dielectric constant measurements, Argue and Maass (6) resorted to a measurement of the dielectric constant of the water adsorbed on cellulose, in an effort to throw more light on the cellulose-water relationship. The results proved highly interesting.

The present investigation is a continuation of the work initiated by Argue and Maass. It was undertaken for the two-fold purpose of ascertaining the reproducibility of their results, and also to investigate the cellulose-water relationship under conditions different from those under which these previous workers had made their measurements.

The findings of Argue and Maass were verified for the most part. Certain discrepancies in their measurements, which they attributed to experimental error, were shown, however, to be real differences. Inasmuch as a more precise evaluation of their results had been hindered by a lack of the absolute value for the dielectric constant of standard cellulose, it was decided to measure this constant. Since no method existed for the determination of the dielectric constant of fibrous materials, it was necessary to develop such a method. This was done and the dielectric constant of cellulose was determined. Actually, the measurement of the dielectric constant of the adsorbed water was carried out prior to the measurement of the dielectric constant of cellulose but a more logical treatment of the subject is afforded if the latter is discussed first. Such an order has been adopted in presenting this thesis.

SECTION I.

DISCUSSION OF THE MEASUREMENT OF THE DIELECTRIC CONSTANT

SECTION I

Discussion of the Measurement of the Dielectric Constant.

The principal methods employed for the measurement of the dielectric constant can be divided into three classes. The method to be mentioned last, which is the one employed in this investigation, is by far the most useful. The other two are of no special interest here and only a brief reference is made to them.

(1) The dielectric constant can be calculated from Coulomb's Law from a measurement of the electric force acting through a dielectric. This method was first used by Silow (7). Improvements were added in turn by Perot (8), Carman (9), Quincke (10), Michaud and Balloul (11), and Furth (12).

(2) A determination of the velocity of propagation of electromagnetic waves through a material, which is proportional to the square root of the dielectric constant of the material, was introduced as a method of dielectric constant measurement by Drude (13). Modifications have been subsequently added by Holborn (14), Mesny (15) and Wachsmuth. (16)

(3) The dielectric constant of a material is given by the ratio C_x/C, where C_x is the capacity of the condenser filled with the material, and C is the capacity of the condenser empty. The accuracy of this method obviously depends upon the accuracy with which the capacity measurements can be made. There are three general methods for capacity measurement, namely (a) the bridge method (b) the resonance method (c) the heterodyne beat method. Nernst (17) was a pioneer in the use of the first method. Hertwig (18) and Joachim (19) later added contributions to the field. The second method has been employed by Tank (20), Falckenberg (21), Walden, Ulich and Werner (22) and others. The third method, which is the one actually used in this research, has been investigated by Herweg (23), Isnardi (24) and Williams and co-workers (25) (26). The theoretical considerations involved can best be treated elsewhere and have therefore been left for a later section.

For a more comprehensive treatment of the subject of dielectric constant measurement, the reader is referred to the publication of Smyth (27) from which the material for the above discussion has been taken.

SECTION II.

APPARATUS FOR CAPACITY MEASUREMENT AND METHOD OF USE

SECTION II

Apparatus for Capacity Measurement and Method of Use.

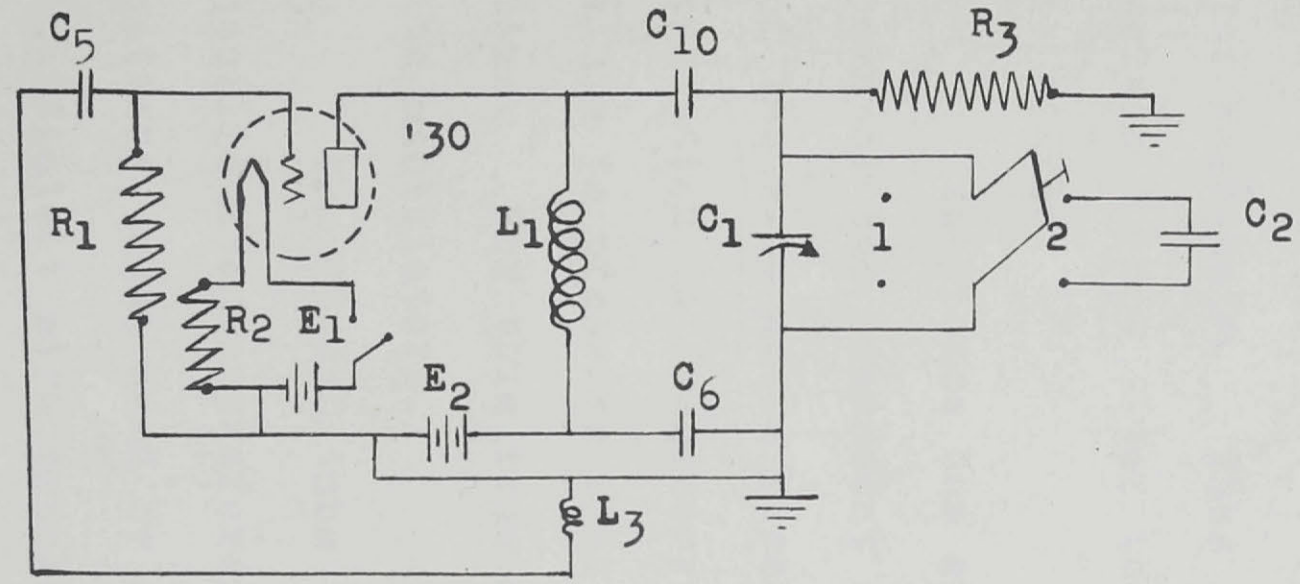
1. Apparatus

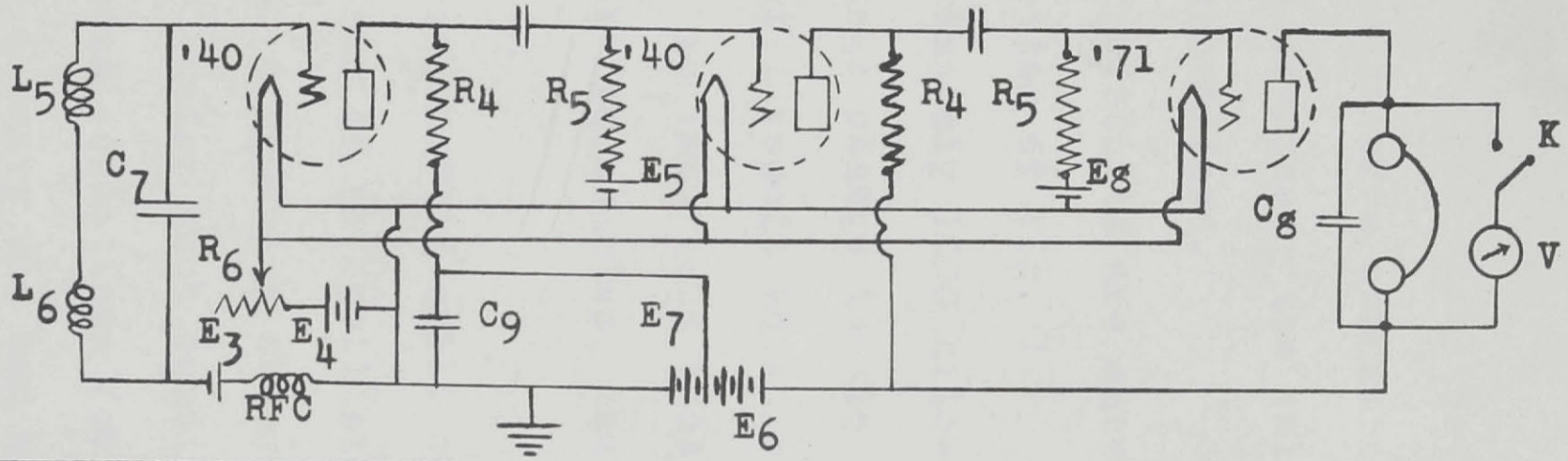
The resonance method for capacity measurement was employed in this investigation. The apparatus was originally described by Smyth (27) but has been considerably modified by other workers (28,29) in this laboratory as well as by the writer. The apparatus consists essentially of two high frequency oscillators of the vacuum tube type which are allowed to beat against each other. If the two oscillators have the same frequency, that is, are in resonance, no beat-note results. Now the frequency of an oscillating system in which only the capacity is varied, can be expressed by the relation:

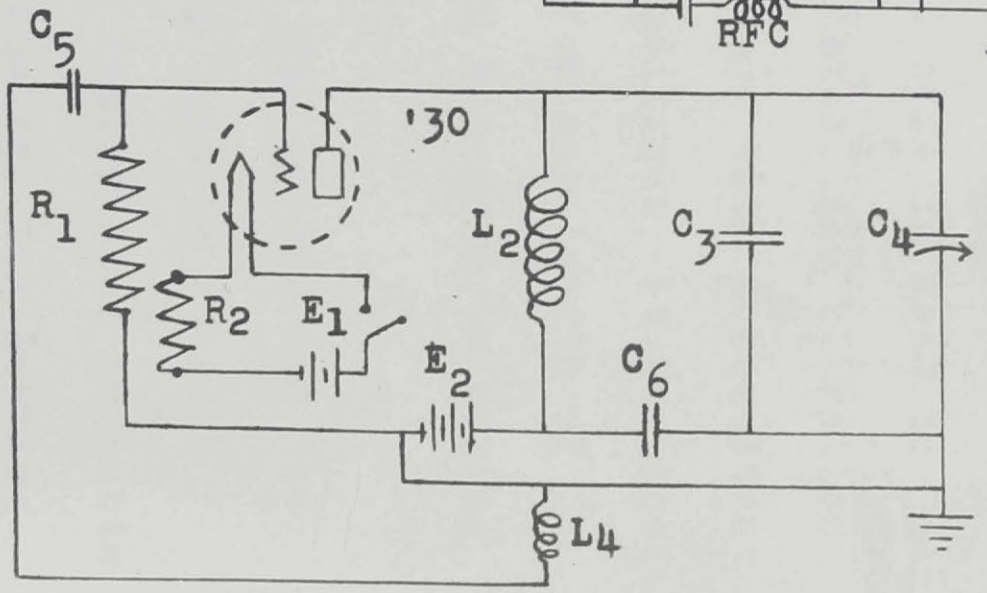
$$f = \frac{k}{\sqrt{c}}$$

where: f is the frequency,
c is the capacity,
k is a constant.

It follows, therefore, that the introduction of additional capacity into one of the oscillators will result in the production of a beat-note since the frequency of that







R_1 = 50,000 ohms
R_2=15 ohms
R_3=12,500 ohms
R_4=0.25 megohms
R_5=5 megohms
R_6=6 ohms

E_1=3 volts
E_2=90 volts
E_3=1.5 volts
E_4=6 volts
E_5=3 volts
E_6=135 volts
E_7=45 volts
E_8=27 volts

C_1=500 mmfd.
C_2=cell.
C_3=500 mmfd.
C_4=1,200 mmfd.
C_5=0.001 mfd.
C_6=0.01 mfd.
C_7=0.00025 mfd.
C_8=0.002 mfd.
C_9=2 mfd.
C_{10}=0.1 mfd.

F I G U R E I

oscillator will change. By reducing the capacity in the same circuit by means of a standard condenser until zero beat is again obtained, the value of the added capacity can be ascertained.

The two oscillator circuits are shown, respectively, at the top and bottom of Fig. 1. These operate at a frequency of approximately 1000 kilo-cycles. A relatively small percentage change in the frequency of one of the oscillators will result in a large change in the beat-note. Thus it is important that these of themselves do not alter their frequencies, that is, they must be stable.

Experience has shown that if small wire is used to connect the component parts of an oscillator, the vibration of the wire gives rise to a capacity change with a resultant variation in frequency. Under such conditions, it is impossible to preserve zero beat conditions for any length of time. For this reason, a heavy bus bar was used in wiring the oscillators.

The UX-230 tube (a dry cell tube) was chosen for the oscillators in preference to the UX-201A type (a storage battery tube) used by Argue (30). The latter tube is quite inefficient with respect to the power required for heating the filaments. A comparison between the two tubes (which

otherwise have the same operating characteristics) shows this.

Tube	Filament Voltage	Filament Current	Power
UX-201A	5 volts	0.25 amperes	1.25 watts
UX-230	2 volts	0.06 amperes	0.12 watts

Furthermore, in view of the fact that the oscillators must be entirely shielded, it is much simpler to achieve this when dry cells, rather than storage batteries, are used.

The frequency of an oscillator is dependent upon the filament voltage. Certain precautions were taken to ensure that this remained constant during measurements. The voltage E_1 was supplied by four dry cells connected in series-parallel to give three volts. Such an arrangement was used to minimize the current drain from each cell and thus provide a more constant voltage source. R_2, a fixed resistor, replaced the conventional rheostat which, due to the oxidation of the resistance wire, often gives rise to a poor contact in the filament circuit. Also from the stand-point of a constant voltage source, the necessity of using "A" batteries in good condition can hardly be too strongly emphasized. It was shown during this work, that frequency instability results if any one of the "A" batteries has reached the state where it gives

a current of less than fifteen amperes on short circuit test instead of the thirty amperes or more which a new cell can furnish.

Frequency is also dependent upon the plate voltage. Instability was traced on one occasion to a "B" battery in poor condition. This battery when tested with a voltmeter furnished the rated voltage of forty-five volts. However, the latter instrument draws such a small current that it does not indicate the voltage of the battery under operating conditions, that is, under appreciable current drain. The voltage of this battery was then tested with its terminals shunted by a thousand ohm resistor. Under this load, the voltage was found to have fallen ten volts below the rated value. (A good battery similarily tested shows no such voltage drop). The voltage of a battery in such poor condition has a tendency to vary during operation.

Due to the voltage fluctuations which both the A and B batteries undergo when the filament circuits of the oscillators are first closed, it is necessary to let the latter run for some time prior to taking measurements. It was found that fifteen minutes to half an hour usually sufficed in order that steady conditions be realized.

The inductances L_1 and L_2 consisted respectively,

of sixty-four and seventy turns of number fourteen insulated copper wire wound on a cylinrical form three and a quarter inches in diameter. The inductances L_3, L_4, consisting respectively of thirty-two and thirty-five turns of wire, were wound over L_1 and L_2.

The capacitance C_1 was a precision condenser of five hundred micromicrofarads (General Radio, Type 247 E). C_2 was the experimental condenser containing the substance whose dielectric constant was to be measured. C_3 was approximately equal to C_1 in capacity. It is shown in the diagram as a fixed capacity as it was not necessary to vary this during experiment. C_4 (about 1200 micromicrofarads) was used to offset the capacity of the long leads employed in conjunction with C_1, C_2. A one-plate vernier condenser attached to C_4 afforded a very fine adjustment. The shafts of this condenser protruded through the sheet metal boxes used for shielding. In order to avoid stray capacities, it is necessary to include these condensers in the oscillating circuit such that the shafts are grounded.

During an actual measurement, the value of C_4 is not varied so that the oscillator including it is termed the "fixed oscillator". On the other hand, the value of

C_1 is changed so that the oscillator containing it, is termed the "variable oscillator".

Some means must be used to indicate when the two oscillators are in resonance. This was accomplished by means of the detector-amplifier unit (centrally placed in Figure 1). The oscillators were loosely coupled to it by means of L_5 and L_6, each of which consisted of four turns of #22 wire on a bakelite form, two and a half inches in diameter. The necessary leads were run from one unit to the other by means of holes in the boxes.

The detector-amplifier unit, with minor changes in circuit design, was the same as that described by Smyth (27). A UX-240 tube was used in the detector stage followed by another tube of the same type as a voltage amplifier. A UX-171 was employed in the output stage.

In the original hook up, since the condenser C_7 was not variable, the circuit composed of L_5, L_6, and C_7 was only approximately tuned, (that is, infinite impedance not offered to every signal). In order to remedy this without making C_7 variable, a radio choke RFC was added. This resulted in an increase in the power output.

The voltage on the plate of the detector tube was reduced from 135 volts to 45 volts as the former value was considered too high for efficient detection. This like-

wise resulted in an increase in power output.

