

EFFECT OF
SURROUNDING MEDIA
ON CELLULOSE

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THE EFFECT OF SURROUNDING MEDIA
ON CELLULOSE

A Thesis

by

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General Introduction

The importance and wide-spread uses of cellulose and its derivatives, and the recent phenomenal development of new cellulose products, has caused the whole subject to become of even greater interest than previously. Along with this development has come the need for a more complete theoretical knowledge of the physico-chemical nature of cellulose, and the best way of obtaining this knowledge is by research.

The nature of water sorption on cellulose has been the subject of a great deal of controversy, and in order to clarify the discussion of experimental results, it is desirable to introduce this work with a brief outline of the most generally accepted views (1) of the physico-chemical structure of cellulose.

Cellulose consists of long chains made up of glucose units. From X-ray data it has been shown that the unit cell of the cellulose crystal is monoclinic in structure and contains four glucose units. The glucose residues in the form of amylose rings are arranged parallel to the "b" dimension of the unit cell, with one cellobiose group on each edge and one through the center. These form long primary valence chains (3) arranged parallel to the fibre axis and approximately 60 of these chains are held together laterally by secondary valence forces to form the cellulose crystallite or micelle. The glucose units in the primary valence chains are arranged spirally about the longitudinal axis in such a way that a half

turn in the screw axis occurs for each unit cell height. It is this periodicity that is responsible for the observed sub-molecular unit.

Cellulose is formed in the plant in the presence of free water, that is, under conditions of 100% relative vapor pressure. Where contact between micelles occurs, crystal forces or secondary valencies come into play, similar to those holding the chains in the micelle. The remaining micelle surfaces which are not in contact may conveniently be called the inner free surface of the cellulose.

Because cellulose is not peptized when placed in liquid water, these naturally-occurring cellulose-to cellulose bonds must be stronger than the cellulose-to-water bonds which might replace them.

When the cellulose is dried, further cellulose-to-cellulose bonds are formed, but because of the mode of their formation these new bonds are under a strain, and are disrupted when adsorption of water takes place. It is generally agreed that these strained bonds are caused by union between free hydroxyl groups.

Gas molecules can penetrate into the fibre and reach the inner free surface, but the cellulose micelles are impenetrable. Adsorption of gases can take place on this inner free surface, and the first portion of water vapor to enter the dried fibre is held in this way. The line of demarcation between water of constitution and surface-bound water is by no means sharp; in general it is agreed that the first portion

of water adsorbed is held with great tenacity; but whether a surface compound is formed, or whether the effect is simply a strong adsorption, is, in the last analysis, merely a matter of degree.

Water entering subsequent to that which has saturated the inner free surface will condense in the capillaries of the intermicellar spaces.

The amount of water held by the cellulose for a given vapor pressure depends on whether water has been added to the dried cellulose or abstracted from the saturated cellulose. That is, adsorption is followed by hysteresis when desorption takes place. From this and the form of the adsorption isotherms, it follows that the water also increases the inner free surface in the sense that contact areas between micelles are disrupted and the forces between cellulose and water replace those between cellulose and cellulose. It must be clearly borne in mind that these cellulose-to-cellulose bonds which are replaced, are those which were formed when the original saturated cellulose was dried; the bonds originally present between micelles are not disrupted.

The transition between surface-bound water and water held by capillary forces also appears to be gradual: all the available data on sorption by cellulosic materials give smooth sigmoid moisture content-relative vapor-pressure curves, and the first inflection point is generally believed to mark this transition.

After the water vapor required to saturate the inner free surface has been adsorbed, subsequent addition of water vapor creates more surface, and the lowering of the vapor pressure is greater than need be accounted for by the curvature of the liquid water surface in the intermicellar capillaries. Water held on the freshly created surfaces will require a lower vapor pressure to be removed before the cellulose surfaces can join up again. This is the mechanism of hysteresis.

In addition, it is reasonable to suppose that the inner free surface is not uniform in its adsorptive capacity. The ends of the micelles will differ from the sides in having a greater amount of free valencies. The surface will be covered with active centers which initiate adsorption, the tendency for the formation of cellulose-water bonds gradually falling off.

The second point of inflection is much more gradual than the first and is due to the fact that the capillaries have a wide range of diameters, and thus the vapor-pressure changes slowly and smoothly as larger and larger capillaries become filled, until finally the vapour pressure of bulk water is reached at a relative vapor pressure of unity.

For a number of years, investigations of the physical-chemical properties of the system cellulose-water have been carried out in the Physical Chemistry Laboratories of McGill University. Of the many researches performed only those directly relating to the present work will be mentioned in this introduction.

Argue and Maass (4), using an adiabatic calorimeter, measured the heats of wetting of cellulose containing different amounts of adsorbed and desorbed water; from their data, they calculated the heats of adsorption of water vapor on cellulose. It was considered of sufficient importance to determine sorption isotherms experimentally, calculate the heats of adsorption, and compare the results with those of Argue and Maass. This problem is treated in Section I.

Another problem, investigated by Filby and Maass (5) was the density of water adsorbed on cellulose. The apparatus used in this research was of a new type, and some uncertainty existed about the experimental accuracy obtainable. In Section II of this thesis, research is described in which the apparatus has been rebuilt on a larger scale and somewhat modified in design. The density of adsorbed water has been determined with a higher degree of accuracy.

More recently, Patrick (6) has attempted to show that the hysteresis which is observed in the adsorption and desorption of water on cellulose is apparently due to small quantities of

permanent gases; this partly contradicts the theory of the physical chemical structure of cellulose as outlined above, so an investigation was carried out to determine if any change in the hysteresis could be observed under conditions of low and high vacuum. This work is reported in Section III.

As well as continuing the above mentioned investigations, the present work also treats two problems related to the question of moisture adsorption on cellulose: The rates of moisture sorption by paper under various conditions of relative humidity, temperature and air pressure; and the conditioning effect of high relative humidities on the extension of paper. These two problems are described in Section IV.

SECTION I

The Temperature Coefficient of the Sorption of Water Vapor on Cellulose

Introduction

Heats-of-wetting data are of considerable importance in thermodynamic considerations of swelling; Argue and Maass (4) have recently measured the heats of wetting of a number of cellulosic materials, and one interesting point brought out by their investigation was that the heat of wetting of cellulose containing a definite proportion of water depended on whether the water had been adsorbed, or left by desorption.

There is a definite relation between the temperature coefficient of the heat of sorption and the sorption isotherms, and although it cannot be applied accurately without a complete knowledge of the temperature coefficients of all the specific heats involved, yet by determining two isotherms at different temperatures, a number of the errors ought to compensate each other.

The object of this investigation is to determine adsorption and desorption isotherms experimentally for standard cellulose prepared in the same way as that of Argue, and then to calculate the heats of adsorption from the data obtained,

and make comparisons with the values calculated by Argue.

Previous Work

The method of calculating heats of adsorption has been used (19,20) by other investigators, but their results agreed only in part with Argue's. From a comparison of results, it is apparent that the slope of the curve, heat-of-wetting against moisture content as obtained by Argue is different from the slope obtained by previous investigators.

The greater amount of experimental data is presented in the form of adsorption isotherms. Masson and Richards (7) found the adsorption isotherms of cotton were of the characteristic sigmoid type. Schloessing (8) and Hartshorne (9) obtained nearly identical isotherms except at the higher relative vapor pressures. This point will be mentioned later under "Discussion of Results".

The most important work has been performed by Urquhart and Williams (10, 11, 12, 13, 14) who have carried out extensive sorption measurements on cotton. They and their co-workers definitely established the form of the isotherms.

Pidgeon and Maass (15) and Filby and Maass (3) have made measurements of the moisture-content-relative vapor pressure relationships of cotton using the same method as is used in the present work. These investigators also obtained the normal sorption curve, and hysteresis effect.

Theory

The differential heat of wetting-moisture content relationship can be calculated from moisture-content relative vapour-pressure data at different temperatures, using the integrated form of the Clausius-Clapeyron equation, in which the differential heat of wetting

$$\Delta H = \frac{R T_1 T_2}{M (T_2 - T_1)} (\ln h_2 - \ln h_1)$$

Where ΔH is the heat of wetting occurring when one gram of the liquid is added to an infinite amount of cellulose at a moisture content in equilibrium with the humidity h_2 at T_2 and h_1 at T_1 . R is expressed in calories and M is the molecular weight of the liquid.

The theory of water sorption on cellulose has been treated in the "General Introduction".

Apparatus

The cellulose was purified by the following procedure: Best quality absorbent cotton was refluxed over a water bath with a 1% NaOH solution for twelve hours and the liquor poured off. The sample was washed with distilled water and the procedure repeated seven times. The cellulose was then acidified with 1% acetic acid and washed free of acid with distilled water. The excess water was pressed out and the purified sample air-dried for one day. It was then oven-dried at 100°C for two days and

transferred to a storage bottle. The absorbent cotton used was "Perfect Absorbent Cotton - Johnson and Johnson".

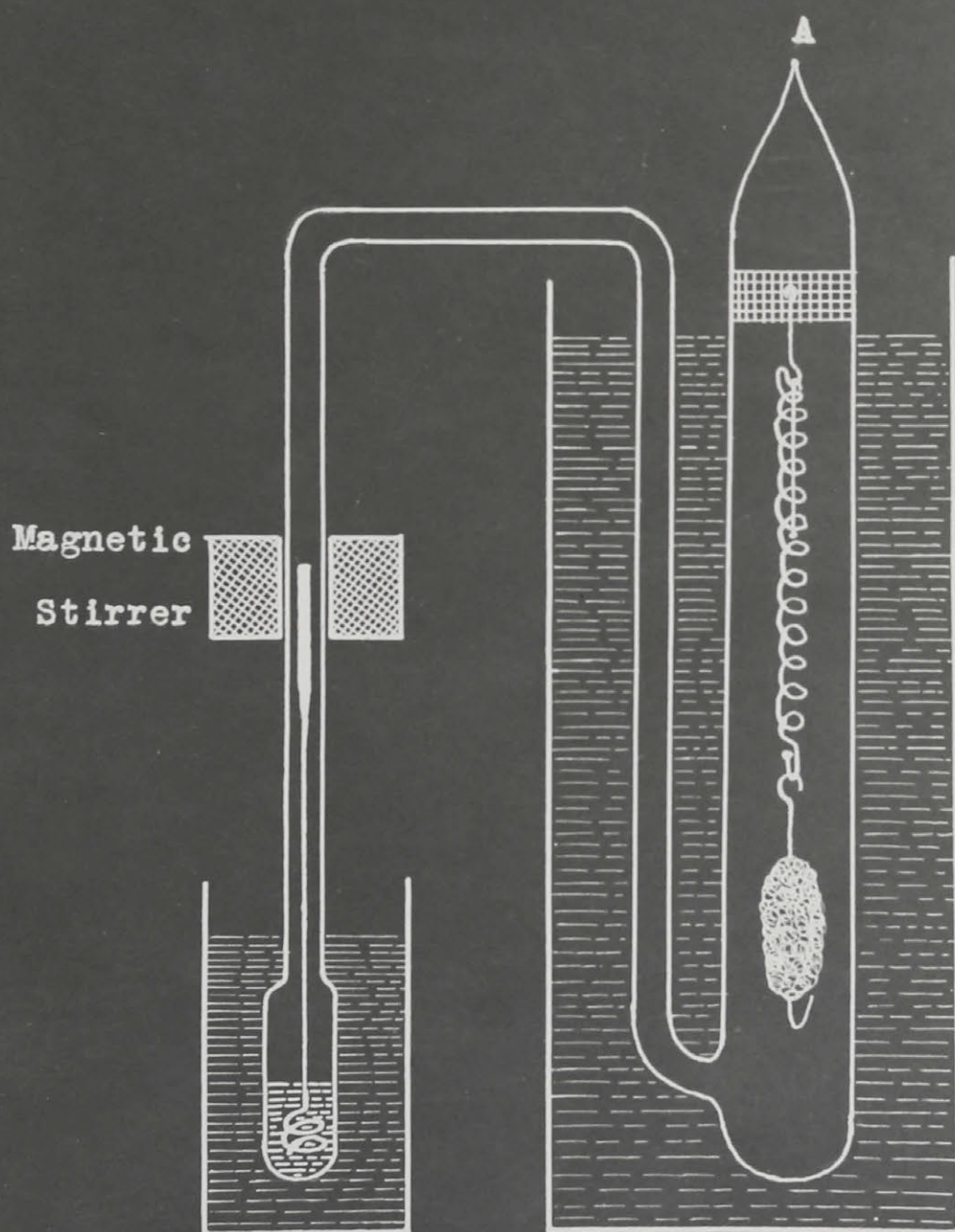
The sample was suspended on a quartz-fibre balance completely enclosed in glass and connected to a bulb containing liquid water. The temperature coefficient of extension of the loaded spring was determined with a weight equal to that of the cellulose sample used, and the spring was tested and found to obey Hooke's Law perfectly.

The sample was thermostated by an oil bath held to $\pm 0.05^{\circ}\text{C}$. and the temperature of the water bulb was controlled by another thermostat which could be set for any temperature from -35 to $+100^{\circ}\text{C}$. with a variation of $\pm 0.1^{\circ}\text{C}$. Since this thermoregulator is a rather ingenious device, and is used in some of the other sections of this thesis, a diagram of it is shown in Figure II. The tube connecting the water bulb to the sample was wrapped with resistance wire to prevent condensation at the higher humidities. A magnetic stirrer was placed in the water bulb to keep the surface of the liquid broken and thereby insure more rapid attainment of vapor-pressure equilibrium. Figure I is a diagram of the sorption apparatus.