As a result of these modifications, the power output was of sufficient level to warrant the use of a loudspeaker. The diaphragms were removed from the phones and each of the latter was placed against the bottom of a "tin can". This arrangement gave loud-speaker volume.

In order to increase the accuracy with which the standard condenser could be read, it was placed in the centre of a circular wooden platform five feet in diameter. A small mirror attached to the rotor shaft reflected a line image on to a millimetre scale fastened to the circumference of the platform. With this arrangement readings could be estimated to 0.1 millimetres. In order to avoid body capacity, a pulley arrangement was utilized to rotate the rotor from the edge of the platform. A vernier dial used in conjunction with the pulley system afforded a fine adjustment.

Because of the experimental set up, it was necessary to use long leads to connect the standard condenser and the experimental condenser to the variable oscillator. These were shielded by placing the individual wires in copper tubing and grounding the latter.

The switch S (a rocker type switch) had to be

placed near the cell and consequently was some distance from the capacity measuring equipment. In order to facilitate the taking of readings, S was closed by means of an auxilliary magnetic switch conveniently located. This was constructed in the following manner. To the movable part of S was fastened a bakelite strip, to one end of which was attached a spring which normally pulled the switch into position 1. From the other end of the strip, there was suspended, by means of a cord, an iron rod which extended half-way into a coil. When the auxilliary circuit was closed, the rod was pulled into the coil, thereby causing S to take up position 2.

2. Method of Operation.

To determine capacity with this set up, the following is the procedure adopted. Switch S is left in position 1. The standard condenser C_1 is set to read zero on the scale. C_4 is then rotated until zero beat condition obtains. To ensure that the null point has been approached from the proper direction, it is determined again, this time rotating C_1. (The "proper direction" refers to the fact that the null point is not sharp but exists over a definite "dead space". One edge of this dead space is considered the null point so that it is necessary that this edge always be taken. This will be true if C_1 is rotated for all readings in the same direction in approaching the null point.) It is not necessary that this null point coincide exactly with the zero on the scale as slightly positive or negative values for "zero" may be taken. The standard condenser is then rotated until zero beat conditions are again established. The difference between the two readings is then a measure of the capacity of C_2.

It was found that the null point could be determined more accurately and more simply by means of the voltmeter V (the three volt range of a Weston Voltmeter

Model #290) than by use of the phones or loud-speaker. The procedure is as follows: The reading of the voltmeter is adjusted to a suitable value by means of R_6. With key K open, the region of zero beat is determined by means of the loudspeaker. K is then closed. As zero beat is approached, the reading given by V gradually increases. Just prior to the null point, the voltmeter needle begins to oscillate about a given value. (This value is the same as that obtained when the frequencies of the two oscillators are so far apart that no audible note is produced in the loudspeaker). The closer zero beat conditions are approached, the wider is the amplitude of the oscillating needle. At the exact null point, however, the needle suddenly drops to the "no audible note" value mentioned above. The dead space by this method is equal to approximately 0.15 centimetres which is considerably less than when the loudspeaker alone(or even the phones) is used. Under these conditions,it was found that capacity measurements could be reproduced with differences less than 0.10 centimetres .

The use of a voltmeter to indicate zero beat conditions in the manner indicated above, is strongly dependent on the grid bias of the output tube. If the

grid bias be chosen on the straight portion of the grid voltage versus plate current curve, then the increase in plate current on the positive swing of the incoming signal is exactly offset by the decrease on the negative swing. Accordingly, there is no resultant increase in plate current. If, on the other hand, the grid bias be chosen on the non-linear portion of the curve, the increase of plate current on the positive swing of the incoming signal will be larger than the decrease on the negative swing. There is thus a resultant increase in the plate current, which is indicated on the voltmeter as a larger drop in potential across the phones. Now in radio work where an undistorted output is desired, the tube is made to function on the linear part of the curve and the grid bias recommended by the manufacturer has been chosen accordingly. Such a value is obviously unsuitable for this work. After trying various voltages, a bias of twenty-seven volts was found to give satisfactory results. Reference to the curves for a UX-171 tube will show that this value lies on the non-linear portion of the curve

Chretien (32) describes a visual method for the determination of the null point in which he employs a sensitive galvanometer. This arrangement, however,

lacks the ease of operation that is found in the above method.

Several experimental difficulties had to be overcome before the above set-up fundtioned satisfactorily. These are indicated briefly below.

When the apparatus was first assembled, considerable annoyance was caused by radio broadcasting stations. (This was probably due mostly to a station located in the immediate vicinity). Instead of a single null point, a series of zero beats were obtained. This would indicate that the oscillators were beating against the carriers of broadcasting stations. This was undoubtedly the case for at times speech and music were obtained. It was found that the long leads to the standard condenser, even though grounded, were acting as antennae. When these were removed from the circuit, only one null point was obtained. A fixed capacity of 500 micromicrofarads was added to each of the oscillating circuits so as to change their frequencies and thus shift the latter from the broadcasting band. This, however, did not remove the difficulty. It was then decided to filter out the incoming signals. This was accomplished by means of R_3 and C_{10}. The value of the blocking condenser is not critical but it should be

large enough to offer but slight impedance to the current of the frequency of the oscillator. A value of 0.1 microfarads was chosen. The value of R_3 was found, on the other hand, to be quite critical as values less than 10,000 ohms killed oscillation while values greater than 15,000 ohms did not remove the interferring signals. A value of 12,500 ohms was actually used. No such filter circuit was found necessary for the fixed oscillator as it did not include any long leads.

The closing of the auxilliary switch, mentioned above in connection with the switch S, was found to influence the oscillators in a peculiar manner. The mere opening and closing of the auxilliary switch (which had no physical connection with any part of the oscillator circuits) changed the reading of C_1 for zero beat conditions after the latter had once been established. This was not due to drift as the apparatus was found to be otherwise quite stable. The difficulty was overcome by shunting the terminals of the auxilliary switch by a one microfarad condenser.

3. Calibration of the Standard Condenser.

In the subsequent determination of the dielectric constant, the assumption is made that there exists a straight line relationship between capacity of the standard condenser and the scale readings. Actually, this is not true so that it is necessary to apply a correction. The aberration from linearity may be due partly to the construction of the condenser and partly to the fact that the latter may not be centred exactly in the circular platform.

Almost all the previous workers (28,29,30,33,34) in this laboratory failed to calibrate the standard condenser. Linton (35) found by measuring the capacity of a given condenser over various parts of the scale, that the relationship between capacity and scale readings was not linear. He states that a correction was applied but he does not give the method employed. Inasmuch as the zero readings were not taken in an ordered manner along the scale, it must have been somewhat difficult and uncertain in application.

The following was the procedure adopted in this investigation. A small capacity was introduced in the circuit of the variable oscillator in the position usually occupied by the experimental cell. The dis-

placement of the null-point produced by this condenser over successive parts of the scale was determined. These are given below. Each value is the average of five measurements expressed to the nearest 0.05 centimteres. It will be noticed that the final reading of each determination has become the zero reading of the next one.

Zero Reading	Final Reading	Difference	Deviation
0.00	20.50	20.50	1.35
20.50	40.15	19.65	0.50
40.15	59.50	19.35	0.20
59.50	78.85	19.35	0.20
78.85	98.10	19.25	0.10
98.10	117.25	19.15	0.00
117.25	136.50	19.25	0.10
136.50	155.65	19.15	0.00
155.65	174.85	19.20	0.05
174.85	194.15	19.30	0.15
194.15	213.45	19.30	0.15
213.45	232.95	19.50	0.35

The lowest deflection 19.15 is taken as the unit or "correct" value. The choice of this is quite arbitrary but by selecting the lowest value, all the

corrections are made in the same direction, that is, are negative. The differences between this value and those obtained are listed under the heading "deviation".

During actual capacity measurements, the true zero was always used. Under these conditions, the correction to be applied to any experimentally obtained value becomes the sum of the separate deviations from zero to that value. These are shown in the table below.

Displacement from Zero	Correction
0.00	0.00
20.50	1.35
40.15	1.85
59.50	2.05
78.85	2.25
98.10	2.35
117.25	2.35
136.50	2.45
155.65	2.45
174.85	2.50
194.15	2.65
213.45	2.80
232.95	3.15

A curve was drawn from the above figures so that the correction to be applied to intermediate values could be determined.

The accuracy of this method of applying the correction was next investigated by measuring the capacity of a condenser over various parts of the scale. A comparison between the corrected and uncorrected values is shown below.

Actual Zero	Actual Final Reading	Difference	Corrected Zero	Corrected Final Reading	Difference
0.00	53.70	53.70	0.00	51.70	51.70
30.20	82.50	52.30	28.60	80.25	51.65
59.60	111.50	51.90	57.55	109.15	51.60
89.80	141.70	51.90	87.50	139.25	51.75
109.10	161.00	51.90	106.75	158.55	51.80
139.50	191.50	52.00	137.05	188.85	51.80

This method of applying the correction is apparently justified as the above figures show. The maximum deviation from the mean is equal to 0.90 centimetres for the uncorrected values of the capacity of the condenser but only 0.10 centimetres for the corrected ones.

Reference to the previous tables will show that the aberration from a linear relationship is greatest at the ends of the condenser. This is to be expected from its

manner of construction. There is, therefore, no justification in the assumption that a correction can be applied in these regions in a linear fashion. The following measurements show this.

Actual Zero	Actual Final Reading	Difference	Corrected Zero	Corrected Final Reading	Difference
11.20	64.00	52.80	10.45	61.90	51.45
169.80	222.20	52.40	167.30	219.25	51.95

For these measurements, the deviation for the corrected values from the mean given above is 0.25 centimetres. It is obviously only justifiable to apply a correction for the end regions as a whole. Thus initial and final readings that lie in the regions 0.00 to 20.50 and 213.45 to 232.95 have been avoided for the most part throughout this work.

4. The Calculation of The Dielectric Constant

The dielectric constant, as previously mentioned, is given by the ratio C_x/C where C_x is the capacity of the condenser filled with the material and C is the capacity of the condenser empty. The capacity measurements actually taken under the above conditions, however, include the capacity of the leads which connect the condenser to the measuring equipment. It therefore becomes necessary to allow for these in calculating the dielectric constant from the experimentally obtained values.

We may write for the condenser

(a) <u>when empty</u>

$$L + C = xd_1$$

(b) <u>when filled</u>

$$L + C = xd_2$$

where L is the lead capacity,

C is the capacity of condenser empty,

C_x is the capacity of the condenser filled with the material,

d_1 is the measured deflection for the condenser empty plus the leads,

d_2 is the measured deflection for the condenser filled plus the leads,

x is the proportionality factor connecting capacity and deflection.

We may write for the leads,

$$L = xd_3$$

where $\underline{d_3}$ is the measured deflection of the leads.

The dielectric constant E will be given in terms of scale by the relation

$$E = \frac{xd_2 - xd_3}{xd_1 - xd_3}$$

$$= \frac{d_2 - d_3}{d_1 - d_3}$$

It is thus seen that the proportionality factor x does not appear in the final expression for the calculation of the dielectric constant and we are therefore not concerned with its value. Capacity measurements have been accordingly expressed in this work, in terms of centimetres deflection of the standard condenser.

SECTION III.

THE MEASUREMENT OF THE

DIELECTRIC CONSTANT OF CELLULOSE

SECTION III

The Measurement of the Dielectric Constant of Cellulose.

1. The Dielectric Constant of Solids

The measurement of the dielectric constant of solids is rendered somewhat uncertain due to the difficulty of obtaining a homogeneous layer between the plates of the condenser. Stoops (36) in measuring the dielectric constant of cellophane, overcame this difficulty by placing mercury on both sides of the material, the mercury acting as the plates of the condenser. Campbell (37) used a similar method in measuring the dielectric constant of sheets of solid cellulose. This method, however, possesses several disadvantages among which are the following: (a) the true capacity of this condenser (rather than the more easily obtainable relative capacity) must be calculated from its physical dimensions. The distance between the "plates" of this condenser is obtained by measuring the thickness of the dielectric which may or may not be uniform, (b) it is difficult to shield such a condenser from stray capacity, (a matter that will be discussed in detail later). Some investigators (37) have placed the solid dielectric in a condenser, the plates of which could be pressed onto the solid, thus ensuring that the space between the plates was entirely

filled with the substance under examination. There is still another method (38) which is more or less standard, that consists of inserting the solid dielectric, without actually making contact, between the plates of the condenser. From the volumes of the solid and remaining air space, and the values for the capacity of the condenser with and without the solid, the dielectric constant of the latter can be calculated. All of these methods, however, fail completely if the dielectric is of a fibrous or porous nature.

Lichtenecker (39) has found that if the dielectric is in the form of very small particles distributed at random in the air space in the condenser, the following relation holds:

$$\log E_m = \frac{V_2}{V} \log E \qquad (1)$$

where E_m is the dielectric constant of the compound dielectric of air and the solid under examination,

E is the dielectric constant of the solid,

$\frac{V_2}{V}$ is the volume percentage of the material.

It has been shown by Campbell (37) and independently by Argue and Maass (6) on theoretical grounds, that if the solid dielectric is in a regular arrangement in layers parallel to the surface of the plates with air spaces between the layers, the following relationship holds:

$$E_m = \frac{1}{\frac{V_1}{V} + \frac{V_2}{VE}} \qquad (2)$$

where E_m is the dielectric constant of the compound dielectric of air and the solid,

$\underline{E}$ is the dielectric constant of the solid,

$\frac{V_1}{V}$ is the volume percentage of air,

$\frac{V_2}{V}$ is the volume percentage of the solid,

If the solid dielectric, however, is arranged at right angles to the surface of the plates, that is, the material forms a continuous path across the air gap between the plates with alternate layers of air and solid, the following relationship holds:

$$E_m = \frac{V_1}{V} + \frac{V_2}{V} E \qquad (3)$$

where the symbols have the same significance.

2. Discussion of the Values for the Dielectric Constant of Cellulose

From a consideration of the above discussion, it is hardly surprising that there is no generally accepted value for the dielectric constant of a fibrous material like cellulose. The International Critical Tables state that E lies between 3.9 and 7.5. They fail, however, to list the source of these data so that it is impossible to determine the methods by which these were obtained. Karo (40) in a review of the physical constants of cellulose assigns a value of 6.7.

This is also the value found listed in Physikalisch-Chemisch Tabellen (41) which is the one determined at 25° C. by Campbell (37) using low frequency currents. (This value will be discussed in detail later.) By use of the formulae which have been given in the preceeding section, Afgue and Maass calculated the dielectric constant to be 4.11 from equation (1) and 13.21 from equation (3). The application of equation (2) to their results gives a negative value. They considered it improbable that the dielectric constant of cellulose should be as high as 13 inasmuch as that for a carbohydrate like sugar is 4. On the other hand, they came to the conclusion, from theoretical considerations, that the value of 4.11 was probably low. Stoops (36) has recently measured the dielectric constant of cellophane (which is pure regenerated cellulose) and found it to vary from 6.7 to 7.7 at 25° C. depending on the frequency of the measuring current. A thorough survey of the literature yielded no further values.

3. The Theoretical Considerations of a Method for Measuring the Dielectric Constant of Fibrous Materials

The equations given in a previous section relating fibre distribution in the condenser space and resulting dielectric constant, can be written in a more general form for any two substances, A and B, as follows:

$$\frac{C_{x_1}}{C} = E_{m_1} = \frac{1}{\frac{V_A}{V E_A} + \frac{V_B}{V E_B}} \qquad (4).$$

and

$$\frac{C_{x_2}}{C} = E_{m_2} = \frac{V_A E_A}{V} + \frac{V_B E_B}{V} \qquad (5).$$

where E_A, E_B are the dielectric constants of the two substances,

$\frac{V_A}{V}$, $\frac{V_B}{V}$ are the volume percentages,

E_{m_1}, E_{m_2} and C_{x_1}, C_{x_2} are respectively the resultant dielectric constants and the capacity of the condenser under the conditions represented by equations (4) and (5),

$\underline{C}$ is the capacity of the empty condenser.

It is thus seen that the resultant dielectric constant (and therefore the capacity of the condenser) will be different for given volume percentages of A and B depending upon their distribution relative to the condenser plates. If, however, we put $E_A = E_B = E$ then both equations (4) and (5) reduce to the same equation, that is,

$$\frac{C_{x_1}}{C} = E_{m_1} = E = \frac{C_{x_2}}{C} = E_{m_2}$$

In other words, the measured dielectric constant of the compound dielectric is equal to the separate values for A and B

and is independent of the particular distribution of A and B relative to the condenser plates. Inasmuch as equations (4) and (5) represent the extreme cases of fibre distribution, that is, parallel to the plates and at right angles, the same relation holds for any intermediate manner of distribution.

The above considerations has suggested a method of measuring the dielectric constant of a fibrous material. Let us consider a condenser partly filled with such a substance. If the space unoccupied by the fibres is filled with a second substance, obviously a liquid, that has the same dielectric constant as the fibrous material, the dielectric constant of the compound dielectric will be the same as that of the liquid alone. A liquid that has the same dielectric constant is obtained in the following manner. Two completely miscible liquids, A and B, are chosen such that the dielectric constant of the material under examination lies between the two values for the liquids. The dielectric constants of solutions of A and B ranging from 100% A to 100% B are measured. A curve is drawn showing the relationship between dielectric constant and percentage composition. The condenser used in the above determinations is then partly filled with the fibrous material. The solutions of A and B are introduced into the condenser and the resultant dielectric constants determined. A second curve is then drawn showing this relationship.

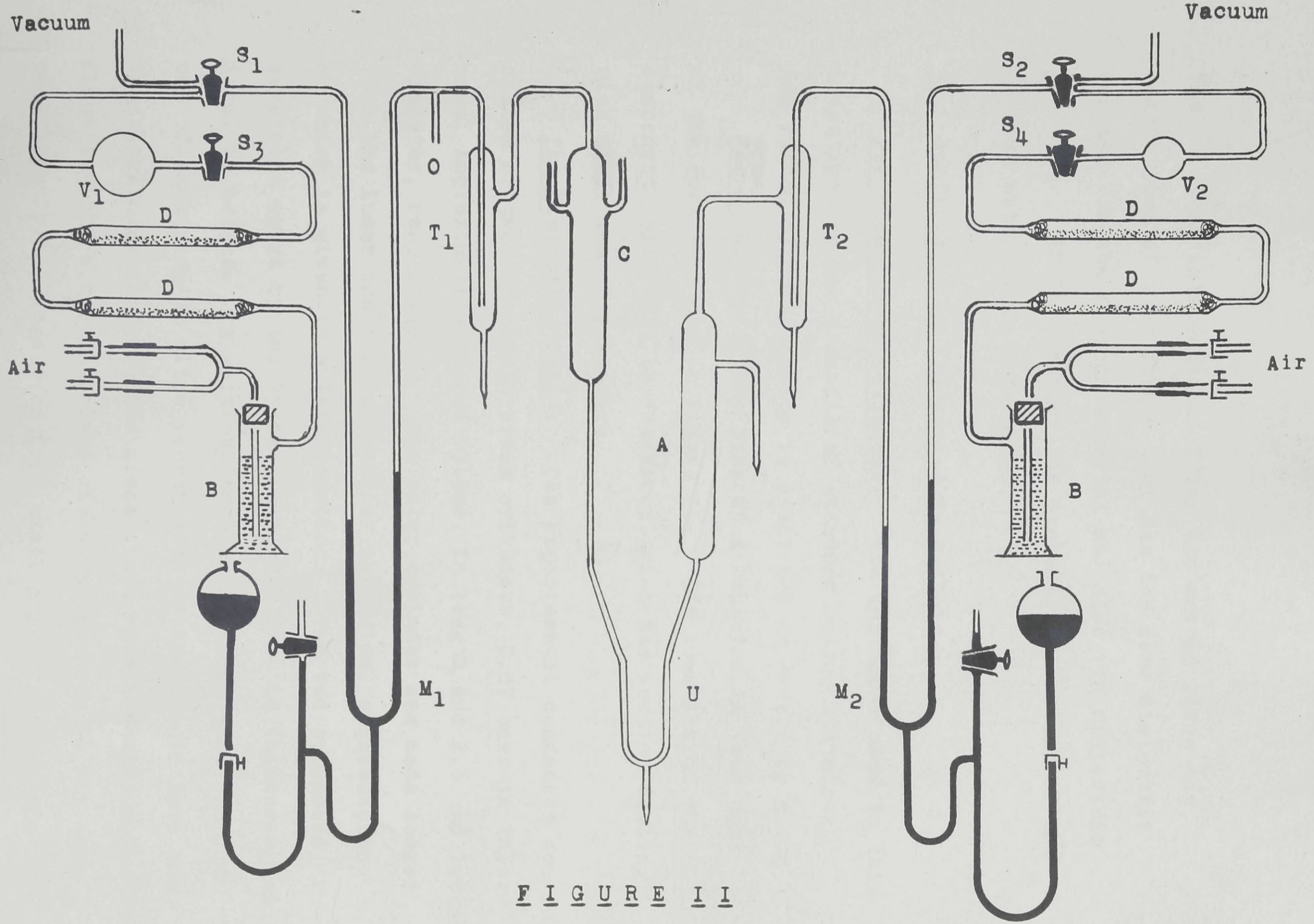


FIGURE II

The point of intersection of the two curves gives the composition of that liquid that has the same dielectric constant as the fibrous material and also its dielectric constant. In this manner the dielectric constant of the fibrous material is determined.

4. Application of the Method to Cellulose

Purification of Cellulose : The cellulose used in this investigation was a sample of standard cotton cellulose. Its method of purification is described in detail by Argue (30).

The Apparatus : The apparatus employed in this part of the work is shown in Figure II. The function of the component parts will be described under the section dealing with experimental procedure.

The Dielectric Cell : The experimental condenser consisted of two concentric brass cylinders, 0.07 cms. in thickness, approximately 18 and 17 cms. in length, and 2.6 and 1.6cms. in diameter, respectively. The outer cylinder was made longer than the inner one for purposes of shielding, a discussion of which is given in a later section. The two cylinders were kept apart by two Pyrex rings, 0.5 cms. in thickness and 1 cm. in height. A vertical section 0.7 cms. wide was cut out of each ring to allow penetration of the liquid into the inter-cylinder space. The glass rings were actually made first and the brass cylinders chosen afterwards to fit them very tightly. There were four small projections on the

bottom of the outer cylinder, bent inwards, upon which one of the glass rings rested. Approximately half a centimetre from the bottom of the inner cylinder, there were four projections, bent outwards, which rested on the glass ring. The other ring was similarily placed at the top of the condenser. This arrangement prevented any movement of the two cylinders relative to each other.

The condenser was placed in a Pyrex cell of about 3.2 cms. inside diameter and 35 cms. in length. The shape of the cell is shown by C in Figure II. The additional length of the cell (over that of the condenser) was required in order that it could be sealed off without heating the cellulose which the condenser was eventually to contain. Electrical connection was made to the cylinders by two fine copper wires, a section of each being replaced by a small piece of thin platinum foil, in order that a glass-to-metal seal could be subsequently made by the method of Campbell (42) These leads were brought out of the cell by means of the two arms, situated on opposite sides. These arms were placed as far apart as was conveniently possible (about six centimetres) so that the lead capacity might be a minimum. The capacity of the condenser plus the internal leads was found to be equal to 24.40 cms. (No use however, is made of this figure in subsequent calculations and it is only given here

as a matter of interest). The capacity of the condenser plus the internal and external leads amounted to 53.65 cm. It was necessary to include the condenser in the circuit in such a manner, that the outer cylinder be grounded, in order to avoid stray capacities. Under such conditions, the condenser gave the same value for capacity, independent of whether or not the dielectric cell was surrounded by the bath liquid.

The Bath : The dielectric cell was immersed in a water bath. A Pyrex cylinder, 7 cms. in diameter and 32 cms. in height was employed as the container for the bath fluid. Stirring of the liquid was accomplished by means of compressed air which was forced through an o-shaped glass tube in which there were holes, the tube being placed at the bottom of the bath around the cell. The temperature of the bath was hand controlled. The water could be cooled by sending a stream of cold water into the bath through the stirrer or it could be heated by using a mixture of air and steam for stirring. A by-pass on the steam valve, from which steam constantly issued in a small jet, assured a constant supply. Steam from the latter was also used to maintain the temperature of the room close to the bath temperature. Small changes in the latter were made, at times, more conveniently by simply adding small

amounts of hot or cold water to the bath. A constant level device was used to prevent overflowing. Under the above mentioned conditions of control, the temperature of the bath could easily be kept within two tenths of a degree of the desired temperature.

The External Leads: It was essential that the external leads which connected the dielectric cell to the capacity measuring equipment, should not undergo any movement (with a resulting change in capacity) during the series of measurements. The two leads, which consisted of a #18 copper wire with a wax-impregnated cotton covering, were tightly twisted together, and then incased in a glass tube. The latter was fastened securely to the framework of the apparatus. At a point near the top of the dielectric cell, the glass tube branched, each branch housing one of the leads. The ends of these leads were situated directly over the arms of the dielectric cell, such that they could be soldered to the leads coming from the condenser. A coating of DeKhotinsky cement was applied to the ends of the external leads and the glass tube, to prevent any possible movement of the lead wires relative to the glass tube. These leads were found to have a capacity of 29.25 cms. (No use is made of this value in subsequent calculations).

The necessity of using lead wires with a wax-impregnated covering is indicated by Campbell (37) who found that

lead capacity changed enormously with variations of humidity in the case of wires with un-protected insulation.

Preparation of The Liquids : Inasmuch as there was considerable doubt concerning the value of the dielectric constant of cellulose, it was necessary to choose two liquids whose dielectric constants were somewhat far apart. It was also necessary to choose liquids which would not be adsorbed by the cellulose. The hydrocarbons, which are ideally suitable from the stand point of no adsorption, all possess low dielectric constants. It was one of these, benzene, (dielectric constant 2.27) that was chosen for the liquid of lower dielectric constant. There are, however, very few liquids that are not likely to be adsorbed that possess a high dielectric constant. Such compounds as those containing oxygen, hydroxyl groups, nitrogen and unsaturated carbon atoms, which are those that exhibit high dielectric constants, are also those that are most likely to be strongly adsorbed. It was eventually decided to use ethylene dichloride (dielectric constant 10.1 to 10.8) as it appeared likely that it would fulfill sufficiently well the above-mentioned requirements.

The benzene used was of Merck's C.P. grade and the ethylene dichloride was the "99% pure" grade supplied by Eastman Kodak Co. The purity of the latter was of no

consequence in as far as its dielectric constant was concerned as no assumptions were made with respect to the latter. On the other hand, it was necessary to ascertain whether or not any of the impurities present might be adsorbed. (Water is undoubtedly the worst offender in this connection). A consideration of the impurities reported present, however, showed that the latter type of substances were present in negligibly small amounts. It was later demonstrated experimentally in two ways that neither ethylene dichloride, benzene nor any of the impurities present were adsorbed on the cellulose to an extent that would influence the measurement of the dielectric constant of the latter.

About 800 cc. of each of seven solutions ranging from 100% benzene to 100% ethylene dichloride were prepared. The separate weights of each liquid in the solutions were weighed with an accuracy of at least one part in five thousand but it was later found that such accuracy was hardly necessary. The percentage composition by weight of these solutions is given below.

	% Benzene	% Ethylene Dichloride
#1	100.00	0.00
#2	76.48	23.52
#3	60.87	39.13
#4	40.64	59.36
#5	27.99	72.01
#6	16.45	83.55
#7	0.00	100.00

Experimental Procedure and Results : It was first necessary to introduce the various solutions into the dielectric cell when the experimental condenser was empty. For this part of the work, the tube coming from the bottom of the cell was not connected to the "U" tube, (as shown in the diagram). Instead, the lower end was left open so that the liquids could be drawn up into the cell. It was also necessary that the capacity of the internal leads be kept the same for this and subsequent measurements. For this reason, the platinum foil was included in the leads although the glass-to-metal seals were not made at this stage of the work. Inasmuch as the cell was not to be subjected to any conditions of high vacuum here, the fine copper leads were brought out of the arms of the cell through a cork and the seal was completed by applying a layer of DeKhotinsky cement over it and the glass tubing

in immediate contact. This was found to be sufficiently air-tight for the work at this stage.

The capacity of the condenser, filled with the liquid, plus the internal and external leads, was measured for each of the seven solutions. This was performed as follows. About 150 cc. of the liquid, contained in a tall cylinder, was placed under the open end of the tube coming from the bottom of the cell. With stop cocks S_3 closed and S_1 open, the volume V_1 (about 150 cc.) was evacuated. S_1 was then closed and S_3 slowly opened. This caused the liquid to rise into the dielectric cell. When the liquid had risen to the desired height, S_3 was closed. (This arrangement of stop cocks and volume V_1 was necessary in order to obtain a sufficiently smooth control over the height of the liquid). The level of the liquid slowly fell after S_3 was closed due to the increase in pressure caused by the evaporation of the liquids. For this reason, the liquid was always raised above the level finally chosen. When the level had ceased falling, the liquid was brought down to the desired height by raising the mercury level in the cut-off M_2.

All measurements were made with the liquid at the same height. The latter was chosen at a point about one centimetre above the top of the condenser. Preliminary

experiments showed that the height of the liquid could be varied several millimetres without making any measurable change in the capacity of the system. (This was to be expected due to the small capacity of the internal leads). After the liquid had been adjusted to the proper height, five or more capacity measurements were made. These usually agreed within 0.1 cms. The average of these readings expressed to the nearest 0.05 cms. was taken as the capacity value.

The liquid was allowed to remain in the cell about twenty minutes in order that temperature equilibrium be reached. These measurements were all made with the bath temperature at $25.0^\circ \pm 0.2^\circ$ C.

Preliminary experiments also showed that the capacity of the condenser was often several millimetres higher when the liquid was allowed to flow out of the cell after the first determination, and then drawn up again. This was undoubtedly due to the fact that the cylinders of the condenser were not thoroughly wetted the first time). The average value for succeeding measurements usually agreed with the average value for the second one within 0.1 cms. In subsequent measurements, the condenser was washed several times with the liquid several times before any capacity determinations were made.

At the conclusion of the measurements, the liquid was drained from the cell and a current of air (dried by means of the sulphuric acid tower B and the two phosphorus pentoxide tubes D, D) was passed through the latter. At the same time, the bath temperature was raised to about 90°C. A test tube surrounded by a cooling mixture was placed at the opening of the tube coming from the bottom of the cell, in order to catch the vapors. The cell was considered to be dried when further condensation of the liquid in the test tube ceased. This usually occurred after twenty minutes.

The capacity of the system comprised of the internal and external leads and the experimental condenser, filled in turn with each of the above-mentioned solutions, is given below. These values are correct to at least ± 0.1 cms.

Solution	Capacity in Cms.
# 1	76.75
# 2	94.05
# 3	108.20
# 4	131.90
# 5	152.10
# 6	175.55
# 7	221.50

An independent check of these values was given in a subsequent series of measurements.

It was now necessary to remove the dielectric eell from the bath in order to fill the condenser with cellulose. Before doing this, however, measurements were taken of the position of the cell relative to its surroundings so that it could be replaced as nearly as possible in its original position. Following its removal, the cell was broken open and the condenser taken out. It was now only necessary to remove the upper glass ring and stuff cellulose into the condenser. (The relative position of the glass ring had been noted).

Although a given volume may appear to be filled with cellulose, it actually occupies only a small fraction of the total volume, due to its fibrous nature. With this in mind, an attempt was made to pack as much cellulose as possible into the inter-cylinder space. After this had been accomplished, the glass ring was replaced.

It was necessary to exercise considerable care in sealing off the cell as an excessive heating of the cellulose had to be avoided. The technique adopted was as follows. The condenser was placed in the glass cell and the lead wires drawn through the arms. The cell was then clamped to a stand in an inverted position. Inasmuch as the glass cell

was about fifteen centimetres longer than the condenser, the end of the latter was removed by that distance from the point of sealing. A wet towel was wrapped around the cell below this point to prevent conduction of the heat to the condenser by the glass. After the cell had been sealed, it was placed in an upright position and the platinum-to-Pyrex seals in the arms were made using the method of Campbell (37). (In this method the glass tubing surrounding the platinum foil is softened and the two opposite sides are gently squeezed together with a pair of pliers).