Experimental Technique

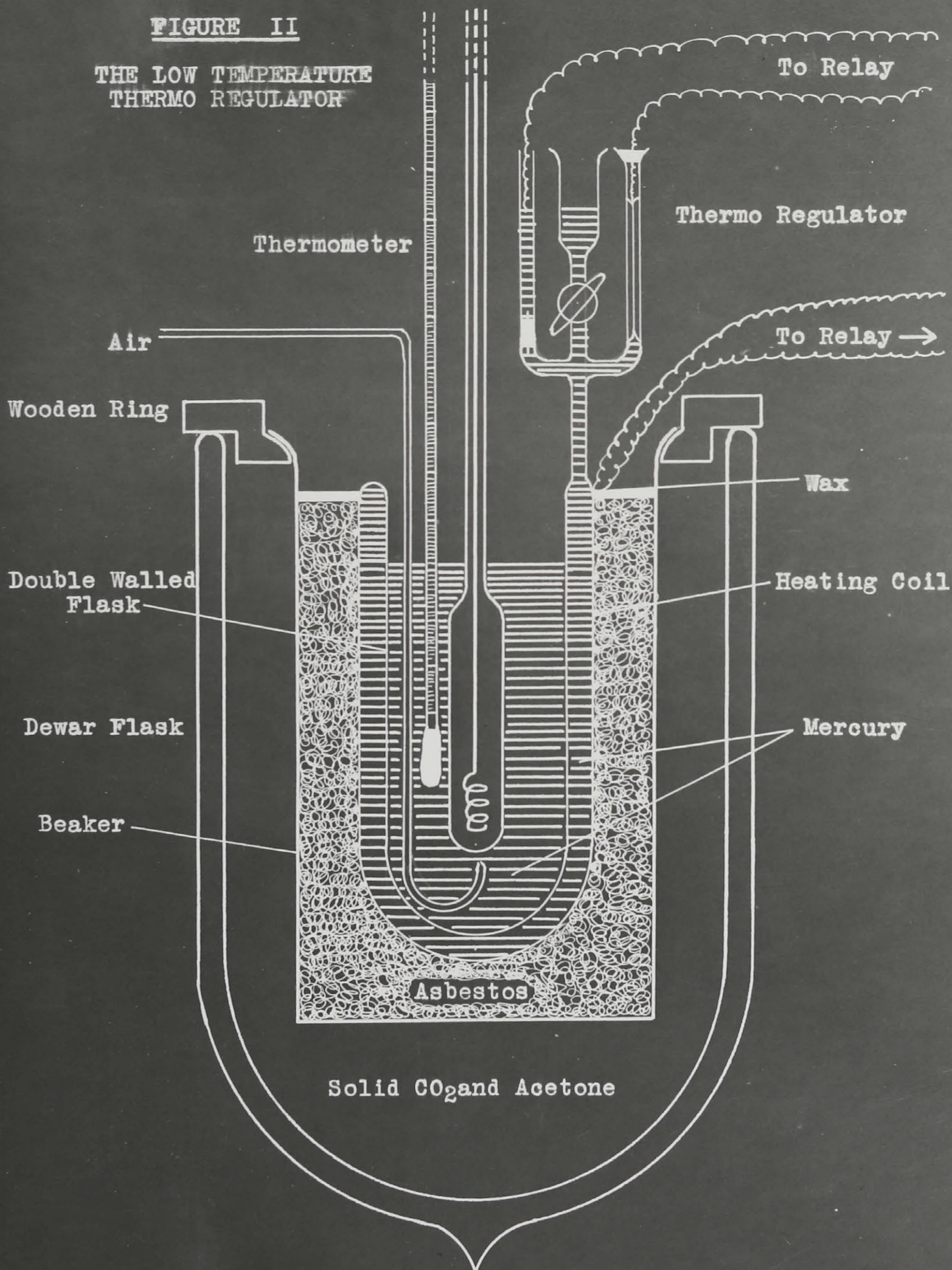
The apparatus was assembled, and the glass portion containing the sample and water bulb were evacuated to .001 mm. of mercury. The water bulb was kept immersed in solid carbon dioxide and acetone; the vapor pressure of water over this refrigerant is 0.0005 mm. The system was isolated from the pumps

FIGURE 1
THE SORPTION APPARATUS



Constant Temperature Baths

FIGURE II
THE LOW TEMPERATURE
THERMO REGULATOR



occasionally and the ice allowed to melt, in order to remove dissolved air. When the sample ceased to lose weight and the extension of the quartz balance became constant, the system was sealed off at A. The water bulb was then immersed in liquid air for a day, and the extension due to the dry cellulose recorded.

The temperature of the sample was fixed at $25.00 \pm .05^{\circ}$ C. and complete adsorption and desorption isotherms determined at this temperature. At the lower relative humidities, when the magnetic stirrer was frozen, equilibrium was reached in five or six hours, and at the higher humidities fifteen to twenty-five hours were required.

Equilibrium was assumed to have been reached when duplicate readings of the extension of the balance, taken ten hours apart, agreed within the error of reading the cathetometer.

A second complete cycle was obtained at 50° C.

Experimental Results

The experimental results are tabulated in Table I.

(Table I on Page 12.)

TABLE I

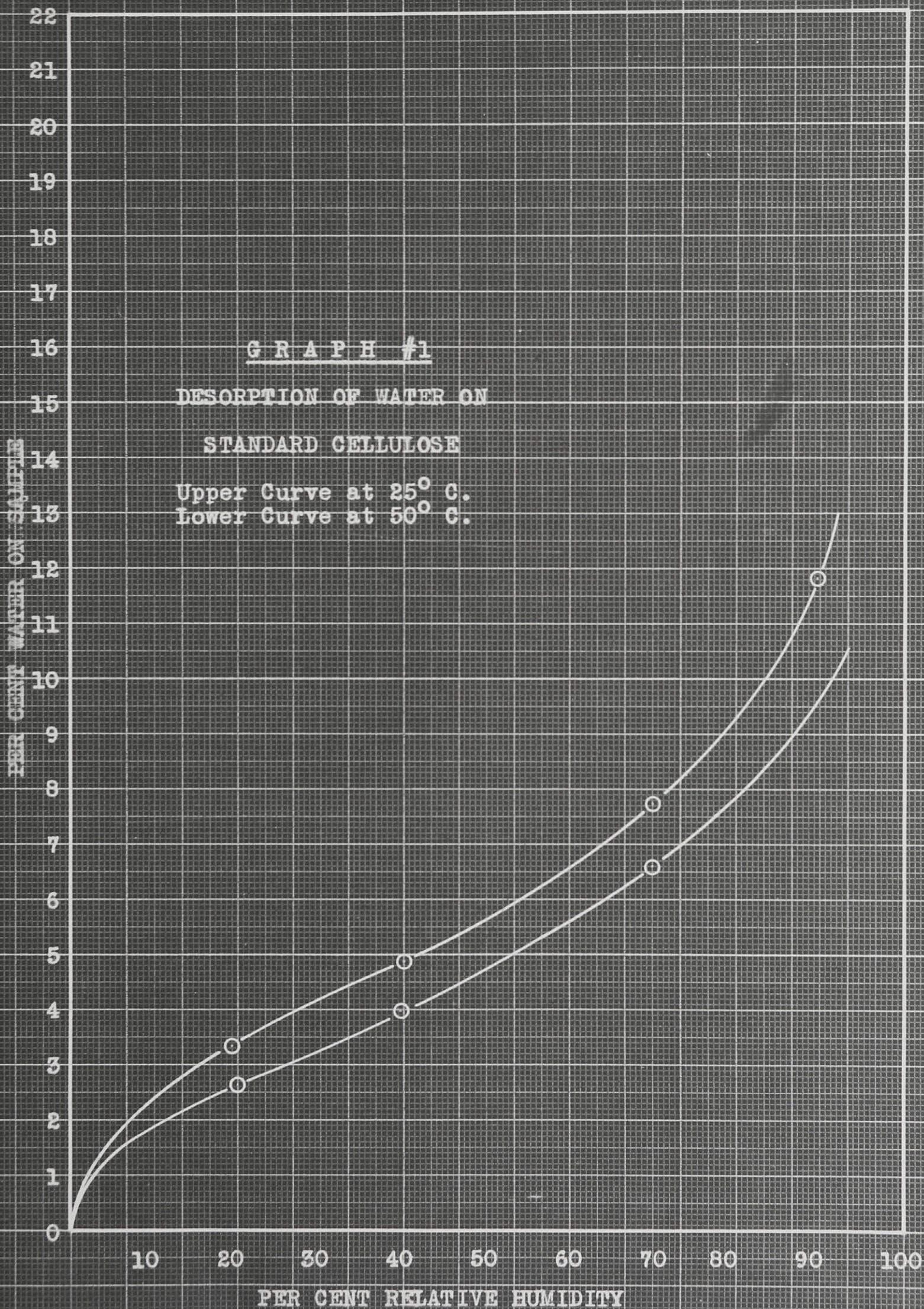
A D S O R P T I O N

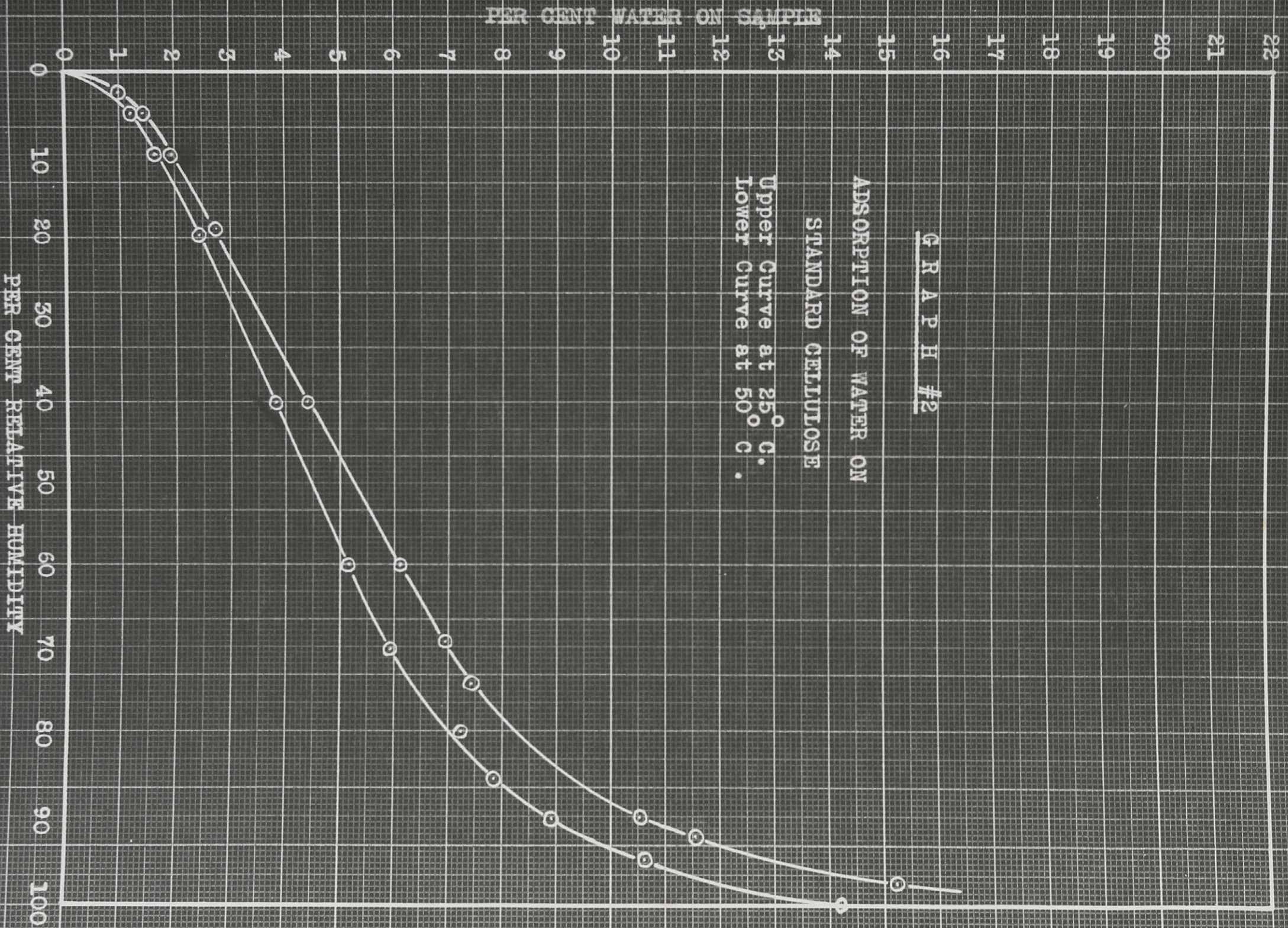
25° C.			50° C.		
<u>Time,</u> <u>Hrs</u>	<u>R.V.P.</u>	<u>%</u> <u>Water</u>	<u>Time,</u> <u>Hrs</u>	<u>R.V.P.</u>	<u>%</u> <u>Water</u>
13	2.5	1.03	7	2.18	0.76
7	5.0	1.44	6	4.94	1.24
8	10.0	1.98	17	9.85	1.67
12	19.27	2.75	26	19.67	2.47
16	40.00	4.41	20	40.0	3.83
10	60.0	6.10	8	60.0	5.17
15	69.4	6.98	17	70.1	5.94
12	74.4	7.47	8	80.2	7.25
18	90.0	10.54	16	85.4	7.88
15	92.1	11.57	10	90.0	8.92
15	97.5	15.22	10	95.15	10.63
			24	100.0	14.20

D E S O R P T I O N

25° C.			50° C.		
<u>Time,</u> <u>Hrs</u>	<u>R.V.P.</u>	<u>%</u> <u>Water</u>	<u>Time,</u> <u>Hrs</u>	<u>R.V.P.</u>	<u>Water</u>
40	89.7	11.82	50	70.0	6.60
15	70.0	7.74	24	39.61	3.98
12	40.0	4.88	24	20.0	2.64
7	19.27	3.33			

These results are plotted on Graphs I and II.





Discussion of Results

Duplicate runs were made in some cases, especially at the higher humidities, and it was found that the second run of each pair always showed a very slightly increased adsorption. This is in accord with previous work on cellulose, and is known as the Von Schroeder effect. Elastic gels, including cellulosic materials, show a greater sorption of water when immersed in liquid water than when brought to 100 per cent relative vapor pressure in the vapor phase. Sheppard and Newsome (16) believe that additional surface is made available in the liquid phase, as a result of the release of stresses which, in turn, result in the release of mutually satisfied hydroxyl groups.

An examination of the results shows that the hysteresis effect decreases with temperature increase, which is in harmony with some observations of Urquhart and Williams (11-14).

The adsorption isotherms agree very well with those of Urquhart and Williams up to 60% relative vapor pressure, but above this value the adsorption appears to be considerably smaller. This may be due to a difference in the methods of preparation of the cellulose: It is known (17) that the previous thermal history of the cellulose has an effect on the amount of water adsorbed at the fibre saturation point. Up to 60% relative vapor pressure, the results are closer to Urquhart and Williams than they are to Filby's. It is also noteworthy that, due to

the indefiniteness of the line of demarcation between water of constitution and surface-bound water, total sorption determinations on cellulosic materials are dependent upon the arbitrary dry weight used, which varies somewhat with the method of drying. Undoubtedly some water remains fixed on the fibres even under a high vacuum and at a temperature of 110° C.