The completed cell was replaced in the bath and was joined to the rest of the apparatus in the manner indicated in Figure II.

It was now necessary to remove the adsorbed water from the cellulose. The bath was left at room temperature and the system was evacuated through S_1 using a Langmuir diffusion pump in conjunction with a Hy-Vac pump. Evacuation was continued for three hours at the end of which time the bath temperature was slowly raised to 100° C. (It is preferable to remove most of the water at the lower temperature). The removal of the water was followed by measuring the capacity of the condenser at regular intervals. At the end of six hours of evacuation at the higher temperature,

the capacity reached a constant value (no change was noted on further heating). The cellulose was now considered to be in a dry condition, so that further evacuation was stopped and the bath allowed to come to room temperature.

With the system still under vacuum and the bath temperature at 25°C , the capacity of the condenser was measured . The capacity of the condenser, filled with cellulose, plus the internal and external leads, was equal to 60.15 cms., which was 6.50 cms. greater than the corresponding measurement with the condenser empty. Air, dried by passage through the two drying units, was then slowly let into the system to atmospheric pressure. This process occupied about forty-five minutes. The capacity of the condenser was then measured but it was found that no change had taken place, thus indicating that the air had been sufficiently dried inasmuch as no water had been adsorbed by the cellulose. (The presence of the air would not be expected to produce a measurable change in the capacity of the system under the above conditions of experiment due to the very small difference between the dielectric constants of air and vacuum).

It must be pointed out here that the method of introducing the liquid into the cell filled with cellu-

lose had at first presented several difficulties. It was highly important that the system be in an evacuated condition when this was carried out, in order that the possibility of air bubbles being trapped among the cellulose fibres, be reduced to a minimum. It was obviously impossible to use stop cocks as the means of introduction of the liquid. The difficulty was overcome by the use of frozen seals of the same composition as that of the liquid to be introduced into the cell. The use of frozen mercury seals to withstand high pressures (34) is common practice but the above use of frozen seals is thought to be original.

During the introduction of the liquid into the U-tube, it was important that no moist air from the atmosphere be allowed to come in contact with the cellulose. The following was the method adopted. First compressed air was introduced into the system by way of the drying unit shown on the left. At the same time, the sulphuric acid tower (shown on the right) was disconnected from the phosphorus pentoxide tubes, by removal of the piece of rubber tubing that joined them, in order to allow a point of exit for the air. The tip on the arm of A was then broken off with a pair of pliers. A loosely-stoppered test tube, containing about twenty cc. of the liquid, was placed under the open arm. The supply of compressed

air was shut off and the sulphuric acid tower again connected to the system. A Dewar flask containing solid carbon dioxide and acetone was placed around trap T_2 so as to prevent the vapors of benzene and ethylene dichloride from passing through the Hy-Vac pump in subsequent operations. The freezing mixture surrounded the trap from this point to the end of the run. Volume V_2 was then evacuated. With S_2 closed, S_4 was partly opened. This caused the liquid to rise into the arm of A and finally to flow into the U-tube. When the arms of the latter were filled to a height of approximately ten centimetres, S_4 was closed. The height of the liquid in the left hand arm was finally adjusted to five centimetres by introducing a slight amount of compressed air into this side of the system. A Dewar flask containing solid carbon dioxide and acetone was now placed under the tip of the U-tube such that about one centimetre of it was immersed in the freezing mixture. The liquid was then raised an additional centimetre. This process was repeated until all the liquid in the left hand arm was frozen. Atmoshperic pressure was then established on both sides of the frozen seal.

Some liquid was always left on the right hand side of the seal, in order that there would always be a supply

ready to flow into the space resulting from the contraction that the liquid first underwent on freezing, and then on reaching thermal equilibrium with the freezing mixture. It was not desirable to leave any liquid in the left hand arm inasmuch as this side of the system was to be eventually evacuated.

It was next necessary to partly fill the vessel A (volume 300 cc.) with the liquid. A covered flask containing the latter was placed under the arm and by application of a suitable vacuum at S_4, about 250 cc. of the liquid was drawn into the vessel A. The flask was then removed and a current of dried air was passed through the arm to remove as much as possible of the liquid remaining in it. Some difficulty was at first encountered in attempting to seal off this arm due to the fact that the charring of the liquids prevented the making of a good seal and also because the liquids were slightly inflammable. This difficulty was overcome by using an asbestos-covered cork to close off the arm and then gently heating the latter before attempting to seal it. This proved quite successful.

The system to the left of the frozen seal was next evacuated for a period of five to ten hours at the end of which time the pressure was usually in the neighborhood

of 10^{-3}mm. of mercury. The pressure above the liquid in A was then reduced to the vapour pressure of the liquid and a small amount of the latter was allowed to boil off in order to drive out as much air as possible. It was essential that the difference between the air pressures existing in the evacuated spaces over both sides of the frozen seal, be as small as possible in order that the liquid might not be pushed beyond the dielectric cell on the subsequent thawing of the seal.

Care had to be exercised in thawing the seals inasmuch as benzene and ethylene dichloride expand on passing into the liquid state. It was therefore essential that no liquid be trapped between two solid phases. For this reason, the seal was allowed to thaw by lowering the freezing mixture a half a centimetre at a time, until the arch of the "U" was reached. At this point, the melting of the solid was hastened by briskly rubbing the inner part of the arch with the fingers. Following the removal of the seal, the liquid rose into the dielectric cell but to a height never more than five centimetres above the bottom of the condenser.

The liquid was raised to a height slightly below a given point, (the same as that used in the previous determinations) by allowing air to slowly expand from V_2 (about 50 cc.) into the space above the liquid in A.

The finer adjustments in the level were made by raising the mercury in M_2. About half an hour was allowed for the liquid to reach thermal equilibrium with the bath before any capacity measurements were made. (A slightly better control of temperature was achieved during these determinations, the bath being kept between 25.0° to 25.2°C.). After the capacity of the system had been determined, the liquid was pulled out of the dielectric cell by application of a vacuum at S_2. Thus by alternate use of pressure and vacuum, by means of which the cell was filled and emptied, a series of capacity measurements could be made on the same solution. It was necessary to wait at least twenty minutes before attempting to take any measurements after the liquid had risen into the cell for the following reason. In pulling the liquid out of the cell after the previous capacity determination by the application of a vacuum, some of the vapors had been drawn out along with the air. After the liquid was again raised into the dielectric cell by letting air into A, the total pressure in the latter slowly increased due to the liquid attaining its equilibrium vapor pressure. This caused the level of the liquid in the cell to rise higher and higher so that it was impossible to take measurements during the establishment of the equilibrium noted above.

At the conclusion of a set of capacity determinations, the liquid was removed in the following manner. Air was first let in on both sides of the system. Next the liquid was drained from the cell by breaking the tip on the tube below the U. Air was then passed through the cell by way of the left hand drying unit.

Considerable difficulty was experienced in attempting to seal off the tube below the U after the liquid had been drained from the cell. Inasmuch as the cellulose held back a considerable amount of the liquid, there was a continuous drip of the latter into the U. As mentioned previously, the charring of the liquid on strong heating, prevented the making of a satisfactory seal. An attempt was made to keep the tubing, below the cell and above the U, gently heated (in an effort to drive the liquid back into the cell) and at the same time to make the seal. This did not prove satisfactory. The difficulty was finally overcome by the use of a solid carbon dioxide trap, which was constructed as follows. Just below the cell, a piece of asbestos was wrapped around the glass tubing in the form of a cone. This was filled with very finely-powdered solid carbon dioxide. To protect the latter, and the glass tubing in immediate contact from the subsequent heating, a second asbestos cone was placed below the first one. Prior to the making of the seal, the

open tube was closed with an asbestos-covered cork, and the U and connecting tubing was heated. Under these conditions, a satisfactory seal could be easily made.

The residual liquid was removed by evacuating the system through the trap T_2 (surrounded with solid carbon dioxide and acetone). By a measurement of the capacity of the condenser, it was found that all the liquid was removed from the cellulose in three hours of pumping or less. At the end of this time, evacuation was stopped and air let into the system. The solid that collected in T_2 was carefully thawed and then removed by breaking the tip at the bottom of the trap. The volume of liquid which had been trapped in T_2 usually amounted to 50 cc. T_2 was subsequently sealed off, a current of dry air passing through the apparatus from left to right during this operation.

It would have been impossible to successfully carry out the above experimental procedure without the inclusion of the mercury cut-offs in the system, as the vapors of the liquids had a tendency to attack the stop-cock grease. The mercury in the cut-offs was kept accordingly raised at all times unless otherwise necessary. The presence of the mercury in the system is of no consequence as far as the measurements are concerned as it has been shown

by Russel, Maass and Campbell (43) that mercury is not appreciably adsorbed by cellulose. On the other hand, they found that the mercury would readily distil from the cut-offs, at low pressures, to other parts of the system if the latter fell to a lower temperature. Such a state of affairs was avoided in the present investigation by keeping the temperature of the room always below that of the dielectric cell.

Several preliminary runs brought out the following facts. The capacity of the condenser was found to successively increase the first five or six times the liquid was pulled out of the cell and sent up again. Following this, however, a constant capacity was attained. The difference between the initial and final values was often as high as six centimetres. This would indicate that at pressures even as low as 10^{-3}mm., the cellulose fibres trapped some air bubbles, which were removed a few at a time at each bathing of the cellulose with the liquid. During some runs, the liquid was sent into the dielectric cell, such that it took about thirty minutes to fill the latter. It was thought that this might prevent the formation of air spaces. Such was not the case as the capacity measurements showed the same trend as previously. That all the air spaces were not removed,

even when the capacity of the condenser had attained a constant value, was indicated by the fact that the "constant value" was not the same for an entirely independent set of measurements on the same solution. Differences as much as one centimetre were obtained. This pointed to the fact that some of the air bubbles that formed were difficult to dislodge and also that the number of this type that formed was different for different runs. It was accordingly necessary to modify the experimental procedure in the manner given below.

Subsequent to the thawing of the frozen seal, the liquid was sent into the cell and pulled out about twelve times, in order to remove as much of the trapped air as possible. After the liquid had been adjusted to the desired height, the frozen seal was again renewed in the U. Air was then let into the space above the liquid in the cell to atmospheric pressure. It was reasoned that any bubbles that had formed in the liquid at an air pressure of 10^{-3} mm., would most certainly be reduced to a negligible size when the external pressure was increased to atmospheric. The results indicated that this was true. It was found that, due to the contraction of the air spaces subsequent to the establishment of atmospheric pressure above the liquid, the level of the latter dropped, on the average, about

three millimetres. To offset this, the liquid was raised about the same distance above the proper level before the frozen seal was made. This was probably not necessary inasmuch, as has been shown previously, the internal lead capacity was so small that such a difference in the liquid level was of no consequence.

It was considered improbable that the dielectric constant of cellulose was as low as that of solutions #1 and #2. Accordingly, the series of capacity measurements were begun with solution #3 and continued with solutions of higher dielectric constant until the point of intersection of the two curves, mentioned previously, was satisfactorily established.

The capacity of the condenser filled with cellulose and each of the solutions from #3 to #6 is given below. A check run was carried out for each of them.

Solution	Capacity in cms.	
	Run #1	Run #2
#3	122.20	112.20
#4	133.70	133.70
#5	151.80	151.85
#6	172.20	172.15

From the results, it is seen that the capacity measurements could be reproduced from run to run under the above conditions of experiment within 0.05 cms.

It has been indicated elsewhere, that experimental evidence was obtained in two ways to show that neither benzene nor ethylene dichloride nor any of the impurities present, were adsorbed by the cellulose to an extent that would influence the measurement of the dielectric constant of cellulose. These will be discussed in turn below.

Prior to taking one of the capacity measurements in which the solution was sent into the condenser filled with cellulose, only the part of the frozen seal immediately below the condenser was allowed to melt. This resulted in the evacuated space being filled with the vapors of the liquids. The system was allowed to stand thus for about thirty minutes. At the end of this time, the capacity of the condenser was measured but no increase in the latter (over the normal capacity of the cell filled with cellulose) was found. Neither had any change in the pressure of the vapors taken place, as was indicated by the mercury levels in M_1. This definitely shows that neither benzene nor ethylene dichloride is adsorbed to an extent that influences the measurement of the dielectric constant of cellulose. It has recently been shown by Walker (44)

that at a relative humidity of sixty percent, the time to half-value for the adsorption of water by a sample of cellulose, freely suspended, is three minutes. Work carried out by the writer on the dielectric constant of water adsorbed on cellulose, in which the latter was tightly packed in a condenser similar to the one used here, showed that the adsorption of the first amounts of water was extremely rapid and was determined, for the greater part, by the rate at which the vapor could be supplied to the system. These facts are presented to show that thirty minutes is ample time to allow for adsorption.

The above experiment, however, does not prove that the impurities present are not adsorbed, under the conditions existing during an actual run, to an extent that might be reflected in the measurement of the dielectric constant, for the following reason. The actual weight of the liquids in the vapour state is small. Inasmuch as the impurities present in any one of the solutions is not greater than one percent, the weight of the impurities in the vapour state is negligible. Thus in the above experiment, even if all the impurities were adsorbed, their amount probably would not be sufficiently great to influence the capacity measurement. During an actual

run, however, the cellulose is bathed in the liquid, and in this instance, the amount of impurity that comes in contact with the cellulose in appreciable.

The following evidence is presented to show that nothing more than negligible amounts of impurities (and at the same time benzene and ethylene dichloride) could have been adsorbed. After the liquid had been drained from the cell at the conclusion of a run, it was found that the capacity of the condenser (filled with cellulose) returned to its normal value in three hours of pumping through a solid carbon dioxide-acetone trap. In the work on the dielectric constant of water adsorbed on cellulose, the following facts were established. It was found that while sixty-five percent of the water, that had been adsorbed at a relative humidity of eighty-five percent, was removed in ten minutes subsequent to the introduction of the above type of trap into the system (pressure of air in the latter 10^{-3}mm.), it required thirty hours to reduce the amount of water held from eleven percent to three percent,and this final amount was not removed in the following twenty-four hours. This evidence points definitely to the fact that the cellulose in the present investigation cannot have adsorbed an appreciable amount from the liquids and it points to the absence of anything but mere traces

G R A P H #1

#1 #2

CAPACITY IN CENTIMETRES

225
220
215
210
205
200
195
190
185
180
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75

0 10 20 30 40 50 60 70 80 90 100

PERCENT ETHYLENE DICHLORIDE

of water in the latter.

In Graph #1 is shown the relation "capacity of the condenser" versus "composition of the liquid" for the sets of measurements in which (i) the condenser was filled only with the liquid (curve #1), (ii) the condenser was filled with cellulose and liquid (curve #2). The point of intersection of these two curves is not very well defined in the small graph which is given here. The point of intersection, however, was not determined from the above curves but from those drawn on a graph 50 cms. by 40 cms. On this latter graph, capacity measurements were plotted to the nearest 0.1 cms. and composition values to the nearest 0.05%. The two curves merged into one for a distance given by the capacity as 146.2 to 147.6 cms. and by the composition as 68.50 to 69.50%. The mean of these values was taken as the true point of intersection. This is given by 146.9 cms. for the capacity and 69.00% for the composition.

A liquid of the above composition (actually 68.99%) ethylene dichloride) was prepared and introduced into the cell containing the cellulose. The capacity of the condenser was found to be equal to 147.05 centimetres. This compares favourably with the above value.

It must be pointed out that the agreement between

the value taken from the graph and the experimentally obtained value is no proof that this point is the point of intersection of the two curves. It simply shows the extent of the agreement that can be obtained between points taken off curve #2 and experimentally determined values. (It also shows, of course, that the solution has been correctly prepared).

To prove conclusively that the value obtained for the point of intersection of the two curves was not far from the correct one, it was decided to introduce the above solution into the empty condenser. (This solution will be termed 4a henceforth). The dielectric cell was therefore dismantled and the cellulose removed. It was then replaced in the bath and the capacity of the condenser, filled with solution 4a was determined. It was found to be equal to 147.00 cms. (compared to 147.05 cms.). This shows definitely that the point represented by solution 4a lies on both curves #1 and #2. It was accordingly only necessary to determine the dielectric constant of this solution in order to arrive at a value for the dielectric constant of cellulose. (Attention is drawn to the fact that in the above treatment of the subject, we have not been concerned with the actual values of the dielectric constants of the various solutions).