Calculation of the Heats of Wetting

The differential heats of wetting were calculated from the equation given in the section on "Theory": They are tabulated, together with Argue's results in Table II.

TABLE II

A D S O R P T I O N					D E S O R P T I O N				
% Water	h_2	h_1	H	H_1	% Water	h_2	h_1	H	H_1
1	.032	.024	121	193	1	.033	.016	306	226
2	.138	.103	124	140	2	.112	.052	324	160
3	.275	.225	84.2	113	3	.253	.150	221	131
4	.425	.347	85.8	85	4	.402	.285	146	95
5	.577	.468	88.4	68	5	.537	.419	105	72
6	.701	.590	72.8	57	6	.647	.539	77.2	54
7	.790	.700	51.0	48	7	.731	.640	56.2	40
8	.851	.789	31.8	...	8	.800	.720	44.6	...
9	.905	.849	26.6	...	9	.861	.784	39.2	...
10	.936	.885	23.7	...	10	.910	.835	36.5	...
11	.958	.910	21.9	...	11	.946	.875	32.9	...
12	.975	.929	20.1	...	12	.970	.902	31.0	...

In the table above, h_2 and h_1 are the humidities at T_2 and T_1 respectively, required to produce the moisture content in the first column. These water contents and humidities were read off from the graphs shown in Plates I and II. H are the calculated heats of wetting, and H_1 are the heats of wetting as measured experimentally by Argue for similarly prepared cellulose.

Discussion

The values of H , as given in Argue's paper, have been corrected for the heat of vaporization of water by subtracting 582 calories.

At low moisture-content values, the temperature coefficient of ΔH is negligible while at higher values it increases with a decrease in temperature (18). Argue and Maass (4) found that small variations in the thermal history of the cellulose caused quite appreciable variations in the measured heats of wetting.

In view of the above facts, the present measurements are in fairly good qualitative agreement with those of Argue.

The difference between the heats of wetting of cellulose containing adsorbed water and of cellulose containing the same amount of water left by desorption may be explained as follows: For a sample containing desorbed water there is a larger internal area, and since the heat of wetting is a measure of this area, a larger heat of wetting is obtained.

At low water concentrations, there is a large difference in the heat of wetting; it is in this region that swelling takes place, because the surface of the micelle is not saturated, and the predominant factor in the formation of heat is surface adsorption. At a water concentration of about 7%, capillary condensation is the chief effect. Therefore, the greater the initial water content of the cellulose, the smaller are the differences in the heat of wetting of samples containing adsorbed and desorbed moisture.

Cellulose containing desorbed water has a larger internal surface than cellulose containing the same amount of water adsorbed from a dry state. When more water is brought into contact with these samples, both will have the same final surface. Therefore in the former case, less energy is required for surface formation, and the heat of wetting is greater. If no swelling took place in the fibre, no difference could be shown between the heats of wetting on samples containing adsorbed and desorbed moisture.

The results given above show a greater difference between the two heats than do Argue's results, especially for the low moisture contents, where it amounts to about 160%.

SECTION II

The Density of Water Adsorbed on Cellulose

Introduction

When a colloidal material swells in a liquid, the volume of the solid is increased but the total volume solid plus liquid is decreased. X-Ray measurements show no sign of a change in the crystal lattice of cellulose on swelling in water, indicating that the volume change is not within the solid. The shrinkage is believed to be due to the formation of a moderately stable surface compound. Filby and Maass (5) determined the volume change taking place when water is adsorbed on standard cellulose at various concentrations, and since the method used was quite new, some doubt existed as to the accuracy of the experimental results, so it was determined to repeat the measurements with a view to increasing their accuracy.

Previous Work

The work of Filby and Maass (5) is reported on the basis of the apparent density of the adsorbed water because the method used determines only the total volume of the system cellulose plus adsorbed water. For convenience in presentation

of the experimental results, it was necessary to suppose that the volume of the cellulose remained constant, although it was fully realized that such might not be the case. Their results show a slowly decreasing high density up to 4% of water, followed by a more rapid drop until the density at a very high moisture content approaches the value of one in an asymptotic manner. From these results they conclude that (1) Water in the high-density phase adsorbs until the exposed surface is saturated and (2) That further water adsorbs largely in the normal phase, the remaining small fraction of this water going to increase the active surface and being adsorbed in the high density phase.

Stamm, in his "Colloid Chemistry of Cellulosic Materials" (1) uses the term "adsorption compression" in referring to the measurements of Filby and Maass. In their paper, the latter authors did not assume that the adsorbed water underwent any appreciable compression; however, the total volume of the system cellulose plus adsorbed water was less than that of the separate components, because of the formation of something in the nature of a surface compound. Stamm's calculation of the enormous compressive force of 10^5 atmospheres is unjustified, because the density values given were arrived at on the assumption that the volume of the cellulose is unchanged on adsorption of water: this assumption was made only for the sake of convenience in presenting the results, and the density values were not considered to be absolute.

A compressive force of 10^5 atmospheres is about seven and a half times the cohesive force of water. The measurements of Bartell and Osterhof (28) and of Bartell and Jennings (29) have shown that the work of adhesion for a solid wetted by water is only 1.00 to 1.05 times the work of cohesion of water. There is no obvious reason why this should not be the case for cellulose.

Stamm and Seborg (30) have tried to verify the work of Filby and Maass by using a pycnometric benzene displacement method which gives true values at the higher moisture contents. However at the lower moisture contents, the accuracy of the measurements is dependent on the true density of the cellulosic material; this quantity is not known with an accuracy sufficient to warrant making measurements. The measurements in benzene show that the contraction effect definitely extends to the fibre saturation point.

Campbell (31) believes that the observed effects may be only apparent and that because helium and non-polar liquids do not swell the material, they cannot reach any void structure. If this is so, the true density of a cellulosic material could not be determined by an expansion method with helium.

It is the object of the present research to determine with greater accuracy the apparent density of water adsorbed on cellulose.

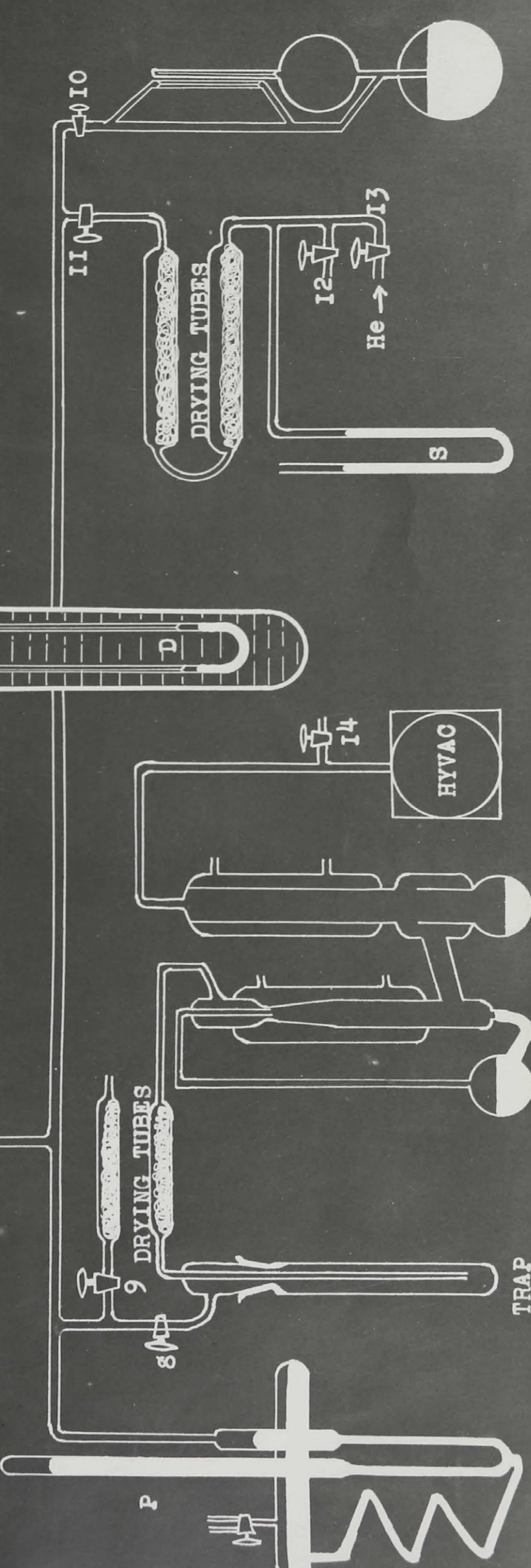
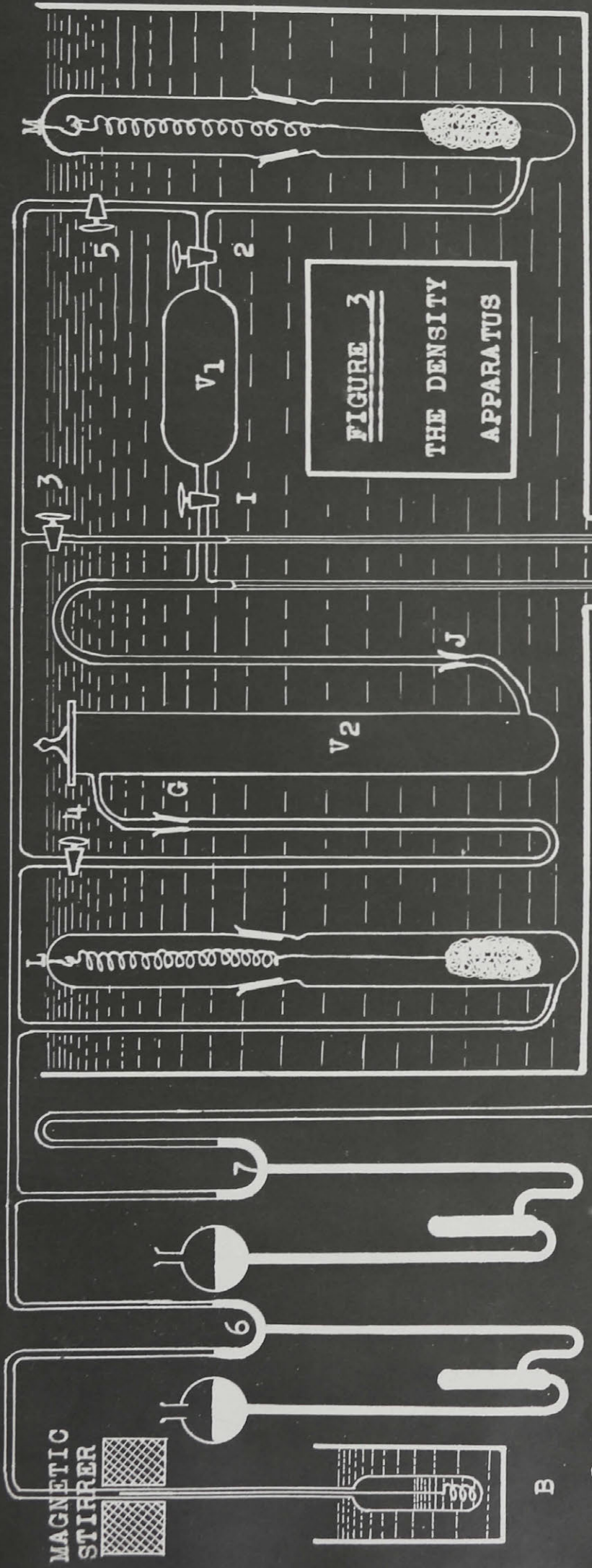


FIGURE 3
 THE DENSITY
 APPARATUS

DRYING TUBES

HYVAC

TRAP

He →

Apparatus

In its essentials, the apparatus employed by Filby and Maass consisted of two glass volumes connected by a stop-cock. One of these volumes was calibrated directly by a gravimetric method, then used to calibrate the second volume by an expansion method with helium. After calibration, the second volume was packed with a known weight of dry cellulose and another expansion made to determine the volume of this cellulose. Definite proportions of water were adsorbed on the cellulose and further expansions made in order to measure the volume of the cellulose plus adsorbed water. From the results obtained, the density of the adsorbed water could be calculated.

The use of helium was indicated for the following reasons: helium is an inert gas and is not adsorbed on cellulose: the small size of the helium molecules favours penetration into the void spaces, thus giving a true value for the specific volume of cellulose. Helium obeys Boyle's Law very well at room temperature and can be used for accurate calibration by expansion methods.

The design of the present apparatus was similar to that used by Filby, except for a few modifications.

Figure III is a diagram of the apparatus. The volumes V_1 and V_2 were made about ten times the size of Filby's, because the accuracy of the method depends on the absolute amount of water adsorbed; at low moisture concentrations this amount is very small unless a fairly large weight of cellulose is used.

When making measurements, the apparatus had to be kept under a pressure of 10^{-2} mm. or less for relatively long periods, so the number of stopcocks used was reduced to a minimum and where stopcocks were essential, especially-ground high-vacuum cocks were used. After trying several stopcock greases, the formula for high-vacuum grease recommended by Shepherd and Ledig (32) was found perfectly satisfactory.

The water bulb B was fitted with a magnetic stirrer to hasten attainment of equilibrium, and the temperature control was the same as that shown in Section I, Figure II. The constant temperature bath surrounding the calibrated volumes was held at $28.00 \pm 0.05^{\circ}$ C.

Two helical quartz balances, L and M were included in the system in such a way that the water-vapor from the bulb B passed first directly into L, through the cellulose in V_2 and then into the second balance M. This arrangement made it easy to determine when adsorption equilibrium had been reached by the cellulose in V_2 .

A pair of ground glass joints, G and J were employed to connect V_2 to the rest of the system, because after calibrating this volume by expansion, it was found convenient to remove it from the system before packing with cellulose. The volume V_2 includes the space from stopcock 4, through the connecting tubing and cell, up to the stopcock 1 and the surface of the mercury in the differential manometer D. In order to reduce that space in volume V_2 which could not be packed with cellulose, it was connected to the differential manometer by

capillary tubing, although this considerably slowed down diffusion. For this latter reason, stopcock 4 was connected to volume V_2 by ordinary shell tubing.