The dielectric constant of solution 4a could have been determined in the manner devised by Williams and Krchma (45). In this method, it is neither necessary to measure the lead capacity, nor to obtain a value for the latter by use of a liquid of known dielectric constant. A condenser similar to the ordinary variable rotary condenser is used. The capacity is determined for two or more exact settings of the condenser surrounded by air and immersed in the liquid. Since the lead capacity is the same for the two or more settings, its value can be eliminated from the calculations and an absolute value of E is obtained. Smyth (27) objected to the condenser employed by the above investigators, on the grounds that the bakelite used as the insulation, came in contact with the liquid whose dielectric constant was to be measured. Allen and Hibbert (46) have overcome this disadvantage by using glass insulators. The above method was not used,however, in this investigation inasmuch as it would have required a considerably modified set-up.

It has been shown previously, that the dielectric constant of a material is simply the ratio between the capacity of a condenser filled with that material and the capacity of the condenser empty. This method can be used if the lead capacity can be measured. The value of the latter could not be directly determined in the case

of the experimental condenser. This was due to the fact that the constant capacity which was set up by the glass rings and those parts of the cylinders in contact with them (and which was in effect a lead capacity) could not be measured. A value for the effective lead capacity, however, can be arrived indirectly. The method is indicated below.

It has also been previously shown, that the dielectric constant E, is given in terms of scale deflection by the relation

$$E = \frac{d_2 - d_3}{d_1 - d_3}$$

where d_1 is the measured deflection for the empty condenser plus the leads,

d_2 is the measured deflection for the filled condenser plus the leads,

d_3 is the measured deflection of the leads.

We can arrive indirectly at a value for d_3 by measuring the capacity of the condenser filled with a liquid of known dielectric constant and the capacity of the condenser empty. Since d_1, d_2 and E are then all known, d_3 can be calculated by means of the above equation.

Because of the ease with which it can be obtained

in a pure form, because it does not decompose readily and is not hygroscopic, benzene has been found to be an ideal liquid with which to calibrate condensers. Colley (47), Tangl (48), Turner (49) , Graffunder (50), Isnardi (51), Hartshorn (52), Ball (53), and Linton and Maass (54) have all found benzene to possess a dielectric constant of 2.27. Cuthbertson and Maass (55) and Grutzmacher (56) give the value as 2.28.

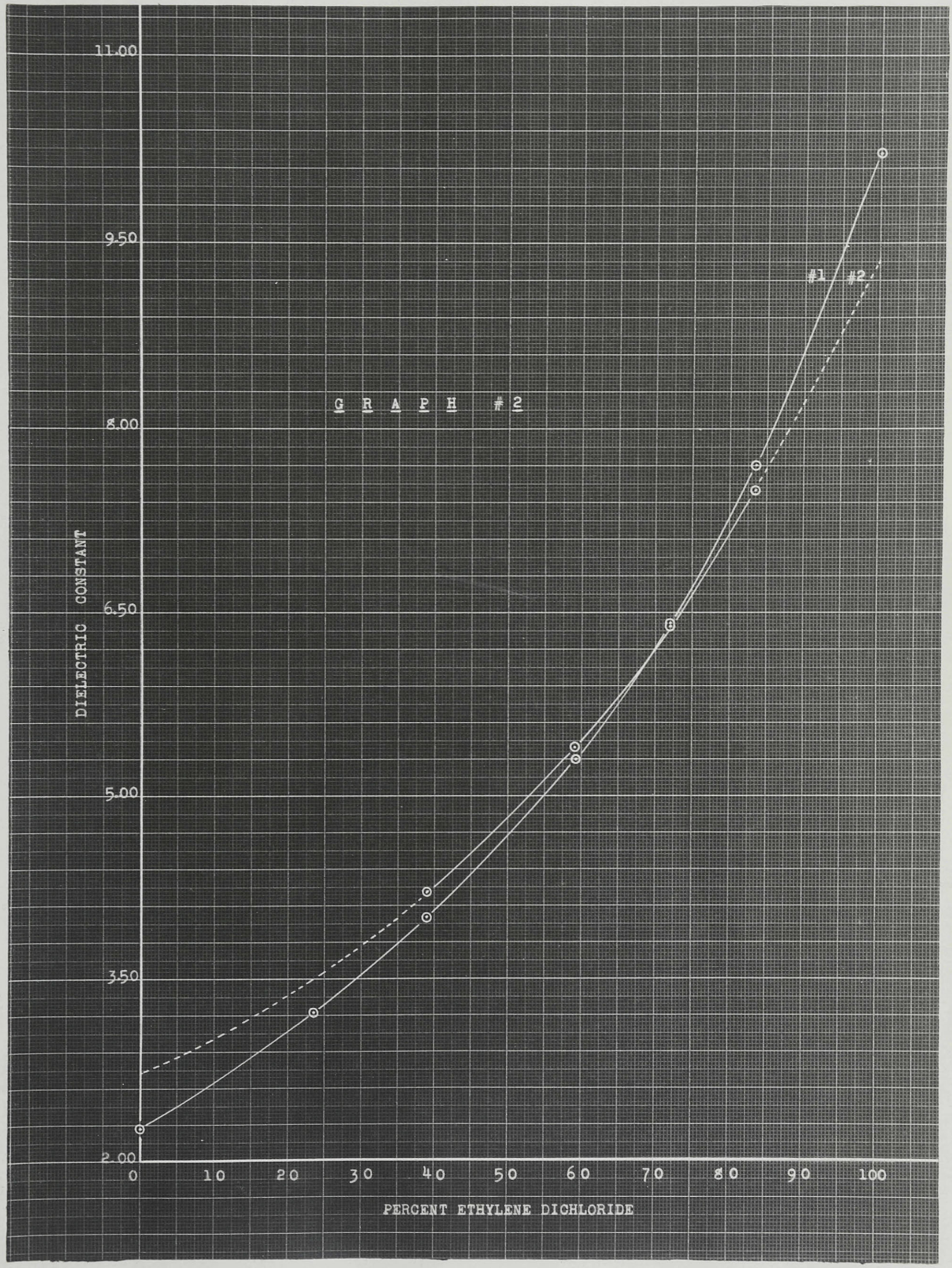
Now the capacity of the experimental condenser filled with benzene, had already been measured when curve #1 of Graph #1 was obtained. (Benzene had been used in the preliminary experiments previously mentioned, so that this measurement had been carried out a number of times). It was therefore only necessary to substitute this value, and the values for d_1 and E, into the above equation in order to determine d_3. This has been done below.

$$2.27 = \frac{76.65 - d_3}{53.65 - d_3}$$

whence $d_3 = 35.45$.

Now by use of this value for d_3 and the above equation, all the previous measurements given in curves #1 and #2 can be expressed in terms of the dielectric constant. The values obtained are given below.

G R A P H #2


11.00
9.50
8.00
6.50
5.00
3.50
2.00
DIELECTRIC CONSTANT
#1
#2
0
10
20
30
40
50
60
70
80
90
100
PERCENT ETHYLENE DICHLORIDE

Solution	Dielectric Constant of Solution (From Curve #1)	Dielectric Constant of Solution and Cellulose (From Curve #2)	
# 1	2.27 *	....	....
# 2	3.22	....	....
# 3	4.00	4.22	4.22
# 4	5.30	5.40	5.40
# 5	6.41	6.39	6.39
# 6	7.70	7.51	7.51
# 7	10.22	....	....

* Assumed.

These values have been plotted in curves #1 and #2 in Graph #2. The point of intersection gives directly the dielectric constant of cellulose. As in the previous case, these values were plotted on a larger scale than in shown here (actually to .01 units) in order to determine this point accurately. It was found that the two curves merged into one for a distance given by the dielectric constant as 6.07 to 6.17. The mean of these, 6.12, was taken as the dielectric constant of cellulose.

It was shown previously that the condenser possessed the same capacity when filled with cellulose and solution 4a, as when it was filled with the solution only. By substituting this capacity measurement (147.05 cms.) into the above equation, a more accuarae value for the dielectric constant can be obtained. This was found to be equal to 6.13.

It is usual to check the accuracy of the calibration of a condenser which has been made with a standard liquid, by measuring the dielectric constant of a second liquid for which this constant is known. This was performed in this investigation by a measurement on chloroform. The values 4.92, 4.92 were obtained at 20°C. in two succeeding runs. This agrees well with the values measured at radio frequencies which are found in the literature,(19,51,57,58, 59) of which the most reliable appears to be that of Walden, Ulich and Werner (59) which is given as 4.9_3.

The Importance of Temperature Control : It was decided to investigate the importance of temperature control. The effect on the capacity measurements of lowering the bath temperature one degree below the normal temperature (from 25.0 to 24.0°C.) was noted for the three cases in which the condenser was filled with (i) cellulose, (ii) solution 4a, and (iii) cellulose and solution 4a. These are given below.

Cell filled with:	Capacity change per degree:
(i) Cellulose	increased 0.1 cms.
(ii) Liquid	decreased 0.5 cms.
(iii) Cellulose and liquid	decreased 0.3 cms.

The algebraic sum of (i) and (ii) should theoretically equal (iii). The agreement is as good as can be expected from a consideration of the accuracy of the capacity measurements and the small temperature interval taken. The results,however, are sufficiently accurate for our purposes. The above explains somewhat why the capacity measurements of the cell filled with the liquid alone, which were taken between the temperatures 24.8° and 25.2°C, were reproducible only to ± 0.1 cms., while the capacity determinations of the cell filled with cellulose and liquid, taken between 25.0° to 25.2°C., were reproducible within smaller limits.

A Second Determination of the Dielectric Constants of the Solutions : As a final check, it was decided to measure the dielectric constants of the various solutions a second time, inasmuch as the importance of temperature control had not been fully appreciated at the time the solutions were originally measured. The bath temperature was kept at 25.0° to 25.2°C., and the time allowed for the solutions to come to thermal equilibrium was raised to thirty minutes. It was found that under these conditions, the actual capacity readings of the two sets of measurements taken were usually not more than 0.1 cms. apart. The dielectric constants of these two sets of determinations are compared below with the original set.

Solution	Previous Values	Set #1	Set #2
# 1	2.27*	2.27	2.27
# 2	3.22	3.20	3.19
# 3	4.00	3.97	3.97
# 4	5.30	5.30	5.30
# 4a	6.13	6.13	6.13
# 5	6.41	6.41	6.41
# 6	7.70	7.70	7.69
# 7	10.22	10.19	10.19

* Assumed.

It will be noticed that there are differences of 0.03 units between the values obtained in the previous determinations and those of the second set for solutions #3 and #7. These do not affect the value previously given for the dielectric constant of cellulose as they lie at the ends of curve #1 on Graphs #1 and #2 and do not influence the point of intersection. It is of interest, however, to attempt to explain the discrepancy. Inasmuch as 0.10 cms. on the capacity scale represents 0.006 dielectric units, it is difficult to give any reason for this difference, in view of the accuracy claimed for these measurements. It is greater than can be explained on the basis of the temperature variation that existed in the original measurements. It might be due

to the incomplete attainment of temperature equilibrium in these two instances but this is rather doubtful.

The dielectric constant of solution #7 (10.2) gives the value of this constant for the 99% pure ethylene dichloride. It is of no importance of itself but it is interesting to compare it with the values found in the literature for the pure liquid. This is given for measurements at 25°C. at radio frequencies, as 10.1 by Harris (60), 10.1 by Walden (61), 10.4 by Linton and Maass (54), 10.5 by Linton (35) and 10.8 by Turner (62)

Discussion of Results ; In the above treatment of the subject, the values for the dielectric constant have been expressed to the nearest 0.01 units. This has been done more to show the accuracy of which the method is capable rather than an attempt to measure the dielectric constant of cellulose to this value. This latter task in itself would be rather a useless one as it is quite probable that the dielectric constants of two samples of standard cellulose might differ by a number of times the above amount.

It has been mentioned previously that the two curves in Graph #2 merged into one over a distance given by the difference between 6.07 and 6.17, that is, by 0.10 dielectric units. This obviously does not give the limits of accuracy of the method. This is indicated by the

fact that the solution that actually gave the same capacity to the condenser, independent of whether or not the latter contained cellulose, was found by measurement to possess a dielectric constant of 6.13 which value is in good agreement with the mean of the limits given by the graph, namely 6.12. It has been shown that under proper conditions of temperature control, the capacity values for curves #1 and #2 can be reproduced within 0.1 cms., or in terms of the dielectric constant within 0.006 units. Since both curves could be displaced by this amount, the point of intersection, theoretically, should not be in error by more than twice this amount, that is, 0.012 units. In actual practice, however, since the shapes given to the curves is somewhat arbitrary, (unless a considerable number of values have been taken), and since it is difficult to ascertain exactly the points where the two curves merge, this error is increased several times or more.

The above sources of error are of no consequence in the measurement of the dielectric constant of cellulose as the value of the latter is only desired to the nearest 0.1 units. It may be given, accordingly, with this accuracy as 6.1 ± 0.0.

There are no values in the literature for the

dielectric constant of standard cellulose. Inasmuch as the properties of cellulose are known to depend to a very marked degree on its method of preparation, it is hardly justifiable to compare the value obtained in this investigation, with those of Campbell (37) and Stoops (36) since the latter were made on regenerated cellulose, which in turn was prepared differently by these two workers. It has been definitely shown that the treatment employed in the production of the latter, alters the crystal structure of the cellulose. The dielectric constant of standard cellulose would, therefore, be expected to differ from that of regenerated cellulose. There is a further complication introduced by the fact that the dielectric constant depends on the frequency of the measuring current. Stoops found that the dielectric constant of cellophane at 25°C. decreased from 7.7 at 60 cycles, to 6.7 at 10^6 cycles. As a matter of interest, however, the various values for the dielectric constant of cellulose at 25°C. have been compared below.

	Frequency		
	60	800	10^6
Stoops	7.7	7.6*	6.7
Campbell	...	6.7	...
This work	...	...	6.1

* Obtained by interpolation.

If a similar percentage change with frequency in the dielectric constant as found by Stoops, can be applied to the value of Campbell, the latter becomes 5.9 at 10^6 cycles, which is not far removed from the value found in this work.

As mentioned previously, the value of the dielectric constant is given in the International Critical Tables as 3.9 to 7.5 but the source of these data is not indicated. In the light of the results obtained in this work, and those of Stoops and Campbell, it is felt that the above value should be given within much smaller limits.

5. Suggestions for Future Work

When this work was initiated, considerable doubt existed concerning the value of the dielectric constant of cellulose. It was accordingly necessary to choose two liquids whose dielectric constants were somewhat far apart. This necessitated the use of a condenser of such size, that its capacity would not be too large to be measured on the scale of the standard condenser when filled with the liquid of higher dielectric constant. (Of course, the capacity of the standard condenser could have been increased but this would have resulted in decreased accuracy). The smaller the size of the experimental condenser, the

smaller is the amount of cellulose that can be packed into it and the closer together do curves #1 and #2 lie. As this lengthens the distance over which the two curves merge, the determination of the point of intersection is made less exact. It is now known that the condenser was of larger size than was necessary. It is also believed that a method could be devised to pack more cellulose into the inter-cylinder space. Furthermore, inasmuch as the dielectric constant of cellulose has now been established between smaller limits, the various solutions could be chosen in a subsequent determination, such that their dielectric constants would lie closer together, than those used in this investigation. As this would more completely define the shape of the curves, the point of intersection could be more accurately determined.

It is suggested that, in addition to repeating the above work on standard cellulose, under conditions that give greater accuracy, measurements be made on various types of cellulose such as, natural cellulose, that obtained from the sulphite process, and that from the soda process, mercerized cotton and others. It would be interesting to follow the changes in the dielectric constant that ensued as a result of the various processes that the cellulose had undergone in its preparation.

SECTION IV.

THE MEASUREMENT OF THE DIELECTRIC CONSTANT OF WATER ADSORBED ON CELLULOSE

SECTION IV

The Measurement of the Dielectric Constant Of Water Adsorbed on Cellulose.

1. Introduction.

Very little work has been carried out on the measurement of the dielectric constant of adsorbed substances. As previously mentioned, Argue and Maass (6) have determined the dielectric constant of water adsorbed on cellulose. Von Tausz and Ruum (63) have measured this constant for the water adsorbed on silica, lignite and tobacco.

Argue and Maass have found that the dielectric constant of the adsorbed water becomes larger with increased adsorption gradually approaching the value for liquid water. They interpret this phenomenon as follows: "The large value of the dielectric constant of a polar liquid is due mainly to the orientation that the liquid molecules, which are free to rotate, assume in an electric field. Adsorbed molecules will not have the freedom that those in the liquid have. The water molecules that form the first adsorbed layer on the cellulose micelle will be strongly held to the surface and will rotate only through a very limited range. The dielectric constant of these adsorbed water molecules will be relatively low.

The molecules in a second adsorbed layer would not be as securely anchored, and would be free to rotate through a larger range under the influence of an electric field. Hence the dielectric constant of the adsorbed water increases with further additions. At a point in the water adsorption where the adsorbed molecules are no longer under the influence of the surface, the dielectric constant of the adsorbed water would reach a maximum value equal to that of liquid water." The relation "dielectric constant of the adsorbed water" versus "water content" is represented by a curve which is sigmoid in shape. This same type of curve expresses other cellulose-water relationships such as the adsorption and desorption isotherms (2, 3, 44). These workers accordingly found in their results a confirmation of the hypothesis of the physical structure of cellulose and the mechanism of adsorption, which had already been drawn from the results of other investigations.

Of the systems investigated by Van Tausz and Ruum, only the tobacco-water system bears any similarity to the one under consideration here. They found that the dielectric constant of the adsorbed water decreased from 90 to 25, when the moisture content was reduced from 19 to 15 percent. These results have been subjected to criticism by Argue and Maass on the grounds that the dielectric constant

of water is actually less than 90 at 25° C and furthermore, the 4% change that occurs in the water concentration in the vicinity of the fibre saturation point, would not be expected to change the nature of the adsorbed water to such an extent. These last-named investigators contend that the only value to be attributed to the results of Von Tausz and Ruum is the indication that with decreased water content, the dielectric constant of the adsorbed water decreases.

2. Apparatus

The Experimental Condenser : The experimental condenser, shown in Figure III, consisted of two concentric brass cylinders 0.07 cms. in thickness, 23.05 and 22.15 cms. in length, and 2.57 and 2.07 cms. in diameter, respectively. The cylinders were kept a fixed distance apart by two bakelite discs. The disc at the lower end of the condenser (which was grooved to receive the smaller cylinder) fitted snuggly into the larger one. The disc at the upper end was similar, except that part of it was cut away to allow penetration of the water vapor into the inter-cylinder space.

It was necessary to know the capacity of the experimental condenser with air as the dielectric. In the initial work, the condenser employed by Argue was used. This had the same dimensions as the one above except that the inner cylinder was 23.60 cms. in length, that is, was longer than the outer one. This condenser was placed in a glass cell, which was then immersed in a glycol bath. It was subsequently connected to the measuring system by suitable leads which were securely fastened to the framework of the apparatus to avoid any movement with resulting change of capacity. The capacity of the condenser and the leads was determined. The condenser was then carefully unsoldered from the leads without

disturbing them and the capacity of the latter was measured. The difference between the two measurements gave the capacity of the condenser.

From a series of measurements under various experimental conditions the following facts were established.

Since the oscillating circuit was so designed that one of the cylinders of the condenser was grounded, there were two possible methods of including the latter in the circuit, that is, either the outer or inner cylinder became the grounded one. It was found that when the outer cylinder was grounded, the capacity of the condenser was equal to 60.75 cms., but that when this applied to the inner one, the capacity was 138.50 cms. Substituting the dimensions given above into the formula for the capacity of a cylindrical condenser, that is,

$$C = \frac{E\ 0.2416\ L}{\log_{10} \frac{r_1}{r_2}}$$

where C is the capacity in micromicrofarads,

E is the dielectric constant of the insulator,

L is the length of the shorter cylinder in cms.,

r_1 is the radius of the outer cylinder,

r_2 is the radius of the inner cylinder,

it was found that C had a value of approximately 60 micro-

microfarads. A rough calibration of the standard condenser gave a value of about one micromicrofarad per centimetre deflection. Obviously 60.75 cms. was closer to the correct value. It was apparent that when the outer cylinder was ungrounded, there existed an additional capacity between it and the bath liquid. This was verified by siphoning the glycol from the bath, under which conditions the capacity was found equal to 65.50 cms. (Apparently there was still an additional capacity existing between the outer cylinder and the metal supports in the bath), otherwise this value would have also been 60.75 cms.).

The influence of changing the level of the bath liquid when the outer cylinder was grounded, was then investigated. When the glycol was siphoned from the bath, the capacity of the condenser fell from 60.75 cms. to 59.75 cms. This was attributed to the fact that inasmuch as the inner cylinder was the longer one, it was not entirely shielded by the outer one from the bath liquid when the latter surrounded the cell. Removal of the liquid resulted in a disappearance of this stray capacity.

As has been previously mentioned, the dielectric constant of a material is the ratio between the capacity of a condenser filled with that material and the capacity of the condenser empty. Even though the same source of error is

operative when the two values are determined, its effect obviously does not cancel out. It is therefore necessary to eliminate any stray capacities.

In order to remove the source of the stray capacity mentioned above, the condenser was re-designed so that the outer cylinder extended, at the top and bottom, about a half of a centimetre beyond the inner one. The capacity of this condenser was found to be 56.60 cms. independent of whether or not the cell was surrounded by the bath liquid.

Purification of the Cellulose : The cellulose was purified by the manner given by Argue and Maass (4) for standard cellulose. About five grams of this was dried for approximately twelve hours in an electric oven at 100°C., at the end of which time, it was removed to a P_2O_5 desiccator and allowed to cool prior to weighing. This weight was considered the dry weight of the cellulose.

The cellulose employed in this investigation was from the same batch as that used by Walker in the determination of the adsorption and desorption isotherms of water (44) and by Morrison (64) in the heats of wetting.

The Dielectric Cell : The cellulose was tightly packed between the cylinders of the condenser. Electrical connection was made to the cylinders by two fine copper wires

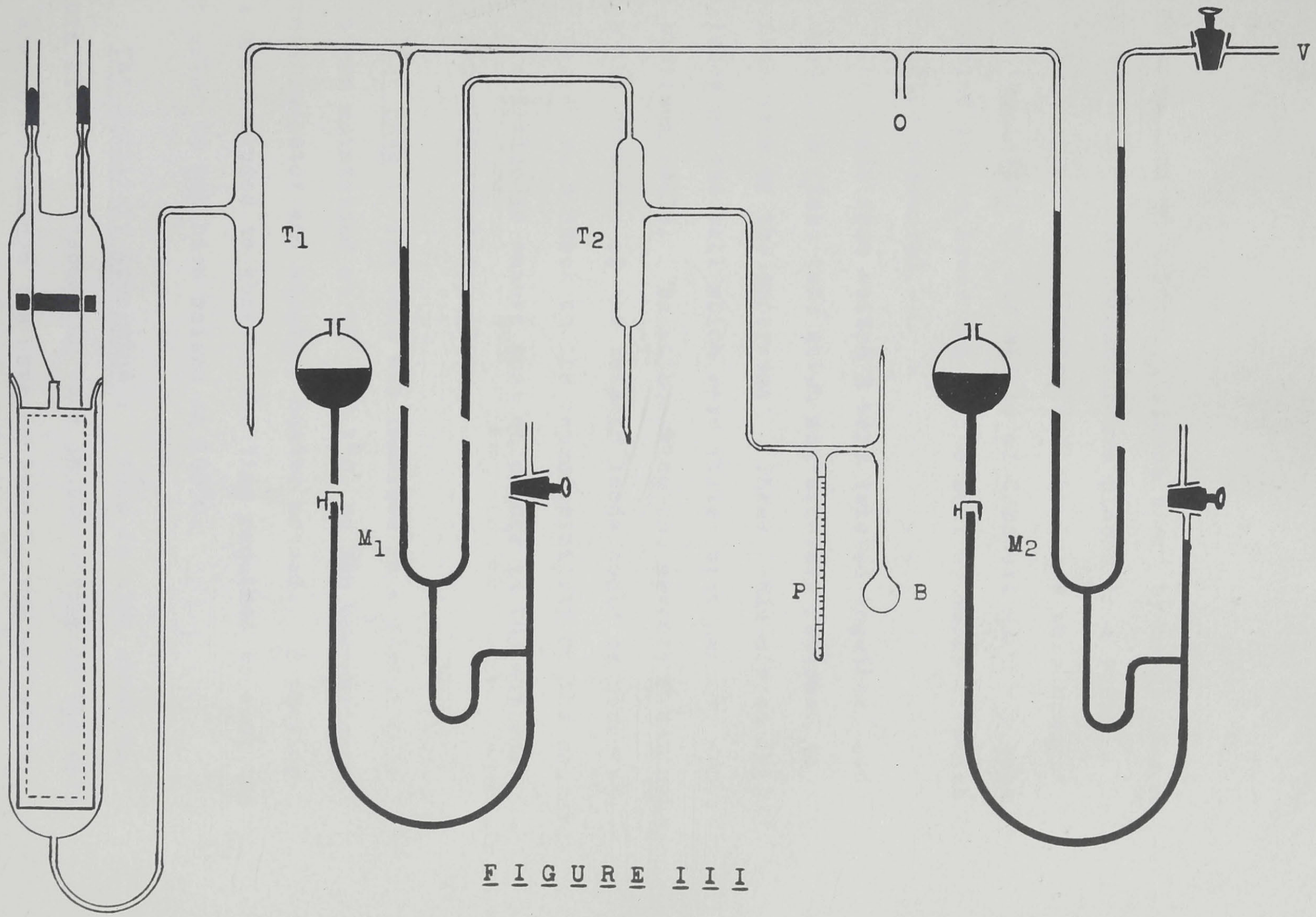


FIGURE III

which were kept at a fixed distance apart by means of a bakelite disc. The condenser was placed in a Pyrex cell about 35 mm. in diameter and the leads were brought out of the latter by the method of Campbell (42) A tube was sealed to the lower end of the cell by means of which it could be evacuated.

The leads from switch S were twisted together, and enclosed in a glass tube which was securely fastened to the framework of the apparatus. These leads dipped into the tubes on the cell which were filled with mercury above the platinum seals. By withdrawing the mercury from these tubes the capacity of the twisted leads could be measured. This served as a check on the reproducibility of the measurements, and also to ensure that no change in the external lead capacity had taken place.

The Bath : The cell was immersed in a glycol bath which was maintained at $25^{\circ} \pm 0.1^{\circ}C.$ by the conventional thermo-regulator and electric heater method. A cooling coil was included to shorten the time required to cool the bath after it had been raised to $100^{\circ}C.$

The Auxiliary Apparatus : This is also shown in Figure III. The evacuating tube on the bottom of the cell was connected through the mercury trap T_1 the cut off M_1,

which served to isolate the trap T_2, the pipette P and the bulb B from the rest of the system. A McLeod gauge was included at O. At V there was connected a Langmuir diffusion pump and a Cenco Hy-Vac pump, by means of which the pressure could be reduced to 10^{-5}mm. The cut-off M_2 served as a seal between the atmosphere and the system, after the latter had been evacuated, and also as a manometer.

It will be noticed that there are no stop-cocks leading directly into the system. This reduced the possibility of any leaks developing during a run.

3. Experimental Procedure and Experimental Results

At the beginning of the series of runs, the bulb B was filled with distilled water. A Dewar flask containing solid carbon dioxide and acetone was placed around it, and the water made to freeze. The mercury in the cut-offs M_1 and M_2 was lowered and evacuation begun. When the pressure had been sufficiently reduced, the cut-off M_1 was closed and the ice allowed to melt. This alternate freezing and melting of the water was repeated several times in order to remove the final traces of dissolved gases.

After the out-gassing of the water, cut-off M_1 was closed and evacuation was continued for twelve hours, with the temperature of the bath at 25°C. The bath temperature was then gradually raised to 100°-105°C., and maintained at this temperature for approximately ten hours. At the end of this time, the bath was cooled to 25°C. After this treatment, it was assumed that the cellulose contained zero percent adsorbed water.

The capacity of the condenser containing cellulose with zero percent water was determined. By lowering the mercury in M_1, a measured amount of water was allowed to evaporate from the pipette into the space in contact with the cellulose. The cut-off was then closed and after equilibrium had been established, the capacity of the con-

denser was again measured. This procedure was repeated until the cellulose had adsorbed an amount of water close to the fibre saturation point. By this method the capacity of the condenser containing cellulose with increasingly larger amounts of adsorbed water was determined.

It was found that the water had a tendency between measurements to distill from the pipette P into the trap T_2, the bulb B and the inter-connecting tubing. In order to again collect all the distilled water in the pipette, the latter was surrounded with a glass vessel containing cold water (about 10°C.) prior to reading P.

It was convenient to take capacity measurements about twelve hours after the water had been introduced into the system. This was found sufficient for the attainment of equilibrium. Whether or not this latter stage had been reached could be determined by ascertaining the pressure of the vapor above the cellulose which was simply the differemce in level between the two arms of M_2. The equilibrium vapor pressure for a sample of cellulose with a given percent of adsorbed water could be obtained from the vapor pressure-adsorption data of either Walker (44) or Filby and Maass (2). The values actually obtained showed much better agreement with the results of the former but this was to be expected since, as previously mentioned, the cellulose employed in this investigation was from the same

batch as used by Walker in obtaining the above data.

(At the conclusions of the series of runs, the glycol was drained from the bath and the Pyrex cell was cut just above the point where the fine copper wires were joined to the condenser. The leads were then carefully unsoldered from the latter, and the total lead capacity, that is, the capacity of the internal and external leads, was measured. This value was subtracted from the capacity of the condenser and leads in order to obtain the capacity of the condenser alone. It is this value that appears below. During the runs, the small internal lead capacity was neglected in the calculations, in order that some indication of the trend of the dielectric constant values might be obtained. The capacity of the internal leads has been used, however, in the calculations of the dielectric constants given below).

The results obtained in Run #1 are shown in Table I. The first column gives the total volume in cc. (or weight in grams) of the water introduced into the system. In the second column is given the percentage of water to the dry weight of the cellulose. (This has been calculated on the assumption that all the water introduced into the system is adsorbed by the cellulose). The relative vapor pressure for a sample of cellulose with a

TABLE I

Run #1.

Volume of Water in cc.	Percent Water.	Percent Relative Vapour Pressure.	Vapour Pressure in mm.	Weight of Vapour.	Volume of Adsorbed Water.	Capacity in cms.	Dielectric Constant of the Mixture (E_m)
0.000	0.0	0.0	0.0	0.000	0.000	69.10	1.221
0.075	1.6	5.5	1.3	0.001	0.074	70.20	1.240
0.100	2.1	11.5	2.7	0.002	0.098	70.80	1.251
0.135	2.8	20.0	4.8	0.004	0.131	72.00	1.272
0.170	3.5	29.0	6.9	0.006	0.164	73.45	1.298
0.245	5.1	48.0	11.4	0.010	0.235	76.50	1.352
0.305	6.3	62.5	14.9	0.014	0.291	79.05	1.396
0.355	7.4	73.5	17.5	0.016	0.339	81.80	1.445
0.405	8.4	81.5	19.4	0.018	0.387	84.75	1.497
0.500	10.4	90.0	21.5	0.019	0.481	93.45	1.650

given moisture content can be obtained from the data of Walker on adsorption (44). This is given in column three and the actual vapor pressure is given in column four. The weight of this vapor, which has been calculated from its pressure and the volume it occupies, is given in column five. (The volume of the evacuated space in contact with the cellulose was found to be equal to 937 cc. by the expansion of air into the system from a known volume). The volume of the water that is actually adsorbed by the cellulose, that is, the difference between columns one and five, is shown in column six. The capacity of the condenser containing the cellulose and the given amount of water is given in column seven.