In the previous set-up, the differential manometer was not of barometric height with the result that it was difficult to avoid blowing mercury into the calibrated volumes. Therefore in the present apparatus, the manometer D was made about 80 cm. long and extended through the bottom of the bath. A glass jacket was attached to the bottom of the bath, and water circulated through it by means of an air-lift (not shown in the diagram) in order to keep the differential manometer at the same temperature as the main part of the apparatus. The level of the water in the bath was kept well over the calibrated volumes and the stopcocks 1, 2 and 4.

The main part of the apparatus, as described above, was connected through the cutoff 7 to the external system which consisted of the following: A constant-level manometer P, McLeod gauge, hyvac pump, diffusion pumps, trap, drying tubes and an arrangement for furnishing dry helium. The manometer P was read by means of a Gaertner cathetometer and pressure readings were reproducible to ± 0.02 mm. A Becker cathetometer was employed to read the extensions of the quartz balances and the cross-hair of a third cathetometer was focussed on the mercury meniscus in one arm of the differential manometer.

Experimental Technique

After the apparatus had been constructed and tested for leaks, V_1 was calibrated by weighing empty and then full of distilled water; it was then sealed on to the rest of the apparatus.

V_2 was now calibrated by expanding helium from V_1 into V_2 . The procedure for this is given in detail below.

I - Calibration of V_2 by Expansion

The bath was adjusted to $28.00 \pm .05^\circ \text{C.}$, and the cutoff 6 left closed throughout the measurements. Starting with atmospheric pressure in the apparatus, stopcocks 1, 2, 3, 4, 5, 8, 10, 11 and cutoff 7 were opened. Stopcocks 9, 12, 13 and 14 were closed and the system evacuated to a pressure of 10^{-3} mm. of mercury. Then stopcocks 8 and 10 were closed and helium let in slowly through 13 until a pressure of a few millimetres above atmospheric had been reached, as indicated by the small manometer S. Stopcock 11 was closed and 9 opened slowly, allowing the dry helium in the apparatus to reach atmospheric pressure. After waiting ten minutes, pressure readings were taken on the manometer P until two consecutive readings agreed within ± 0.03 mm. This pressure was called " p_1 ". Stopcocks 1 and 2 were closed immediately, thus isolating a volume of dry helium in V_1 at known pressure, volume and temperature. The cross-hair of the cathetometer was set on the mercury meniscus in one arm of the differential manometer D, stopcock 9 closed and 8 and 10 opened. After

waiting five minutes for temperature equilibrium to be attained, 3 was opened slowly and by judicious application of atmospheric pressure through 9 and vacuum through 8, the mercury in the differential manometer was caused to return exactly to its position before expansion. The pressure " p_2 " was read on the manometer P and the volume V_2 calculated from Boyle's Law. A typical calibration is given in detail below.

Calibration No. 18

	810.72	810.80
Cathetometer readings	<u>39.50</u>	<u>39.55</u>
Apparent pressure	771.22	771.25
Manometric correction	<u>-2.97</u>	<u>-2.97</u>
	768.25	768.28
True p_1	768.26	mm.
	355.90	355.93
Cathetometer readings	<u>41.48</u>	<u>41.52</u>
Apparent pressure	314.42	314.41
Manometric correction	<u>-1.23</u>	<u>-1.23</u>
	313.19	313.18
True p_2	313.18	mm.

$$p_1 V_1 = p_2 (V_1 + V_2)$$

$$768.26 \times 106.35 = 313.18 (106.35 + V_2)$$

$$\text{Therefore } V_2 = 154.53 \text{cc. at } 28^\circ \text{ C.}$$

Seventeen calibrations were made, as shown in Table III.

Table III

Measured Volume of $V_2 = 106.35$ at 28°C.

Run No.	p_1 mm.	Average error in p_1	p_2 mm.	Average error in p_2	V_2 cc.
1	751.53	0.03	307.29	0.01	153.64
2	776.21	0.02	316.37	0.05	154.58
3	775.56	0.02	315.98	0.01	154.68
4	773.87	0.01	315.05	0.03	154.88
5	773.10	0.03	314.88	0.08	154.76
6	760.28	0.03	309.06	0.00	155.26
7	757.49	0.17	307.50	0.03	155.85
8	765.92	0.02		..	
9	760.36	0.01	309.22	0.02	155.15
10	755.76	0.01	308.31	0.03	154.34
11	753.12	0.02	306.69	0.01	154.76
12	750.77	0.01	306.27	0.02	154.35
13	752.76	0.02	307.60	0.02	153.91
14	764.24	0.01	313.31	0.06	153.06
15	766.89	0.04	313.19	0.00	154.06
16	751.12	0.03	306.38	0.04	154.37
17	755.11	0.03	307.65	0.00	154.68

These calibrations gave $V_2 = 154.52 \text{ cc.} \pm$ average error 0.28 cc. , and since this accuracy was not high enough for the purpose, an attempt was made to decrease the error.

After considerable experimentation, it was found that the greatest source of error lay in levelling the differential manometer. Up to this time it had been levelled by using an objective of 36-inch focal length on the cathetometer, but

after replacing this with a 3-inch objective, the accuracy with which levelling could be effected was greatly increased because of the much larger image obtained.

The results subsequent to this change in technique are tabulated in Table IV.

TABLE IV

Run No.	p_1 mm.	Average error in p_1	p_2 mm.	Average error in p_2	V_2 cc.
18	768.26	0.02	313.18	0.01	154.53
19	769.88	0.00	313.90	0.03	154.48
20	770.60	0.01	314.12	0.03	154.55
21	759.07	0.02	309.39	0.02	154.57
22	760.68	0.02	310.04	0.02	154.57

These results gave $V_2 = 154.54 \pm 0.03$ cc., and this value was considered sufficiently accurate to be used in all subsequent work.

II - Measurements of the Volume of the Dry Cellulose

After V_2 had been calibrated, it was disconnected from the rest of the system and packed as tightly as possible with standard cellulose, prepared as described in Section I. It was found that more cellulose could be packed into V_2 if it was saturated with water. Previous to packing, the cellulose was dried at 100°C. for 24 hours, weighed, and the amount packed into V_2 determined by difference. The two helical quartz balances were loaded with small pieces from the same batch of cellulose.

The whole system was evacuated through a liquid air trap until the extensions of the balances became constant. Each extension was recorded as "the extension due to the dry cellulose". When these readings were taken, the pumps had been in operation for 48 hours and the McLeod gauge indicated 3×10^{-4} mm. pressure. The procedure used in determining the volume of the dry cellulose was as follows: Cutoff 6 was kept closed, stopcocks 1, 2, 3, 4, 5, 8, 10, 11 and cutoff 7 were open, stopcocks 9, 12, 13, and 14 closed; the whole was evacuated to a pressure of 10^{-3} mm. Then stopcocks 1, 3, 4, 8 and 10 were closed, thus isolating the evacuated volume V_2 . Helium was let into the system through stopcock 13 until the pressure was slightly greater than atmospheric. Stopcock 9 was opened slowly, and after waiting ten minutes, the helium pressure read on the manometer P. Stopcock 2 was closed at once, and 1 opened; after expansion the differential manometer was levelled as be-

fore. From the resulting value for the volume of V_2 minus the volume of the cellulose, the latter was obtained by subtraction. The data for these measurements is given below in Table V.

TABLE V

Volume of V_2 empty - 154.54 cc. at 28° C.

Run No.	P_1 mm.	P_2 mm.	V_2 - Vol. of dry Cellulose cc.	Volume of dry Cellulose cc.	Density of dry Cellulose	Spec. Vol. of dry Cellulose
23	757.91	339.86	130.81	23.73	1.577	0.634
24	753.55	337.87	130.84	23.70	1.580	0.633
25	755.82	338.90	130.83	23.71	1.577	0.633
26	765.28	343.17	130.81	23.73	1.577	0.634
Averages			130.82	23.72	1.577	0.633
Av. errors			± 0.01 cc.	0.01cc.	0.007	0.005

These measurements gave the volume of the dry cellulose =
23.72 $\pm$ 0.01 cc.

Incidentally, the value 0.633 for the specific volume of cellulose agrees quite well with Filby's value of .639 to .642 and Davidson's (33) value of .638 to .642 for soda boiled cotton. This serves as a check on the accuracy of the present work.

III - Measurements of the Density of Adsorbed Water

After the volume of the dry cellulose had been determined, runs were made to determine the density of adsorbed water. The following technique was employed:

With stopcocks 1, 2, 3, 4, 5, 9 and 11 closed, and 8 and cutoffs 6 and 7 open, the water in the bulb B was evacuated for ten minutes with the magnetic stirrer in operation in order to remove most of the dissolved air. Cutoff 6 was closed and the water frozen at the temperature of solid CO₂. After several successive freezings, evacuations and thawings the water was air-free. Cutoff 6 was closed and subsequently opened only when there was a good vacuum in the rest of the system.

The whole system was evacuated to less than 10^{-3} mm., and the cutoff 7 closed. The water bulb B was adjusted to a temperature corresponding to the desired relative vapor-pressure and percent sorption as determined in Section I. Stopcock 5 was closed, the cross hair of the cathetometer adjusted to the meniscus in the differential manometer, and cutoff 6 opened. The system was allowed to reach equilibrium, which took one to three days. A rough estimate of when equilibrium was reached could be obtained from the differential manometer: when the mercury had returned to its original position, the vapor pressures on both sides of V₂ were equal. However, enough time was always allowed so that the quartz balances indicated the same moisture contents.

At this point in the procedure, three different ways of making the expansion were tested out, and only one found to give reproducible results. They were as follows:

- A. Stopcocks 1, 2, 3 and 4 were closed, thus isolating V_1 and V_2 which each contained the same pressure of water vapor. The rest of the system was evacuated, flushed twice with dry helium, then filled with helium at slightly over atmospheric pressure. Stopcock 2 was opened for a few seconds at a time until helium ceased to flow into V_1 . In this way no water vapor could diffuse out of V_1 . The pressure p_1 was read as before and the expansion carried out as previously described except that precautions similar to those mentioned above were used to prevent backward diffusion of water vapor. Stopcock 1 was closed after expansion. Run No. 28 was made in this manner and the value of 49.0 g. per cc. obtained for the density of the adsorbed water. Evidently, when expansion took place, the additional water vapor which passed from V_1 into V_2 caused a displacement of the adsorption-relative vapor-pressure equilibrium, because on attempting to read the pressure after expansion, it was found that frequent re-levelling of the differential manometer was necessary for some time. The final pressure obtained was evidently due in part to a shift in the adsorption equilibrium, so this method was discarded.
- B. The method used was identical with that described in A above, except that stopcock 1 was left open after expansion in the hope that since each volume contained the same pressure of water vapor before expansion, the equilibrium which was disturbed

during expansion would be re-established. Run No. 27 was made by this method and the result 0.611 obtained for the density, so this method was also discarded.

C. The procedure finally adopted was as follows: After equilibrium had been reached, only V_2 was isolated from the system; that is, only stopcocks 1, 3 and 4 were closed. Stopcock 2 was left open and the water vapor in V_1 allowed to be flushed out with the dry helium. The procedure from this point was the same as in A; precautions against diffusion of water vapor from V_2 to V_1 were taken during expansion, and stopcock 1 left closed after expansion. Expansion was considered complete when a rapid opening and closing of stopcock 1 left the level of the mercury in the differential manometer unaffected. This technique gave reproducible values for the density of adsorbed moisture, and was adopted in all subsequent measurements.

The data and calculations for a typical run are given below:

Run No. 33

	<u>Balance M</u>	<u>Balance L</u>
Cathetometer readings	12.425	10.590
	<u>1.597</u>	<u>2.797</u>
Gross extension	10.828	7.793
Unloaded extension	<u>1.032</u>	<u>0.409</u>
	9.796	7.384
Dry extension loaded	<u>9.334</u>	<u>7.030</u>
Extension due to water adsorbed	.462	.354

Run No. 33

	<u>Balance M</u>	<u>Balance L</u>
Water, fraction of dry weight adsorbed	<u>.462</u> 9.334	<u>.354</u> 7.030
Water, percent of dry weight adsorbed	4.95%	5.03%
Average water adsorbed	4.99%	

Temperature of bulb B when cutoff 6 closed: 15.800 C.

Corresponding vapor-pressure of water: 13.46 mm.

Manometer readings:

Cathetometer readings	818.30	818.05
	<u>63.60</u>	<u>63.37</u>
Apparent pressure	754.70	754.68
Manometric correction	<u>-3.03</u>	<u>-3.03</u>
	751.67	751.65
True p_1	= 751.66 mm.	

Cathetometer readings	403.62	403.62
	<u>55.92</u>	<u>55.91</u>
Apparent pressure	347.70	347.71
Manometric correction	<u>-1.38</u>	<u>-1.38</u>
	346.32	346.33
True p_2	= 346.32 mm.	

Calibrated volume of V_1 at 28° C. = 106.35 cc.

$$p_1 \frac{V_1}{v_1} + p_1 \frac{V_2}{v_2} = p_2 (V_1 + V_2)$$

Therefore

$$751.66 \times 106.35 + 13.46 V_2 = 346.32 (V_1 + V_2)$$

Whence $V_2 = 129.50$ cc.

Volume of V_2 empty	154.54 cc.
-----------------------	------------

V_2 - volume of (cellulose + adsorbed water)	129.50
--	--------

Therefore,

Volume of (cellulose + adsorbed water)	25.04
---	-------

Volume of dry cellulose	23.72
-------------------------	-------

Therefore,

Volume of adsorbed water	1.32
--------------------------	------

Weight of dry cellulose	37.428 g.
-------------------------	-----------

Moisture on cellulose 4.99% of dry weight

Therefore, moisture on cellulose = 1.867 g.

Therefore, density of adsorbed water $\frac{1.867}{1.32} = 1.41$ g. per cc.

Experimental Results

The experimental results are tabulated in Table VI.

TABLE VI

Run No.	P_1 mm.	P_2 mm.	Volume of cellulose water	Pressure of Water Vapor .	% water adsorbed	Average density of adsorbed water
27	751.93	341.93	25.29	4.58	2.56	0.611
28	773.26	349.30	23.74	4.58	2.56	49.0
29	754.19	341.57	24.32	4.58	2.63	1.64
30	753.87	341.29	24.23	4.58	2.56	1.88
31	746.32	337.93	24.25	4.58	2.56	1.81
32	752.31	346.58	25.01	13.46	5.04	1.46
33	752.66	346.32	25.02	13.46	4.99	1.41
34	749.03	349.89	25.40	21.19	7.86	1.75
35	756.47	350.93	19.83	24.28	7.00	4.50
36	757.62	356.43	21.07	27.32	7.50	1.28
37	751.15	350.56	21.19	25.23	7.64	1.34
38	759.12	341.26	23.78	1.41	1.34	8.3
39	764.07	343.67	23.91	1.30	1.25	1.89

These results are plotted in Graph 3A.

Discussion of Results

Runs 27 and 28 were discarded because the technique used did not give reproducible results.

The results of runs 34 and 35 were erratic due to condensation of water because the temperature of the room was too close to that of the water bulb.

2.50

2.00

DENSITY OF ADSORBED WATER

1.50

1.00

DENSITY OF WATER ADSORBED AGAINST PERCENT OF ADSORPTION

GRAPH NO 3

CURVE A, AVERAGE APPARENT DENSITY

CURVE B, ACTUAL APPARENT DENSITY

A

B

A

B

0

1

2

3

4

5

6

7

8

9

10

11

WATER ADSORBED, PERCENT OF DRY WEIGHT

Runs at the lowest moisture content (about 1.5%) were most important in checking the work of Filby and Maass. In this region, the absolute volume of water adsorbed is very small, and a slight error in measurement produces a large error in the calculated density of adsorbed water. This was the case in Run 38.

The curve A on Graph 3 showing the variation of the average density of water adsorbed with percent of water adsorbed is of the same general shape as Filby's, although the density values obtained for corresponding moisture contents are considerably smaller.

Values for the actual apparent density of water vapor being adsorbed at a particular percentage of moisture may be obtained in the following way: The volume of water adsorbed per gram of cellulose at a definite percentage of water vapor is subtracted from that adsorbed at another, so also are the corresponding weights of this water, and from these results the density of the water being adsorbed at the mean value of the two percentages of moisture may be found. Thus if "X" be the total volume of water adsorbed on one gram of cellulose at A % moisture, and "Y" the volume corresponding to B %, then the density of the water being adsorbed at $\frac{A + B}{2}$ % of moisture is given by the equation

$$d = \frac{\frac{A}{100} - \frac{B}{100}}{X - Y}$$

This calculation was carried out at various intervals of the curve A Graph 3. The results are given in Table VII and plotted at B in Graph 3.

TABLE VII

Weight of Water A/100 - B/100	Volume of Water X - Y	$\frac{A + B}{2}$	$\frac{d}{A - B}$ (x-y)
0.0175 - 0.0150	.00935 - .00795	1.62	1.78
0.0225 - 0.0250	.0135 - .0121	2.37	1.76
0.0287 - 0.0262	.0159 - .0143	2.75	1.55
0.0300 - 0.0275	.0170 - .0150	2.87	1.26
0.0350 - 0.0325	.0207 - .0164	3.37	1.19
0.0425 - 0.0400	.0278 - .0256	4.12	1.10
0.0525 - 0.0500	.0365 - .0343	5.12	1.14
0.0600 - 0.0575	.0432 - .0410	6.87	1.11
0.0725 - 0.0675	.0457 - .0501	7.00	1.08
0.0850 - 0.0800	.0665 - .0617	8.25	1.04

SECTION III

The Effect of Degree of Vacuum on Hysteresis in Water Sorption by Cellulose

Introduction

Hysteresis loops extending from saturation to practically zero relative vapor pressure have been invariably found by investigators who worked with small specimens of cellulosic material under carefully controlled conditions. In all cases the desorption shows higher moisture-content values than adsorption for the same equilibrium relative vapor pressure.

In a recent paper Hamm and Patrick⁽⁶⁾ have claimed that the phenomenon of hysteresis can be completely eliminated by carrying out the sorption measurements in the absence of permanent gases. These results are not explainable on the basis of the theory of water sorption by cellulose as outlined in the general introduction, so the present investigation was carried out with the object of attempting to produce a change in the magnitude of the hysteresis by changing the degree of vacuum under which the measurements were made.

Previous Work

In the case of certain artificial adsorbents such as silica gel, Gavack and Patrick (21) have attributed the hysteresis to the presence of adsorbed air, but Pidgeon (22) has recently shown that the absence of a hysteresis loop in Patrick's measurements was not due to a complete removal of air as he supposed, but due to changing vapor pressure during sorption.

Patrick believes that cellulose differs from inorganic gels only in that permanent gases such as oxygen are removed with greater difficulty. He favors Zsigmondy's⁽²⁶⁾ explanation of hysteresis on the basis of a difference under adsorption and desorption conditions in the curvatures of the menisci of the liquids filling the capillary spaces, but this explanation is hardly applicable to elastic gels such as cellulose.

Urquhart and his co-workers (10, 11, 12, 13, 14, 23, 24 and Campbell (25) were unable to reduce the hysteresis effects for cellulosic materials, working under reduced pressures of 10^{-3} mm. of mercury.

Apparatus

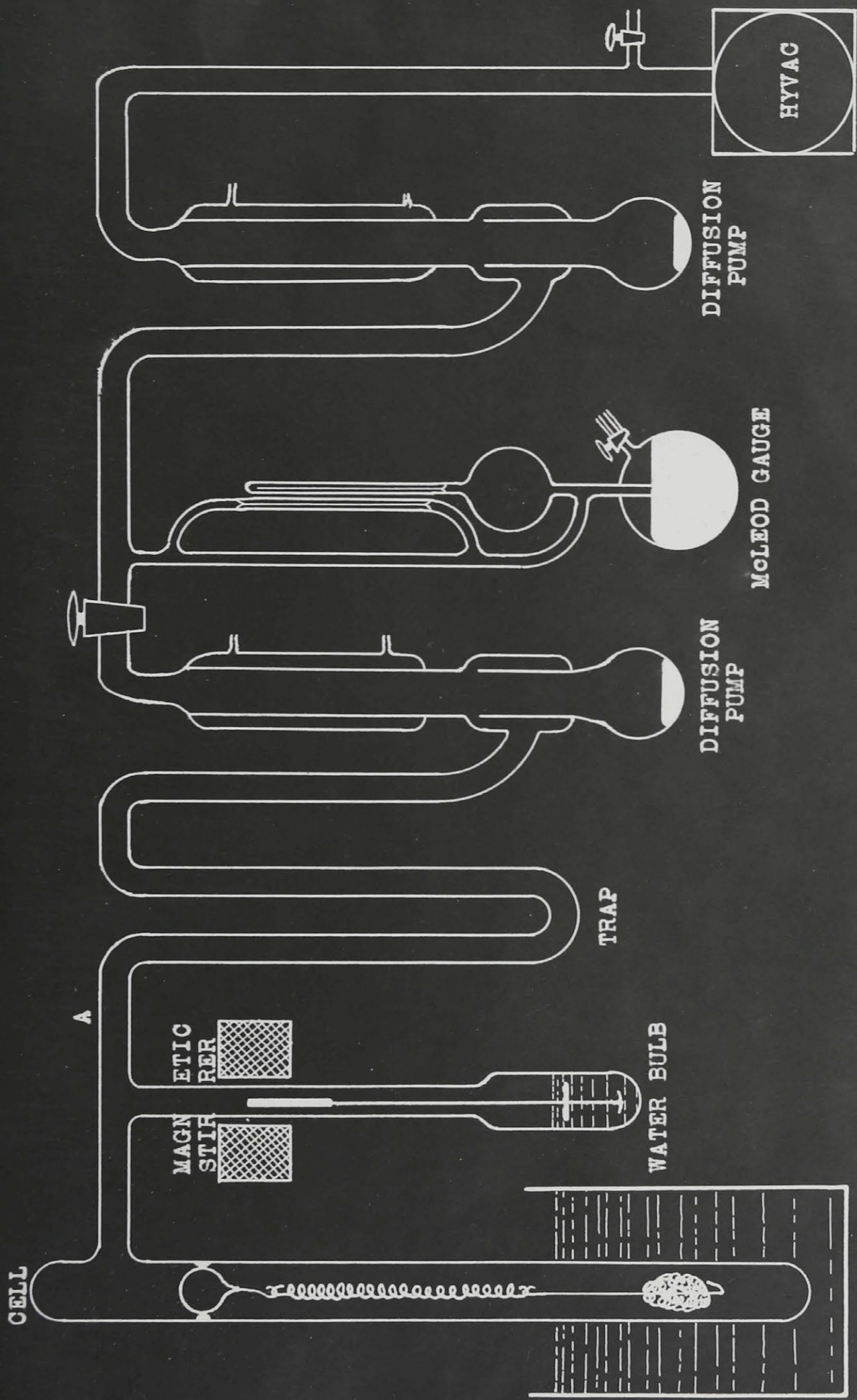
The apparatus was designed with a view to facilitating evacuation to very low pressures, and essentially it consisted of a cell containing a helical quartz balance connected to a source of water vapor.

Figure 4 is a diagram of the final arrangement of the apparatus. The cell, water bulb, and the tubing connecting them to the trap were made of pyrex tubing obtained fresh from the manufacturers, and the inside surfaces were washed once with distilled water because it was realized that glass treated with chromic acid cleaning solution presents a much larger surface for adsorption of gases.

Since speed of evacuation is limited largely by the diameter of the connecting tubing used, the cell was made of 41 mm. O.D. tubing and the trap and connecting tubing of 22 mm. O.D. stock.

A magnetic stirrer was placed in the water bulb, because continual breaking of the liquid surface hastens the attainment of vapor-pressure equilibrium. Due to the fact that metals absorb considerable quantities of gases, the stirrer was completely enclosed in glass.

The cell containing the cellulose sample was thermostated at $28.00 \pm 0.05^\circ \text{C}$. The diffusion pumps used were the Cenco "Supervac" type. The McLeod gauge had a volume of 500 cc. and was calibrated to read 10^{-5} , 10^{-4} , 10^{-3} , and 10^{-2} mm. of mercury. It has been found (5) that in a system containing free mercury, small temperature differences will cause a slow distillation of mercury, so in order to prevent condensation of mercury vapor on the sample, a trap was placed between the cell and the second diffusion pump: this trap was kept cooled by solid CO_2 or liquid air whenever the system was under vacuum.



CONSTANT
 TEMPERATURE BATH
 CELL
 A
 MAGN
 STIR
 ETIC
 RER
 WATER BULB
 TRAP
 DIFFUSION
 PUMP
 McLEOD GAUGE
 DIFFUSION
 PUMP
 HYVAC
 THE HYSTERESIS APPARATUS
 FIGURE 4

The elimination of adsorbed gases from the glass tubing was an important feature of the apparatus. To accomplish this, the tubing connecting the water bulb and cell to the trap was wrapped with resistance wire, as was that section of the cell projecting above the liquid in the constant temperature bath. This enabled the apparatus to be baked out while the pumps were in operation. Only one stopcock was placed in the system, and this was for convenience in making the low vacuum measurements.

Experimental Technique

After the apparatus had been assembled, all joints were tested for leaks with a high-frequency generator. When the apparatus had been made vacuum-tight the preliminary evacuation was carried out as follows: The water in the bulb was frozen, and the trap cooled with solid CO_2 ; the system was evacuated until the McLeod indicated 10^{-2} mm. The stopcock was closed, the ice allowed to melt and then re-frozen. This procedure removed some of the dissolved air. The system was again evacuated to a pressure of 10^{-2} mm. and sealed off at A. The water bulb was surrounded with liquid air for 24 hours and a reading of the extension of the balance due to the dry cellulose obtained.

Measurements of the hysteresis were carried out at this relatively high pressure: Since it was desired only to prove or disprove that the degree of vacuum has an effect on

the hysteresis, it was decided to use one constant vapor pressure of water, namely that corresponding to a temperature of 0° C. This was a convenient point for two reasons: Any temperature control difficulties would be largely eliminated because the water bulb could be surrounded by a large Dewar flask containing enough chopped ice and water to last for the duration of a run. Also, the hysteresis at this relative vapor pressure amounts to a difference in the amounts of water sorbed of about 12%. This is equivalent to about 0.32% of the sample weight, and since the dry cellulose caused an extension of the balance of about 10 cm. which could be read to ± 0.001 cm., the weight of the sample was known with an accuracy of 0.01%. Under these conditions, any change in a hysteresis amounting to 0.32% of the sample weight would be readily measurable.

In order to insure identical conditions for each run, the adsorption points were always approached from a bone dry condition and the desorption points from a thoroughly saturated condition.

In making a run, the water bulb was left in solid CO₂ and acetone for 12 hours, and then a large Dewar flask containing ice and water was placed around the bulb. When the extension of the balance became constant within 0.01 mm. for a ten-hour period, equilibrium was assumed to have been reached and a reading of the extension was taken. The water was removed from the bath thermostating the sample and the ice removed from the water bulb, thus allowing both sample and water to reach the same temperature. After the sample was saturated, which usually took about 12 hours,

the sample was again thermostated at $28.00 \pm 0.05^\circ \text{C.}$, and ice placed around the water bulb. When desorption was complete, a reading was taken as before. The difference between the two amounts of water held gave the magnitude of the hysteresis.

For the measurements under a high vacuum, the sealed-off part of the apparatus at A was re-connected and resistance wire wrapped around that part of the cell projecting from the constant temperature bath. The tubing of the water bulb, and the tubing connecting it to the trap were similarly wrapped.

The water in the bulb was frozen and the hyvac and one diffusion pump were turned on. The water was frozen and melted four times under a pressure of 10^{-3} mm., so as to remove all traces of dissolved gas. Then the water bulb and trap were surrounded with liquid air, and all three pumps turned on. During the evacuation, current was passed through the heating coils so that the inner surfaces of the tubing were kept at about 350°C. A small section of the tubing at A, about 6 inches long, where the apparatus was to be sealed off, was kept at 550°C. , so that when the actual sealing off took place, adsorbed gases would not be given off to any appreciable extent. The constant temperature bath was maintained at 55°C. , in order to decrease to some extent the adsorbed gases on that part of the cell under the surface of the liquid; it is generally agreed that cellulose remains unchanged at this temperature.

After 36 hours under these conditions, the McLeod gauge indicated 1×10^{-4} mm., so it was assumed that the apparatus would be at a pressure of 1×10^{-5} at most, because of the second

diffusion pump. The apparatus was sealed off at A and a check reading made of the extension due to the dry cellulose. Measurements of the hysteresis were made as before.