The assumption made above that all the water introduced into the system is adsorbed by the cellulose, gives a value for the equilibrium vapor pressure which is sufficiently accurate for our purposes. Inasmuch as the weight of water in the vapor stage is at all times small, the error resulting is much less than the accuracy with which the volume of the water could be measured. The more accurate value for the equilibrium vapor pressure is obtained by using the figures given in column six and again referring to the data of Walker. It is this value that showed very good agreement with the experimentally obtained

G R A P H # 3

E_m

1700
1680
1660
1640
1620
1600
1580
1560
1540
1520
1500
1480
1460
1440
1420
1400
1380
1360
1340
1320
1300
1280
1260
1240
1220
1200

.00 .05 .10 .15 .20 .25 .30 .35 .40 .45

TOTAL VOLUME OF ADSORBED WATER IN C.C.

RUN #3

RUN #4

equilibrium vapour pressures.

In the last column of Table I are shown the dielectric constants of the mixtures of cellulose, air and adsorbed water. (The dielectric constant of the mixture is the ratio of the capacity of the condenser with the mixture, to the capacity of the condenser with air as the dielectric.) These results are represented by Curve #1 in Graph 3.

In order to test the reproducibility of the above results, a second run was carried out. The experimental procedure was similar in every detail to that employed in Run #1. These results are shown in Table II, and in Curve #2 of Graph 3.

Curve #2 is seen to lie considerably above Curve #1. This could be explained by an increase in the external lead capacity due to a movement of these leads, but this was highly improbable as the latter were securely fastened to the framework of the apparatus. A measurement of the external lead capacity proved that no such capacity change had taken place. No movement of the internal leads was considered possible and, furthermore, a rather large movement of these would have been required to give rise to the observed capacity change, since these leads themselves possessed a small capacity. A displacement of the two cylinders of the condenser relative to one another, could

TABLE II

Run #2

Volume of Water in cc.	Percent Water.	Percent Relative Vapour Pressure.	Vapour Pressure in mm.	Weight of Vapour.	Volume of Adsorbed Water.	Capacity in cms.	Dielectric Constant of the Mixture (E_m)
0.000	0.0	0.0	0.0	0.000	0.000	69.40	1.226
0.050	1.0	2.5	0.6	0.001	0.049	70.30	1.243
0.085	1.8	7.5	1.8	0.002	0.083	71.30	1.260
0.120	2.5	16.0	3.8	0.003	0.117	72.50	1.280
0.160	3.3	26.0	6.2	0.006	0.154	73.80	1.304
0.200	4.1	36.5	8.7	0.008	0.192	75.30	1.330
0.225	4.7	42.5	10.1	0.009	0.216	76.15	1.346
0.265	5.5	52.5	12.5	0.010	0.255	78.40	1.386
0.325	6.7	67.0	15.9	0.015	0.310	81.35	1.437
0.390	8.0	79.0	18.8	0.017	0.373	85.35	1.508
0.450	9.3	86.0	20.5	0.019	0.431	90.15	1.592

have produced the capacity change but from the manner in which the condenser was constructed, this was considered impossible. An apparent change in the capacity of the system would have resulted if all the water had not been removed due to an insufficient time of heating at 100° - 105°C. This possibility was investigated in the following run. (By following the capacity changes of a condenser filled with cellulose under conditions similar to the above, it has since been shown that six hours of heating at the higher temperature is sufficient to remove the adsorbed water).

The experimental procedure for Run #3 was similar to that employed in the two previous ones, with the exception that the cellulose was maintained at the temperature of 100° - 105°C. for twenty hours instead of ten. The results of this run are given in Table III, and Curve #3 of Graph #3. Curve #3 is seen to lie above the two previous ones.

The dielectric constant of the mixture of air and cellulose containing zero percent adsorbed water (and therefore the dielectric constant of cellulose itself) has apparently increased from run to run. It was possible that the cellulose might have undergone a change due to the heat treatment employed during the desorption of water, which change had resulted in an increase in its dielectric

TABLE III

Run #3.

Volume of Water in cc.	Percent Water.	Percent Relative Vapour Pressure.	Vapour Pressure in mm.	Weight of Vapour.	Volume of Adsorbed Water.	Capacity in cms.	Dielectric Constant of the Mixture (E_m)
0.000	0.0	0.0	0.0	0.000	0.000	69.70	1.231
0.050	1.0	2.5	0.6	0.001	0.049	70.80	1.251
0.080	1.7	6.5	1.6	0.001	0.079	71.75	1.268
0.150	3.1	24.0	5.7	0.005	0.145	74.05	1.308
0.250	5.2	49.0	11.7	0.011	0.239	78.15	1.381
0.350	7.2	72.5	17.3	0.016	0.334	83.55	1.477
0.445	9.2	86.0	20.5	0.019	0.426	90.75	1.603
0.180 *	3.7	26.0	6.2	0.006	0.174	75.10	1.327

* Water left by desorption.

constant. This was investigated in the following run.

The water was removed from the cellulose in Run #4 in the following manner. A mixture of solid carbon dioxide and acetone was placed around bulb B. After the water had distilled from the pipette into the latter, the mercury in cut-off M_1 was lowered. The removal of the water was followed by measuring the capacity of the condenser at regular intervals. This showed a successive decrease up to forty-eight hours. As no measurable change occurred in the succeeding twenty-four hours, it was concluded that no further desorption would take place. The mercury in the cut-off was then raised and the freezing mixture removed from the bulb B. After the water in the latter had melted, it was distilled into the pipette. During the whole of the above procedure, the temperature of the bath was maintained at 25°C.

It was found that all the water previously adsorbed was not removed by this treatment but that an amount equivalent to approximately 0.3 percent of the dry weight of the cellulose still remained.

The results of Run #4 are shown in Table IV, and Curve #4 in Graph #3. These lie on the curve of the previous run within the limits of experimental error.

The cellulose could hardly be expected to show

TABLE IV

Run #4

Volume of Water in cc.	Percent Water.	Percent Relative Vapour Pressure.	Vapour Pressure in mm.	Weight of Vapour	Volume of Adsorbed Water.	Capacity in cms.	Dielectric Constant of the Mixture (E_m)
0.015	0.3	0.5	0.1	0.000	0.015	69.80	1.233
0.050	1.0	2.5	0.6	0.001	0.049	70.60	1.247
0.100	2.1	11.5	2.7	0.002	0.098	72.05	1.273
0.195	4.0	35.5	8.5	0.007	0.188	76.00	1.343
0.300	6.2	61.0	14.5	0.013	0.287	80.80	1.428
0.400	8.3	80.5	19.2	0.017	0.383	86.90	1.536

indefinitely an apparent increase in its dielectric constant with each heat treatment employed during desorption. It should eventually reach a state in which no further change would take place. To show that this state had not been reached at the conclusion of Run #3, (in which case the results of Runs #3 and #4 would have both been represented by the same curve regardless of the method employed for desorption), it was decided to carry out an additional run in which heat treatment was used. In Run #5, the adsorbed water has been removed from the cellulose under the same conditions as given for Run #3, that is, by heating at a temperature of 100° - 105°C. for a period of twenty hours. The results of this run are shown in Table V, and Curve #5 of Graph #3. This curve is seen to lie above all the previous ones.

Inasmuch as certain properties of the cellulose - water system (as moisture content at a given relative humidity) depend on its previous history, it would have been interesting to carry out a series of measurements on the dielectric constant of water which had been left on the cellulose by desorption. The above apparatus, however, was not especially suited for this type of determination. Nevertheless, one such value was obtained during the removal of the water for Run #4. This water was

TABLE V

Run #5

Volume of Water in cc.	Percent Water.	Percent Relative Vapour Pressure.	Vapour Pressure in mm.	Weight of Vapour.	Volume of Absorbed Water.	Capacity in cms.	Dielectric Constant of the Mixture (E_m)
0.000	0.0	0.0	0.0	0.000	0.000	70.50	1.246
0.050	1.0	2.5	0.6	0.001	0.049	71.50	1.263
0.100	2.1	11.5	2.7	0.002	0.098	72.90	1.287
0.200	4.1	36.5	8.7	0.008	0.192	77.05	1.361
0.295	6.1	60.0	14.3	0.013	0.282	81.40	1.438
0.400	8.3	80.5	19.2	0.017	0.383	87.85	1.553
0.450	9.3	86.0	20.5	0.019	0.431	91.80	1.622

actually removed in two stages. Before desorption was complete the mercury in the cut off M_1 was raised and the freezing mixture was removed from bulb B. After the water had melted, it was distilled into the pipette P by surrounding the latter with cold water (about 1°C.). The volume of water in the pipette was noted. (The difference between this reading and that prior to Run #3 gave the amount of water left on the cellulose). The bulb B was again surrounded by the freezing mixture and when all the water had distilled from the pipette, the mercury in M_1 was lowered and desorption continued. The data for the above determination have been given after those of Run #3. The value of E_m for this moisture content was found to lie, within experimental error, on the curve for Run #3.

4. The Calculation of the Dielectric Constant of the Cellulose and of the Adsorbed Water

It has been mentioned previously that equation (3), gives a value for the dielectric solid of cellulose that is closer to the true value than that given by equation (1) or (2). Equation (3) is shown again below.

$$E_m = \frac{V_1}{V} + \frac{V_2}{V} \; E_2 \qquad (3).$$

where E_m is the dielectric constant of the compound dielectric of air and solid,

E_2 is the dielectric constant of the solid,

$\frac{V_1}{V}$ is the volume percentage of air,

$\frac{V_2}{V}$ is the volume percentage of the solid.

The actual distribution of the cellulose fibres in the condenser is obviously more closely approximated by the conditions which hold for equation (3) than by those holding for either equations (1) or (2). Now whatever manner of distribution is possessed by the cellulose, that also must be the form of distribution of the water adsorbed on its fibres. An equation of the same type as equation (3) will therefore give, for the dielectric constant of the adsorbed water, values which are closest to the true ones.

Although the values of the dielectric constant obtained by the use of such a formula are only relative values, they are sufficient to throw further light on the cellulose-water system.

It has been indicated previously that the dielectric constant of cellulose has undergone an apparent increase as a result of the heat treatment employed during desorption. This was based on the fact that the capacity of the condenser containing air and cellulose only, was found to be greater after each of the successive desorptions at the higher temperature. The value of the dielectric constant E_2 has been obtained by use of equation (3). V (40.36 cc.), the volume of the inter-cylinder space, has been calculated from the dimensions of the two cylinders. V_2 (3.00 cc.), the volume of the cellulose, is obtained from the weight of the latter (4.832 grams) and its specific volume (0.62). V_1 (37.36 cc.), is the difference between V and V_2. The values of the dielectric constant E_2, together with the corresponding capacities C_x and the values of the dielectric constants of the mixtures E_m, are listed below.

	Capacity of the Condenser in cms. (C_x)	Dielectric Constant of the Mixture (E_m)	Dielectric Constant of the Cellulose. (E_3)
Run #1	69.10	1.221	3.97
Run #2	69.40	1.226	4.04
Run #3 and #4	69.70	1.231	4.10
Run #5	70.50	1.246	4.30

Argue and Maass (6) noted a similar increase in the capacity of the condenser following desorption but they attributed it to experimental error. Their results have been recalculated so that they can be compared with those obtained in this work. These are given below.

	Capacity of the Condenser in cms. (C_x)	Dielectric Constant of the Mixture (E_m)	Dielectric Constant of the Cellulose. (E_3)
Run #1	74.73	1.241	4.05
Run #2	74.96	1.245	4.10
Run #3	75.10	1.247	4.13

The values of the dielectric constant for various amounts of adsorbed water have been calculated from the formula:

$$E_m = \frac{V_1}{V} + \frac{V_2}{V} E_2 + \frac{V_3}{V} E_3$$

G R A P H #4

OVERALL DIELECTRIC CONSTANT OF ADSORBED WATER

40
35
30
25
20
15
10

RUNS #3 & #4
RUN #5
RUN #2
RUN #1

.00 .05 .10 .15 .20 .25 .30 .35 .40 .45 .50

TOTAL VOLUME OF ADSORBED WATER IN C.C.

where V_3 is the volume of adsorbed water in cc.

E_3 is the dielectric constant of the adsorbed water,

and the remaining symbols have the same significance as above.

The values of E_m taken from the curves of Graph #3 have been used in preference to the actual values that were experimentally obtained. The calculated dielectric constants of the adsorbed water E_3, together with the corresponding values for the volume of the adsorbed water V_3, and the dielectric constants of the mixtures E_m, are given for the various runs in Tables VI, VII, VIII and IX respectively. The results are shown in graphical form in Graph #4.

TABLE VI

Run #1

Dielectric Constant of the Mixture (E_m)	Volume of Adsorbed Water in cc. (V_3)	Dielectric Constant of Adsorbed Water. (E_3)
1.233	0.055	10.27
1.243	0.080	12.11
1.258	0.110	14.68
1.276	0.140	17.01
1.300	0.175	19.37
1.319	0.200	20.78
1.339	0.225	22.24
1.360	0.250	23.41
1.387	0.280	24.93
1.434	0.330	27.02
1.514	0.400	30.56
1.587	0.450	33.81

TABLE VII

Run #2

Dielectric Constant of the Mixture (E_m)	Volume of Adsorbed Water in cc. (V_3)	Dielectric Constant of Adsorbed Water (E_3)
1.246	0.055	16.13
1.264	0.090	18.39
1.285	0.125	20.33
1.298	0.145	21.14
1.319	0.175	22.60
1.337	0.200	23.41
1.374	0.245	25.36
1.425	0.300	27.84
1.486	0.355	30.58
1.556	0.410	33.47
1.620	0.450	36.14

TABLE VIII

Runs #3 and #4

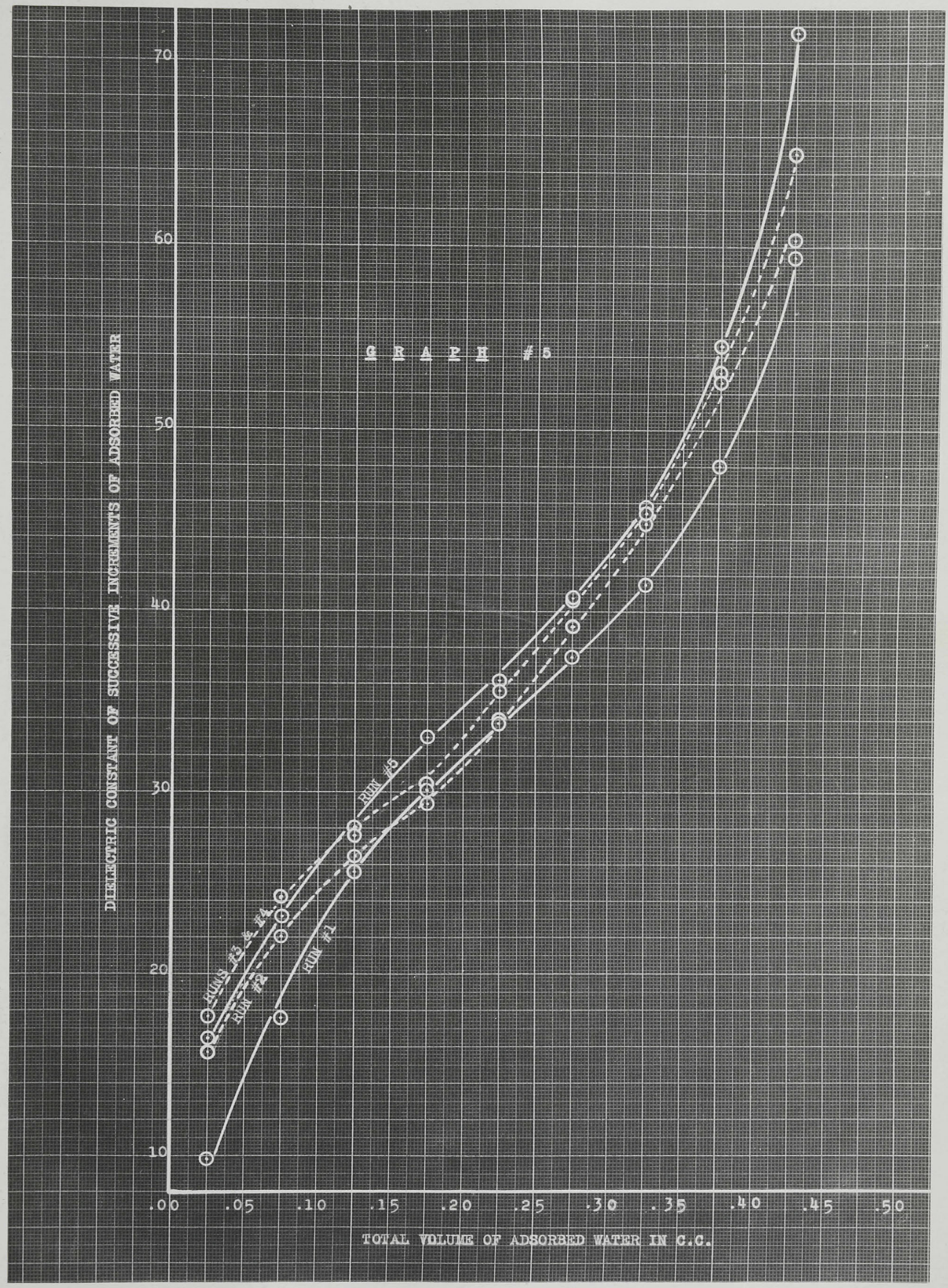
Dielectric Constant of the Mixture (E_m)	Volume of Adsorbed Water in cc. (V_3)	Dielectric Constant of Adsorbed Water. (E_3)
1.258	0.060	19.50
1.280	0.100	20.98
1.296	0.125	22.27
1.320	0.160	23.46
1.350	0.200	25.02
1.402	0.260	27.63
1.442	0.300	29.45
1.496	0.350	31.60
1.564	0.405	34.17
1.642	0.450	37.93

TABLE IX

Run #5

Dielectric Constant of the Mixture (E_m)	Volume of Adsorbed Water in cc. (V_3)	Dielectric Constant of Adsorbed Water. (E_3)
1.267	0.055	16.88
1.277	0.075	18.29
1.295	0.105	19.97
1.312	0.130	21.73
1.326	0.150	22.60
1.345	0.175	23.98
1.410	0.250	27.44
1.514	0.350	31.94
1.578	0.400	34.49
1.658	0.445	38.40

GRAPH #5


DIELECTRIC CONSTANT OF SUCCESSIVE INCREMENTS OF ADSORBED WATER
70
60
50
40
30
20
10
RUN #5
RUNS #3 & #4
RUN #2
RUN #1
.00
.05
.10
.15
.20
.25
.30
.35
.40
.45
.50
TOTAL VOLUME OF ADSORBED WATER IN C.C.

The values of the dielectric constant obtained above, are the mean or overall dielectric constants of all the adsorbed water from zero adsorption up to the amount represented by V_3. Of much more interest, however, are the values of the dielectric constant for successive increments of adsorbed water. Now the additive relationship expressed by equation (3) may be given in the form:

$$E_{V''} \times V'' - E_{V'} \times V' = E\,(V'' - V')$$

where $E_{V''}$, $E_{V'}$ are the dielectric constants when

V'', V' are the volumes of adsorbed water respectively,

E is the dielectric constant of the increment of water.

The values for V'', V' and $E_{V''}$, $E_{V'}$ have been taken from the curves of Graph #4. The value of E for each increment of water is given for the various runs in Tables X, XI, XII and XII respectively. The average value of V'' and V' has been plotted against the corresponding value of E in Graph #5.

TABLE X
Run #1

Range of Water Content (V" - V' cc.)	Dielectric Constant of Increment of Water.
0.00 - 0.05	9.9
0.05 - 0.10	17.6
0.10 - 0.15	25.6
0.15 - 0.20	30.1
0.20 - 0.25	33.8
0.25 - 0.30	37.5
0.30 - 0.35	41.5
0.35 - 0.40	48.0
0.40 - 0.45	59.4

TABLE XI

Run #2

0.00 - 0.05	15.7
0.05 - 0.10	22.0
0.10 - 0.15	26.4
0.15 - 0.20	29.4
0.20 - 0.25	34.0
0.25 - 0.30	39.2
0.30 - 0.35	45.4
0.35 - 0.40	52.6
0.40 - 0.45	60.4

TABLE XII

Runs #3 and #4

Range of Water Content ($V'' - V'$ cc.)	Dielectric Constant of Increment of Water.
0.00 - 0.05	17.7
0.05 - 0.10	24.2
0.10 - 0.15	27.6
0.15 - 0.20	30.4
0.20 - 0.25	35.6
0.25 - 0.30	40.8
0.30 - 0.35	44.8
0.35 - 0.40	53.2
0.40 - 0.45	65.0

TABLE XIII

Run #5

0.00 - 0.05	16.5
0.05 - 0.10	23.2
0.10 - 0.15	28.0
0.15 - 0.20	33.0
0.20 - 0.25	36.2
0.25 - 0.30	40.6
0.30 - 0.35	45.8
0.35 - 0.40	54.6
0.40 - 0.45	71.6

5. Discussion of the Results

In the above investigation the largest probable error resulted from the measurement of the amount of water introduced into the system. The volume of the water in the pipette P was estimated to 0.005 cc. Approximately 0.050 cc. of water was let into the system for the first measurement in any run so that the probable error at this point was a maximum and was equal to 10%. The percentage error diminished as the amounts of water became greater and at the largest value of the latter, approximately 0.500 cc., the error became equal to 1%. (The error does not become accumulative as the volume of the water introduced into the system is taken as the difference between the reading of the pipette at any given time and that at the beginning of the run. Since the pipette is read twice for each volume determination, the maximum error is 0.010 cc. but the probable error is only half of this value). An attempt was made to eliminate this error during the last three runs by choosing the volumes of water such that the levels in the pipette coincided with the scale markings of the latter. Reference to the curves of Graph #3 will show that an error of 0.005 cc. will throw a point considerably off the curve. Since the number of points that do not lie on the curves in not great,

it is felt that this error has been eliminated for the most part.

The probable error in the capacity measurements in terms of scale readings was equal to 0.05 cms. This causes an error in the dielectric constant of the mixtures E_m of less than 0.001 units, which is obviously negligible compared to the error encountered in the measurement of the volume of the water.

The successive increase in the capacity of the condenser filled with air and cellulose following the heat treatment during the desorption of the water, has been treated up to the present as an increase in the dielectric constant of the cellulose. This has been done in order to facilitate the discussion up to this point. Whether or not it is a true change in the dielectric constant will be considered in the paragraphs following.

As previously mentioned, two methods were used for the desorption of the water from the cellulose namely (i) by raising the temperature of the cellulose to 100° - 105°C., (ii) by lowering the vapour pressure in the system by the use of a freezing mixture. As a result of the treatment given in (i), it was found that the capacity of the condenser filled with cellulose and air underwent an increase. This did not happen when

the procedure indicated in (ii) was employed (otherwise Curves #3 and #4 of Graph #3 would not have coincided). Obviously the change in capacity does not result from the adsorption and subsequent desorption of the water at 25°C. The question to be answered is whether the capacity change, as a result of desorption at 100° - 105°C., is due to the removal of the water at the higher temperature, or is due solely to the subjection of the cellulose to such a temperature. The answer is supplied by the following experimental evidence. During the desorption of the water in Run #2, the cellulose was maintained at the temperature 100° - 105°C. for a period of ten hours. This was increased to twenty hours for Run #3. The increase in the capacity of the condenser, however, was the same in both cases. If the change is due solely to the high temperature, the capacity increase in the latter case would be expected to be larger. Moreover on a subsequent desorption employing the higher temperature, the capacity of the condenser showed a still further increase. That the higher temperature alone is not responsible for the rise in capacity was proven conclusively by measuring the capacity of the condenser at regular intervals during desorption, and after desorption was complete. As the water was removed, the capacity

decreased continuously and eventually reached a given value which presumably marked the completion of desorption. Further heating did not result in an increase in capacity.

It has been shown above that the capacity rise is due to a combined effect of the high temperature and the removal of water from the cellulose at that temperature, but the nature of the change that the simultaneous operation of these two factors effects in the cellulose-air system has not been indicated. Such a change might be (i) one that alters the chemical nature of the cellulose and thereby increases the dielectric constant of the latter, (ii) an irreversible physical change in the cellulose that results in a permanent displacement of the fibres relative to each other, this displacement being such that it acts in the direction of an increased capacity of the condenser.

It is highly improbable that the cellulose undergoes a chemical change. No chemical reaction would be expected from the action of a weak reagent like water on a substance as inert as cellulose at the relatively low temperatures employed here. (The results of Bateman and Beglinger (65) tend to show that the chemical composition of cellulose is unaltered at temperatures as high

as 170°C. Destructive distillation is appreciable, however, at 200°C.).

The more probable cause of the increase of the capacity of the condenser, under the conditions noted above, is that of an irreversible physical change in the cellulose, which results in a displacement of the fibres. As can be shown by equations (2) and (3) given previously, the capacity of a condenser filled with a given weight of a material, will be greater if the alternate layers of the latter are arranged at right angles to the condenser plates rather than parallel to them. Thus any change in the position of the fibres will result in a change in capacity. A possible manner in which such a displacement may occur is given in the following paragraphs.

It has been shown from X-ray data (66) that the unit cell of the cellulose crystal consists of four glucose units. Some 50 to 200 of the glucose units are joined together, end to end, to form the cellulose molecule or chain. By means of lateral forces, groups of approximately 70 of these chains are bound together in a parallel arrangement to give a cellulose crystallite or micelle. The fibres of the cellulosic material are composed of groups of crystallites or micelles twisted together in the form of a spiral.

When contact between micelles occurs, crystal forces due to secondary valences come into play. During the process of adsorption of water by cellulose, these intermicellar bonds are broken and replaced by cellulose-water bonds. In the immediate neighbourhood of the point of contact of the micelles, the forces that hold the water are the greatest. During the process of desorption, this water is the last to be removed and some of it may not be removed at all unless such high temperatures are employed that decomposition of the cellulose results (67). During the evaporation of the water the micelles are drawn together by the internal tension of the liquid that exists between them. As the micelles come closer together, the molecular forces come into play, and even after the water has evaporated, the structure is held in a state of internal stress by these forces. This displacement of the micelles naturally results in a shift in the position of the fibre which results in the formation of a new fibre-to-fibre contact. Equation (3) has been developed on the assumption that each cellulose fibre forms a continuous path across the plates of the condenser. Because this does not hold exactly under the experimental conditions, the value of the dielectric constant calculated from equation (3) is too low. As

new fibre contacts are made, the conditions demanded by this equation are more nearly approximated, with the result that the calculated dielectric constant increases. New fibre contacts are made at each desorption and since there is no reason why the old ones should be broken, the number of contacts increases with each desorption.

The reason that there is no apparent increase in the dielectric constant of the cellulose when desorption is brought about at the lower temperature may be two-fold: (i) it is only at the higher temperature that the fibres are sufficinetly flexible to undergo an appreciable permanent displacement, (ii) all the water is not removed at the lower temperature since some of it is held quite strongly; it is the removal of this water, which is held at the point of contact of the micelles, that causes the greatest fibre displacement.

If the increase in the capacity of the condenser, under the conditions noted above, is due to an actual increase in the dielectric constant of the cellulose, then it becomes necessary to apply a correction to the value of the dielectric constant found in Section II. By use of equation (3) in this work, it was found that the dielectric constant of cellulose had increased as a result

of the first two desorptions, by an amount equal to 1.8% and 1.6% respectively. Assuming that the cellulose used in the measurements in Section II underwent a similar increase as a result of desorption, the value of the dielectric constant of cellulose becomes 6.0 instead of 6.1.

A consideration of the Curves of Graph #3 shows that the differences between the values of E_m (or the capacity of the condenser) are greater at given water concentrations higher than zero, than they are at zero concentration. This would be expected on a basis of a fibre displacement from run to run, for if this is such that it acts in the direction of increased capacity of the condenser when the latter is partly filled with cellulose only, it would also tend to increase the capacity due to a change in the distribution of the adsorbed water relative to the condenser. The calculated values of the dielectric constants of given amounts of adsorbed water would therefore be expected to increase from run to run. This is borne out for the most part by the Curves of Graphs #4 and #5.

There is no need to enter into a discussion of the significance of the sigmoid character of the curves of Graphs #4 and #5. This has been amply treated by the previous workers in this field.

Argue and Maass (6) did not realize that the curve showing "E_m" versus "Volume of the Adsorbed Water" shifted towards higher values of E_m at a given water content, subsequent to desorption at 100°- 105° C. This was due to the fact that the distance between corresponding points of their two runs was of the same order of magnitude as the experimental error. They accordingly came to the conclusion that the above results were reproducible from run to run.

From the single determination made on the water left on cellulose by desorption, it would appear that the dielectric constant of the adsorbed water depends only on the amount present and is independent of the previous history of the cellulose-water relationship. This is not true for certain other properties of the cellulose-water system. It is, however, extremely hazardous to draw conclusions from an isolated measurement, so that such conclusions must await the further investigation of this system from the above angle.

6 Suggestions for Future Work.

It would be highly desirable to show definitely that the increase in the capacity of the condenser following desorption at the higher terperature, is not an actual increase in the dielectric constant of the cellulose. This could be readily accomplished by use of the method, given in the first section, for the measurement of the absolute dielectric constant of fibrous materials. This would be carried out in the following steps: (i) the dielectric constant of cellulose would be determined by the above method and simultaneously by use of equation (3) (ii) The cellulose would be subjected to several alternate adsorptions and desorptions of water, the latter process being carried out at 100°- 105° C (iii) The dielectric constant of the cellulose would again be determined by the two methods given above. It is felt that the absolute value of the dielectric constant would be found to undergo no change, even though the values given by equation (3) would differ.

Argue (30) has already pointed out the value of a series of measurements on the dielectric constant of water left on cellulose by desorption. The apparatus used in this investigation should accordingly be modified to permit such determinations to be made.

It has already been suggested in the previous section that it would be desirable to measure the dielectric constant of forms of cellulose that have been differently prepared, in order to determine the magnitude of the change that results in this constant from a different method of preparation. It would be equally interesting to note what differences are to be found in the dielectric constant of the water adsorbed on these different types of cellulose.

SUMMARY

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A visual method for the determination of the null point has been incorporated in the capacity measuring apparatus which apparatus functions on the principle of the heterodyne beat. Other changes in circuit design have raised the power output level to one that affords the simultaneous operation of a loudspeaker. These improvements have removed the need of earphones and the inconvenience attendant with their use.

A new method has been developed for the application of the correction to condensers that do not give a straight line relationship between capacity and angular rotation and the accuracy of the method has been demonstrated.

The design of a condenser composed of two concentric cylinders has been investigated from the point of view of eliminating the effect of the environment on the capacity of the condenser. It has been found that if the inner cylinder is made shorter than the outer one, (provided the latter is grounded) the environment has no effect on the capacity of the condenser.

It has been shown that the capacity of a condenser partly filled with cellulose undergoes an increase when adsorbed water is removed at a temperature of 100°- 105°C

but that no increase results if desorption is brought about at 25°C by the lowering of the vapour pressure in the system through the introduction of a solid carbon dioxide-acetone trap. An explanation has been given for these phenomena on the basis of an irreversible physical change, (which the cellulose is considered to undergo when desorption occurs at the higher temperature) that results in a change in the distribution of the cellulose fibres.

It has been found that the calculated relative dielectric constant of adsorbed water at a given water content increases subsequent to desorption of the cellulose at the higher temperature. This has likewise been explained on the basis of a displacement of the cellulose fibres.

A method has been developed for the measurement of the dielectric constant of fibrous materials. This method has been applied to the determination of the dielectric constant of standard cellulose, an accurate value of which has been obtained for the first time.

Other points of interest that have resulted from the above investigation are given as follows:

It has been shown that neither benzene nor ethylene dichloride is adsorbed on cellulose to an appreciable extent.

Frozen seals of the same composition of the liquid to be introduced into an evacuated space have been used for the first time.

The above statement is likewise a summary of the claims to original work and contributions to knowledge.

The above investigation verified the findings of Argue and Maass (6) that the dielectric constant of adsorbed water increases with the water content in a manner that confirms the hypothesis of the physical structure of cellulose and the mechanism of adsorption.

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