Experimental Results

TABLE VIII

<u>Pressure 10^{-2} mm. R.V.P. 16.15%</u>				
<u>Condition</u>	<u>Time allowed</u>	<u>Time for equilibrium</u>	<u>% Water on sample</u>	<u>Hysteresis</u>
Saturated	18 hrs.	14 hrs.	15.75	
Desorption	19 "	7 "	2.91	
Dry	32 "	8 "	0.	
Adsorption	16 "	4 "	2.59	0.32
Saturated	23 "	14 "	15.74	
Desorption	20 "	7 "	2.90	0.31
Dry	17 "	8 "	0.	
Adsorption	12 "	4 "	2.59	0.31

<u>Pressure 10^{-5} mm. R.V.P. 16.15%</u>				
Saturated	26 hrs.	14 hrs.	15.75	
Desorption	16 "	7 "	2.66	
Dry	28 "	8 "	0.	
Adsorption	12 "	4 "	2.34	0.32
Saturated	24 "	14 "	15.76	
Desorption	13 "	7 "	2.66	0.32

Discussion

From the foregoing experimental results, the conclusion may be drawn that there is no change in the hysteresis over a pressure range of 10^{-2} to 10^{-5} mm.; that is, within the experimental error, there is no effect from a thousand-fold decrease in pressure.

Although Patrick (6) does not quote numerical values in his paper, he gives a graph showing the adsorption and desorption curves to be almost identical in the absence of permanent gases. However, his adsorption and desorption points at 2 1/2% moisture content differ by about 1 mm., which corresponds to 0.29% water on the scale used; this is certainly of the same order as the hysteresis in that region. Several other pairs of adsorption and desorption points at identical relative vapor pressures differ by a similar amount and in general, the conclusion that hysteresis is eliminated seems scarcely justified by the experimental data.

In view of the present results, it seems very doubtful whether a still lower pressure such as 10^{-6} or 10^{-7} mm. would cause any change in the hysteresis. Any effect due to adsorbed permanent gases, at least in the amounts present in equilibrium with a pressure of 10^{-5} mm., which caused a sudden disappearance of the phenomenon of hysteresis would be difficult to explain on a theoretical basis.

SECTION IV

PART A

The Rate of Moisture Adsorption by Paper.

Introduction

The dimensional changes which take place in cellulose due to changes in moisture content, have been the subject of considerable study. Most of such work has been carried out on a microscopic scale with single fibres. It was thought to be of interest to supplement such information by the dimensional changes in paper under varying humidity conditions, bearing in mind that paper is made up of cellulose fibres held together by the secondary valence forces between separate fibres. As a preliminary to a study of this kind, the rate at which equilibrium is established was made the object of a separate investigation.

Previous Work

The rates of moisture pick-up of papers under various conditions have so far only been studied from the practical standpoint in relation to the processing of paper. What information is found in the literature comes from technical journals

and while of an accuracy sufficient for the purpose in view, it is not adequate to supply the information required.

Klemm (34) found that equilibrium is reached "in a few hours", and that all papers have practically the same rate of moisture pick up.

Davis (35) and Griffin (36), studying the effect of changes in atmospheric relative humidity on the extension of lithographic papers, indirectly measured the rate of change of moisture content.

Shotwell (37) studied the rate of regain on a high speed paper machine and found the rate was proportional to the difference between the initial moisture content and the equilibrium moisture content.

McKee and Shotwell (38) used a direct method for measuring the rates; their method is similar to that used in the present work, but is less accurate. They used a series of small humidity gradients and followed the moisture content of the paper by suspending it from one arm of an analytical balance.

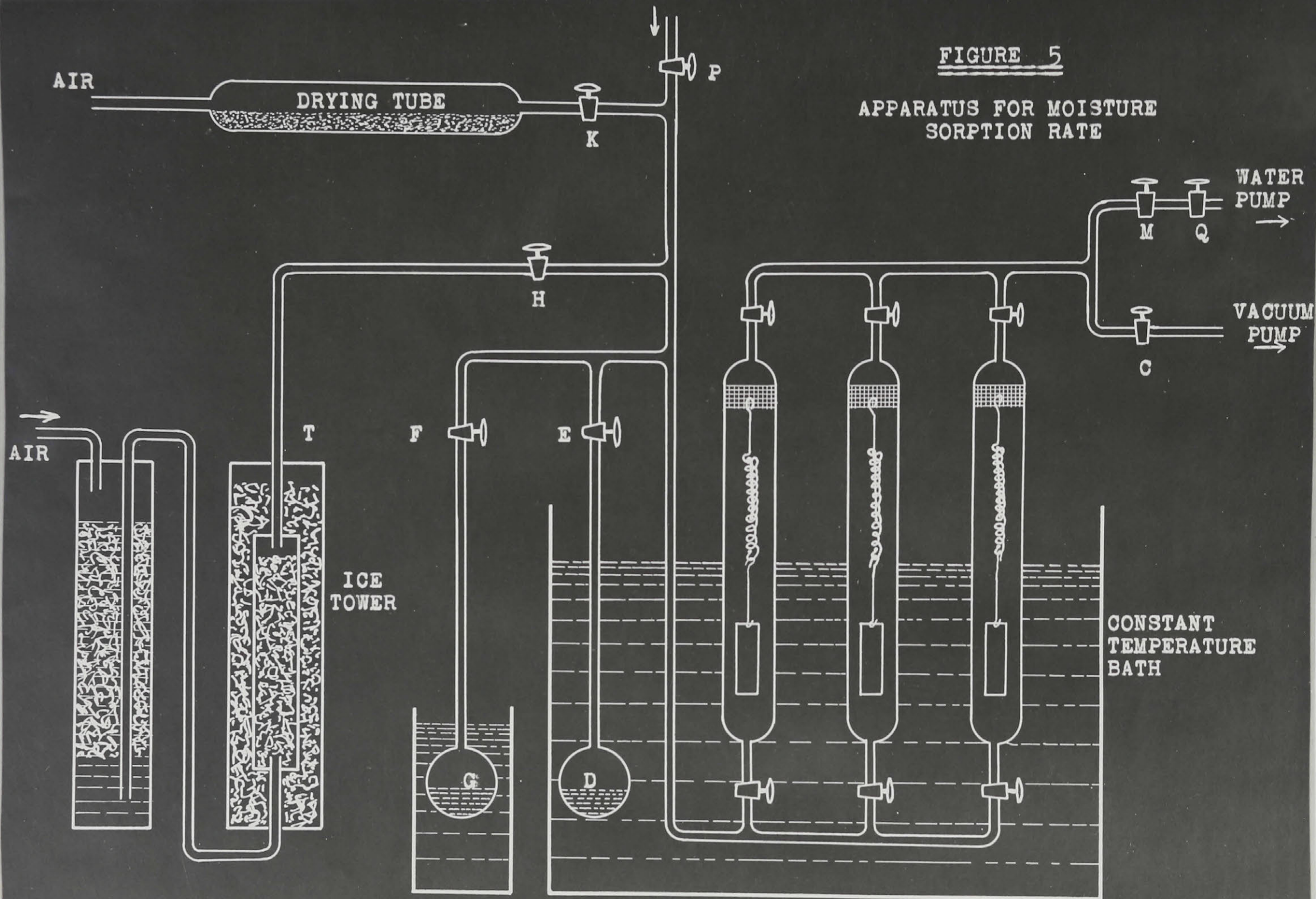
Many investigations on the drying rates of paper have been carried out on a large scale in various paper mills. Montgomery (39), Waters (40), Adams (41), and others have published papers on the results of these investigations. Fisher (42), in his paper "Some Fundamental Principles of Drying", has presented a good theoretical treatment of the subject.

Since previous work on this problem has been carried out mainly on an industrial scale, where uniform methods are seldom used by different investigators, a research performed on a

a laboratory scale under carefully controlled conditions was necessary. The present investigation was undertaken with the above facts in mind.

Apparatus

A diagram of the apparatus is shown in Figure V. The paper samples were suspended on helical quartz balances, completely enclosed in glass, thermostated, and connected to source of water-vapor G and a vacuum pump. Because of the fact that each run lasted only half an hour, the temperature of the bulb G was conveniently controlled by surrounding it with a large dewar flask containing water at the desired temperature. An additional source of water vapor was the bulb D, immersed in the same bath with the paper samples; this gave a constant relative vapor pressure of 68.6% at 30° C., and contained a saturated solution of ammonium chloride and potassium nitrate. For measurements of the sorption rates in air, the vacuum pump was replaced by a water aspirator and two stopcocks M and Q in series, for controlling the rate of air flow. An ice-jacketed ice-tower T was employed to obtain air at a constant low humidity. Air at the higher humidities was obtained most conveniently by humidifying the air in the room by means of steam. Thus the paper samples could be subjected to the following: Water vapor at any relative humidity in the absence of air; dry air; air at one fixed low humidity and air at any high humidity, both the latter flowing at any desired rate. The cells containing the paper samples were arranged in parallel



because only one rate measurement could be made at a time and because it was desired to avoid passing water vapor over any paper sample before it reached the sample undergoing measurement.

The accuracy of the method may be increased almost indefinitely by increasing the sensitivity of the helical springs; this may be effected by decreasing the diameter of the quartz threads because the sensitivity of the balance is inversely proportional to the fourth power of the diameter of the thread.

Experimental Method

Three types of paper were used, bond, newsprint and glassine. Each sample was about 40 sq. cm. in area. The papers were folded once, but in such a manner as to avoid contact between paper surfaces because this would hinder free access of water vapor. The bath surrounding the papers was thermostatically controlled to a temperature of $30.00 \pm .05^{\circ} \text{C}$.

In making runs, all stopcocks except C were closed, and the apparatus evacuated with the hyvac and mercury diffusion pumps. E and F were opened intermittently and the liquids in the bulbs G and D alternately frozen and thawed. In this way, most of the air was removed from the system. Evacuation was continued until the paper samples ceased to lose weight, when the extensions due to the dry papers were recorded.

The method used for the runs in vacuum employed the following procedure: Bulb G was set at a temperature corresponding to the

desired relative vapor pressure and initial moisture content. Stopcock F was opened and one hour allowed for attainment of equilibrium. Then F was closed and the temperature of G changed to correspond to the final humidity required. The cathetometer was focused on the lower reference point of the quartz balance, and F opened. As soon as the balance started to extend, a stopclock was started and readings of the extension taken every 30 or 60 seconds.

The three cells were arranged in parallel, with a separate pair of stopcocks for each, so that when E or F was opened, the water vapor would flow directly on to the required sample without previously passing over either of the other samples.

Readings of the extension were taken until the rate of adsorption became too slow to be conveniently measurable.

For measurement of the sorption rates in air, a water aspirator, connected through two stopcocks M and Q, was used to draw a current of air through the paper samples. First, the papers were dried by a very slow current of air from the phosphorous pentoxide tube; then humidified to the initial low humidity by drawing air through the ice-tower. The air flow rate was adjusted to the desired value and air drawn in from the room through P, H being closed. Measurements of the extension and time were taken as before. The air drawn in from the room was maintained at any constant high humidity by blowing steam into the room and checking the humidity frequently with a sling psychrometer.

The ice tower was not a wholly satisfactory method of obtaining a constant low humidity, so in the later runs moisture was desorbed from the samples by a current of dry air, the desorption being followed with the cathetometer and stopped as soon as the desired moisture content was reached.

Experimental Results

Each run was calculated on the basis of per cent sorption against time, and since the final and initial moisture contents were known, the times to half- and three-quarters-value could be obtained from the graphed results.

The rate curves were reproducible, but only to 1 or 2% due to the fact that the initial water content in duplicate runs varied somewhat because of hysteresis effects. In Table 9 are given experimental results for thirty-one runs including the times for half- and three-quarters-value.

Some representative types of rate-curves are included here in order to show the general shapes corresponding to different humidity gradients.

Table IX on page 51.

TABLE IX

IN VACUUM, 30° C

Relative Humidity Gradient %	Time to Half-Value, mins.			Time to Three-Quarters value, mins.		
	<u>Glass-</u> <u>ine</u>	<u>Bond</u>	<u>News</u>	<u>Glass-</u> <u>ine</u>	<u>Bond</u>	<u>News</u>
14.36 to 68.6	2.1	1.0	1.2	3.9	2.2	2.6
68.6 to 14.36	1.1	0.7	0.7	1.5	1.6	2.8
0. to 14.36	30.5	2.5	0.5	70.(?)	6.0	0.75
0. to 68.6	3.5	1.2	1.0	5.3	2.4	2.0
14.3 to 90.0	3.0	3.5	2.1	8.2	9.5	6.2

IN VACUUM, 40° C

14.3 to 68.6	1.9	0.9	0.9	3.4	2.4	2.4
--------------	-----	-----	-----	-----	-----	-----

IN AIR, 30° C. 1000 cc/min.

17 to 92	...	...	2.5	...	...	6.5
21 to 92	4.0	...	...	10.0	...	...
12 to 92	...	3.5	...	...	8.0	...

IN AIR, 30° C. about 200 ml/min.
(Actual rate in brackets.)

21 to 92	...	...	15(180)	...	...	42 (180)
14.3 to 98	...	20.0 (110)	...	...	60 (110)	...
16.0 to 95	18.5(150)	...	...	50.0(150)	...	...

IN AIR, 30° C. about 500 ml/min.
(Actual rate in brackets)

2 to 98	...	...	5.8(600)	...	...	14.7 (600)
5 to 98	...	8(585)	...	...	22(585)	...
10 to 96	7 (550)	...	...	21(500)	...	...

Glassine	Density	1.2
Bond	"	0.8
News	"	0.6

The details of a typical run are included below:

News No. 10, No. 1 Tube

In vacuum, 30° C.

Relative Humidity Gradient 14.36% to 68.6%

Extension of unloaded balance 0.230 cm.

Extension due to dry paper 7.007 cm.

Upper reference point 12.712.

<u>Time</u>	<u>Reading</u>	<u>Extension</u>	<u>% Sorption</u>
0sec.	5.192	.283cm.	4.04
30	5.030	.445	6.36
60	4.947	.528	7.55
90	4.897	.578	8.27
120	4.863	.612	8.74
150	4.836	.639	9.12
180	4.814	.661	9.44
210	4.796	.679	9.70
240	4.785	.690	9.85
270	4.777	.698	9.98
300	4.767	.708	10.12
330	4.761	.714	10.19
360	4.759	.716	10.22
390	4.752	.723	10.32
420	4.750	.725	10.36
8min.	4.743	.732	10.45
9	4.738	.737	10.52
15	4.725	.750	10.72
30	4.712	.761	10.87
60	4.709	.766	10.95

Discussion of Results

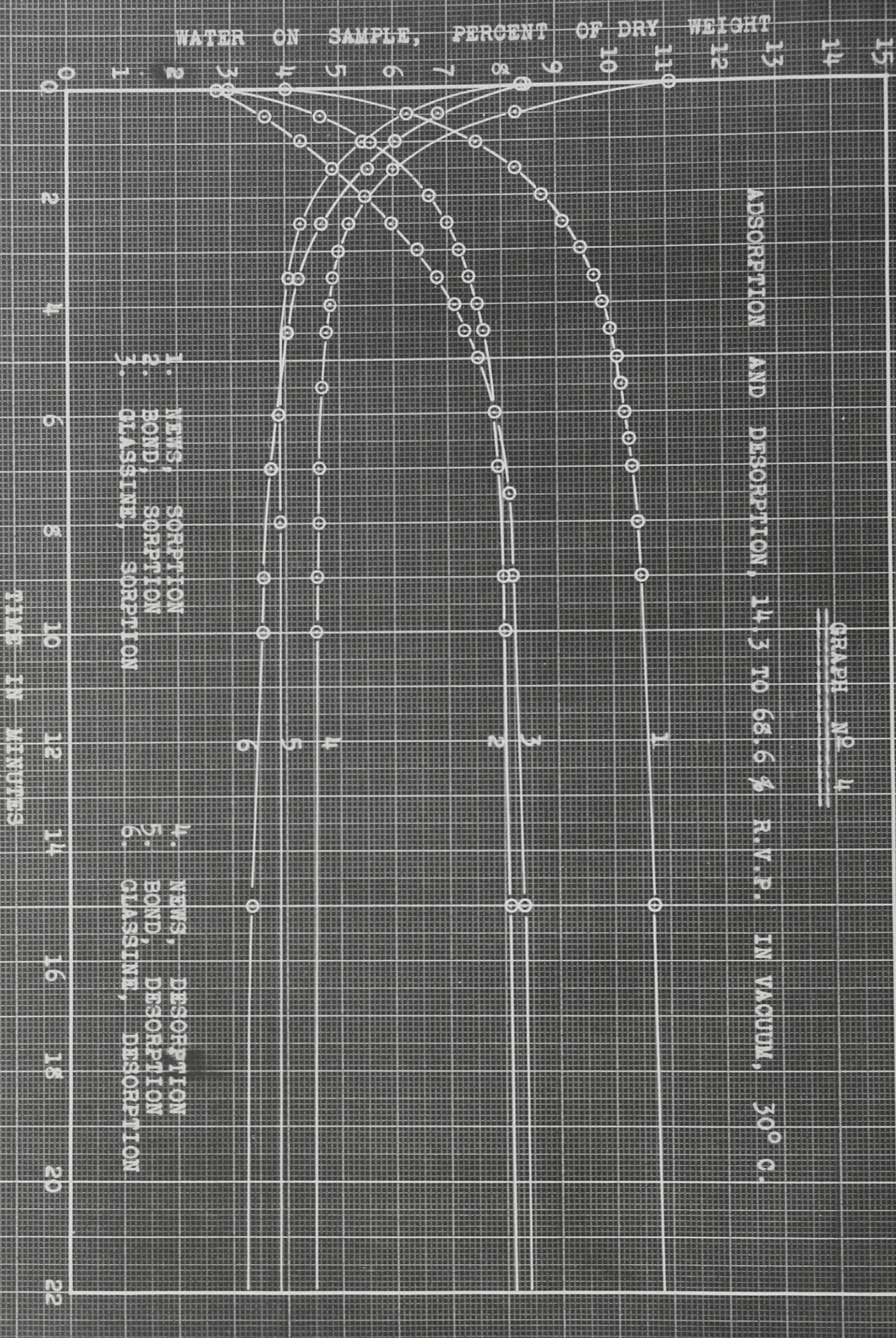
(A.) In Vacuum

On Graph IV are shown the adsorption and desorption rate-curves for the three papers under a moderate humidity gradient of 14.36% to 68.6% relative vapor-pressure. The times to half-value are all of the order of one to two minutes and 95% of the final moisture content is attained in 25 minutes. For all practical purposes, this time may be considered sufficient for attainment of equilibrium. It must be clearly borne in mind however, that these results are for a single sheet where water vapor has free access to the material, and that they do not apply to cases where this condition is not fulfilled. Contrary to what might be expected, the desorption is slightly faster than the adsorption. This may be only apparent, because in calculating the times to half-value, the final moisture content in desorption was assumed to be the same as the initial moisture content in adsorption: this assumption was not strictly justified because of hysteresis effects.

Adsorption from an initial dry state up to a low moisture content shows a much greater variation in the times to half value: these results are plotted on Graph V. Newsprint gives the same general type of rate-curve as it does under a larger relative humidity gradient. There is the same rapid adsorption in the first minute which may be attributed to surface adsorption of water vapor which diffuses rapidly into the porous macrostructure of the paper. This rapid pick-up of moisture may also be

GRAPH NO. 4

ADSORPTION AND DESORPTION, 14, 3 TO 68.6 % R.V.P. IN VACUUM, 30° C.



GRAPH NO 5

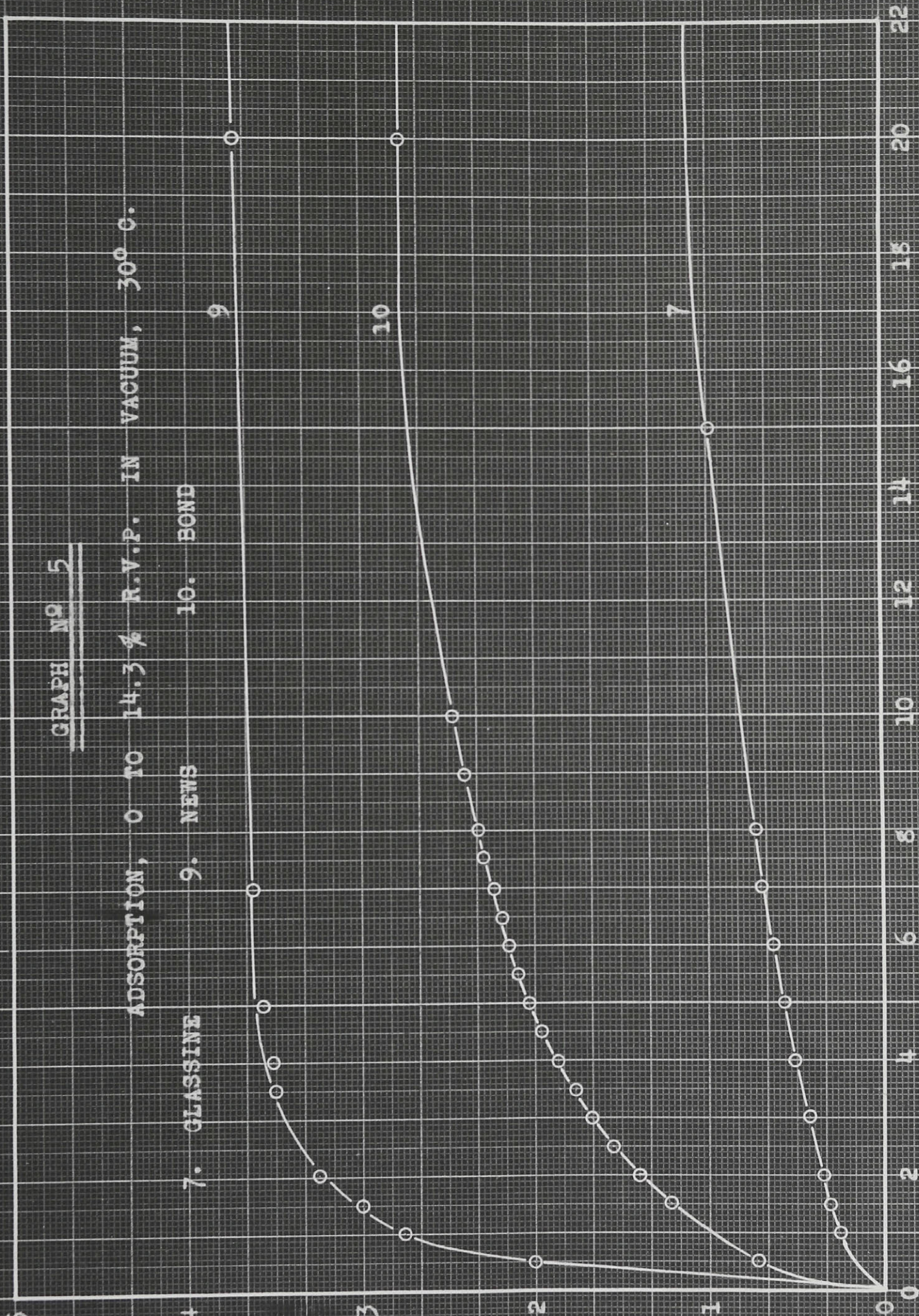
ADSORPTION, 0 TO 14.3% R.V.P. IN VACUUM, 30° C.

7. GLASSINE 9. NEWS 10. BOND

PERCENT OF DRY WEIGHT

WATER ON SAMPLE,

TIME IN MINUTES



attributed to a certain amount of opening up or swelling of the cellulosic material. The glassine paper shows a much slower adsorption rate under the same small humidity gradient. This is probably due to the fact that the density of glassine is double that of newsprint, and the greater density of the paper structure slows down diffusion of water vapor. The time to half-value for adsorption from a dry state up to 2.7% moisture (in equilibrium with 14.36% R.V.P.) is 30.5 minutes. A duplicate run was made to check this value. The bond paper was much more like the newsprint, although they differed more in this humidity range than in any other investigated.

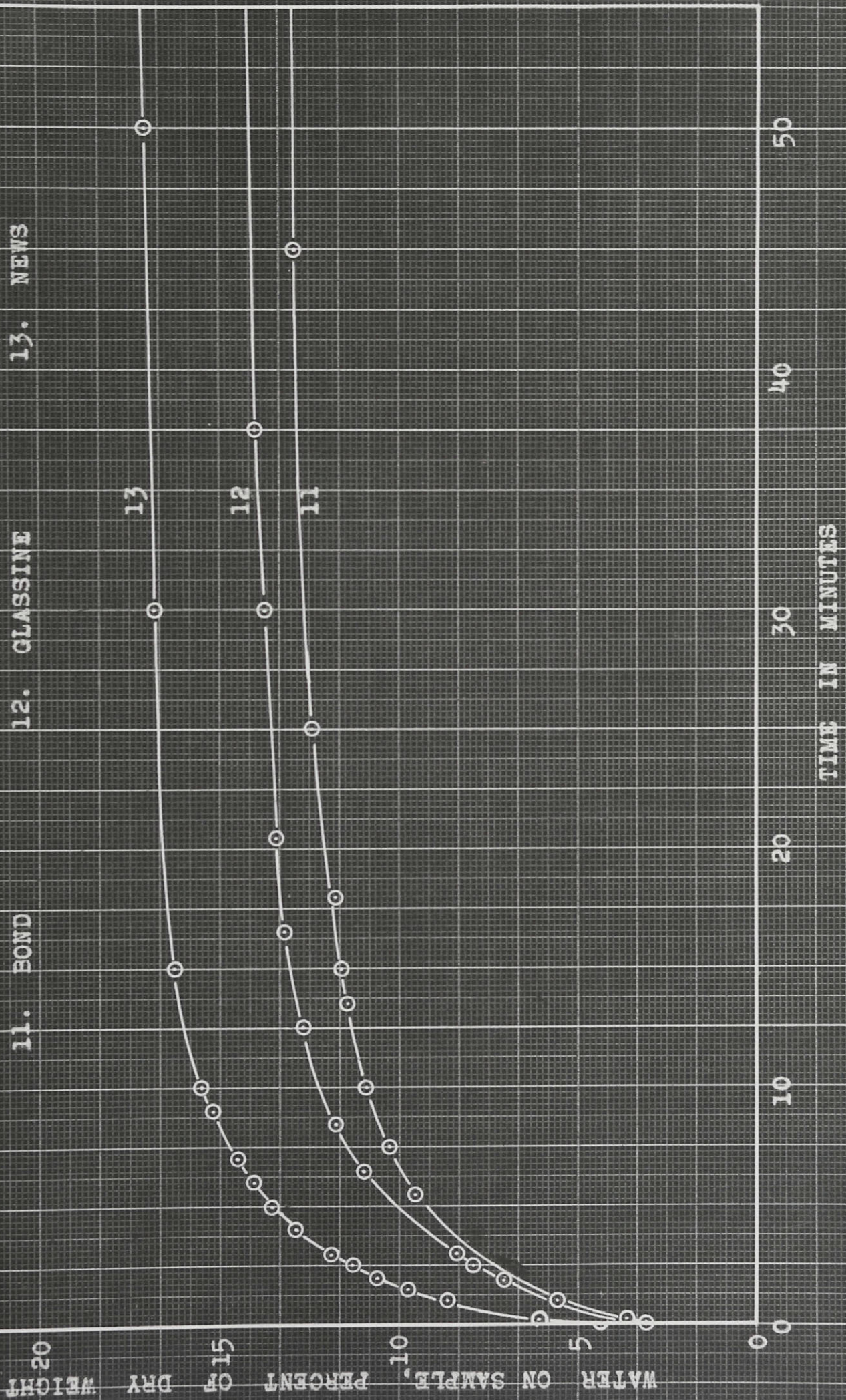
The effect of a ten-degree increase in temperature in the range 14 to 68% relative humidity was very small and resulted in a slight decrease in the times to half-value. This seems to indicate that the determining factor in the rate of adsorption of moisture by paper is a property characteristic of the paper itself. If the rate had depended for instance, on the rate of diffusion of water molecules to the paper, it would be expected that temperature would have a considerable influence on the observed sorption rate, because the diffusion coefficient for vapors is proportional to the square of the absolute temperature.

Over a wide humidity range there is very little difference in the rates and the curves all have similar shapes. This is brought out in Graph VI, and may be interpreted to mean that when the difference between the initial moisture content and the equilibrium moisture content is sufficiently great, the three papers behave in almost exactly the same manner.

GRAPH NO 6

ADSORPTION, 14.36 TO 90 % R.V.P. IN VACUUM 30° C.

11. BOND 12. GLASSINE 13. NEWS



Newsprint is made from ground wood and contains a certain proportion of lignin. It adsorbs considerably more water than the other two papers, which are almost pure cellulose, so that for a given difference between the initial moisture content and the equilibrium final moisture content, the newsprint would be expected to take a longer time to reach half-value. From the experimental results, this is found to be the case in the range 14.3 to 68.6% relative humidity: the newsprint takes longer than the bond, although the glassine is slower than either of the other two.

The density of the three papers seems to play a greater part in the lower humidity range.

It is interesting to compare the times to half-value of these papers in the absence of air with the corresponding value for cotton cellulose. A value of 3.5 minutes was obtained for this material in Section I, using a gradient of 0 to 60% relative vapor pressure. This value was not recorded in Section I, because it was obtained only incidentally.

(B.) In Air

In air, the rates are much slower than in vacuum, both because diffusion of water vapor to the paper is greatly slowed down in the presence of air, and because the absolute amount of water vapor available per unit time is decreased.

The actual rate of moisture adsorption naturally depends both on the nature of the paper and the rate of supply of moisture, so runs were made at various speeds of air flow.

In Graph 7 are shown the results for the glassine paper under a large humidity gradient of 10 to 98% relative humidity and for three different air velocities. The rate at the lowest velocity is at first determined entirely by the rate of supply of moisture, as is evidenced by the initial linear part of the curve. Graphs VIII and IX show similar curves for Bond and Newsprint at different rates.

On Graph X are plotted the times to half-value against rate of air flow for each paper. The corresponding times to half-value in vacuum are indicated on the graph. In the case of newsprint and glassine, it is evident that the times to half-value in air approach those in vacuum as the rate of air flow is increased, and become asymptotic at about 1800 cc. per minute. This corresponds approximately to 25 - 45 cc./min./cm² of paper.

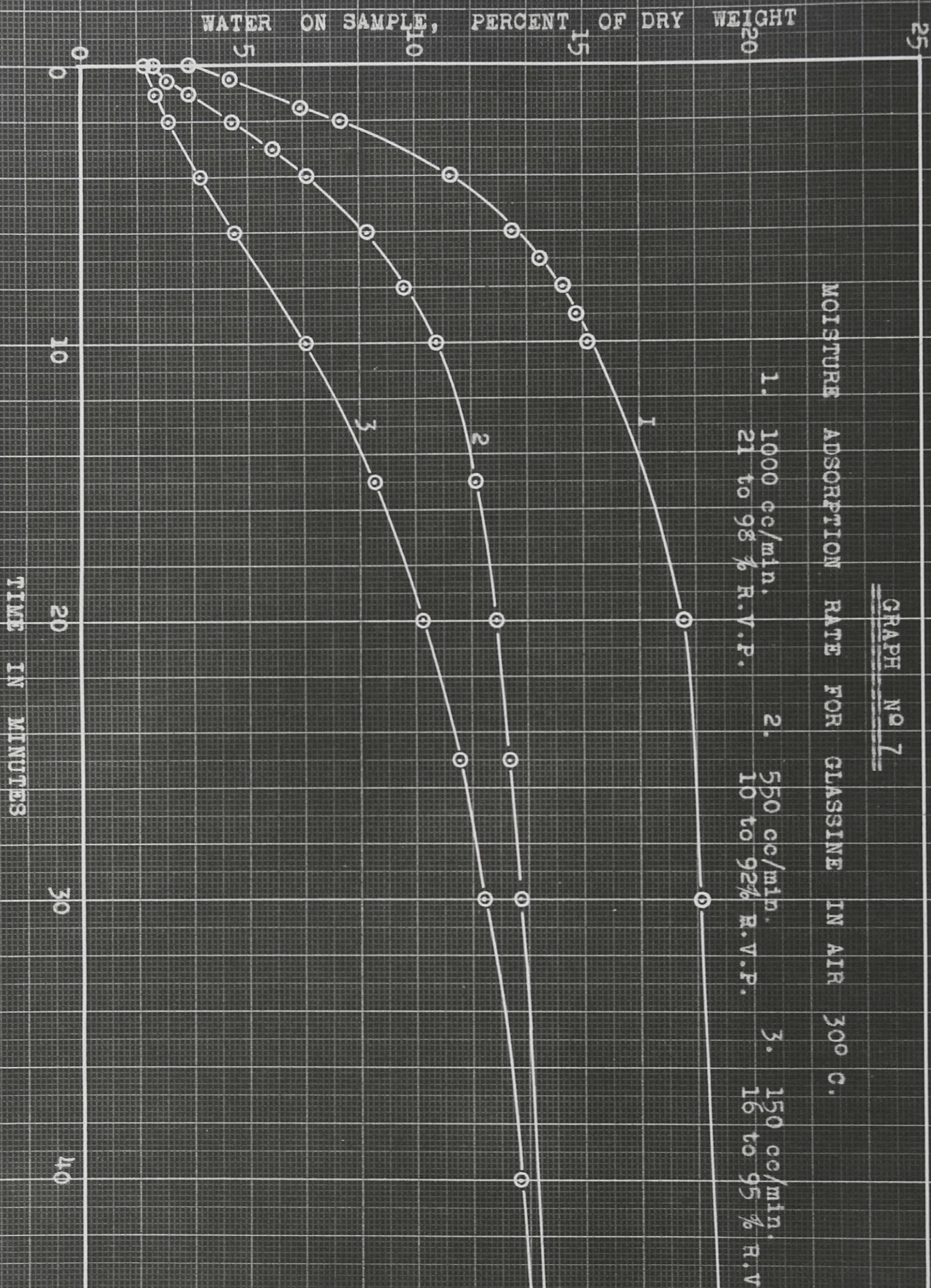
In the case of bond, the curve is not asymptotic to the rate in vacuum. It should not be assumed that the rates in vacuum are necessarily greater than those in air, because of the following considerations:

When water vapor adsorbs on cellulose, the heat of adsorption is given out and this raises the temperature of the surface of the sample, thus decreasing the amount of water held. The magnitude of this effect will be greater for the measurements made in vacuum, because in this case the heat generated is not dissipated as rapidly as when the sample is in a current of air.

GRAPH NO 7

MOISTURE ADSORPTION RATE FOR GLASSINE IN AIR 300 C.

1. 1000 cc/min. 21 to 98 % R.V.P.
2. 550 cc/min. 10 to 92% R.V.P.
3. 150 cc/min. 16 to 95 % R.V.P.



GRAPH NO 8

MOISTURE ADSORPTION RATE FOR BOND IN AIR 30° C.

1. 1000 cc/min.
12 to 92 % R.V.P.
2. 585 cc/min.
5 to 100% R.V.P.
3. 110 cc/min.
14.3 to 98% R.V.P.

WATER ON SAMPLE, PERCENT OF DRY WEIGHT

TIME IN MINUTES

25

20

15

10

5

0

10

20

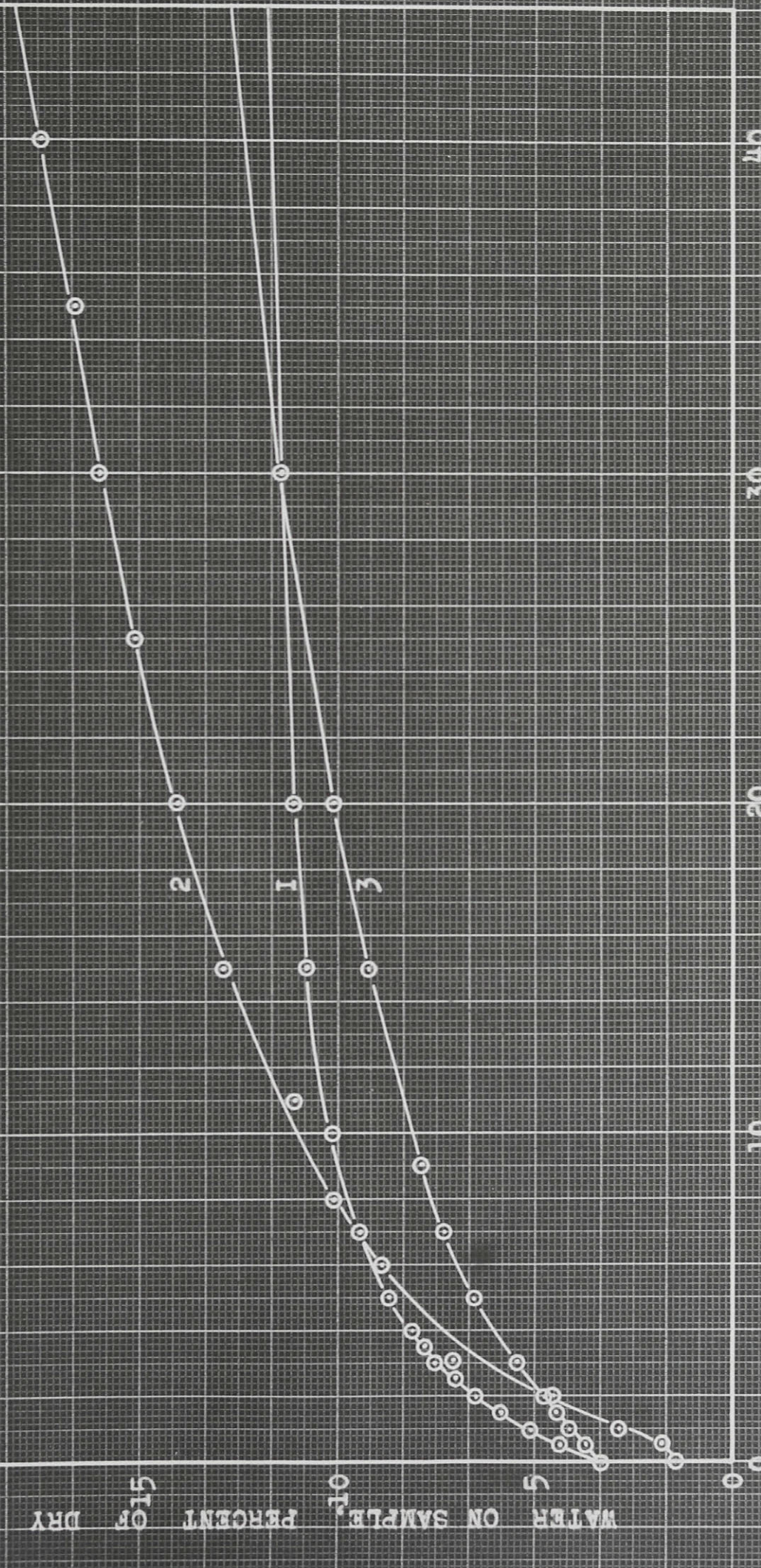
30

40

2

1

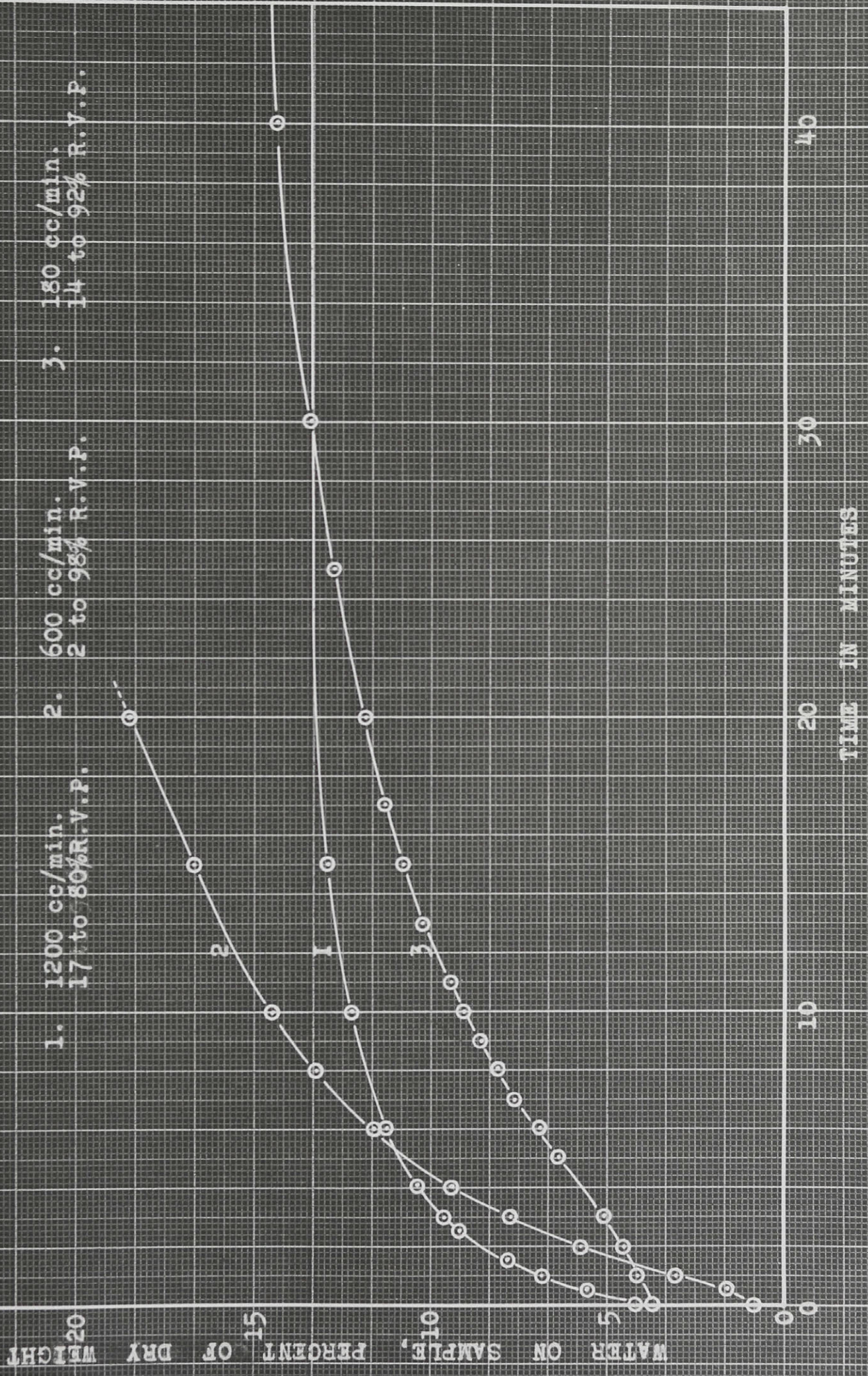
3



GRAPH NO 9

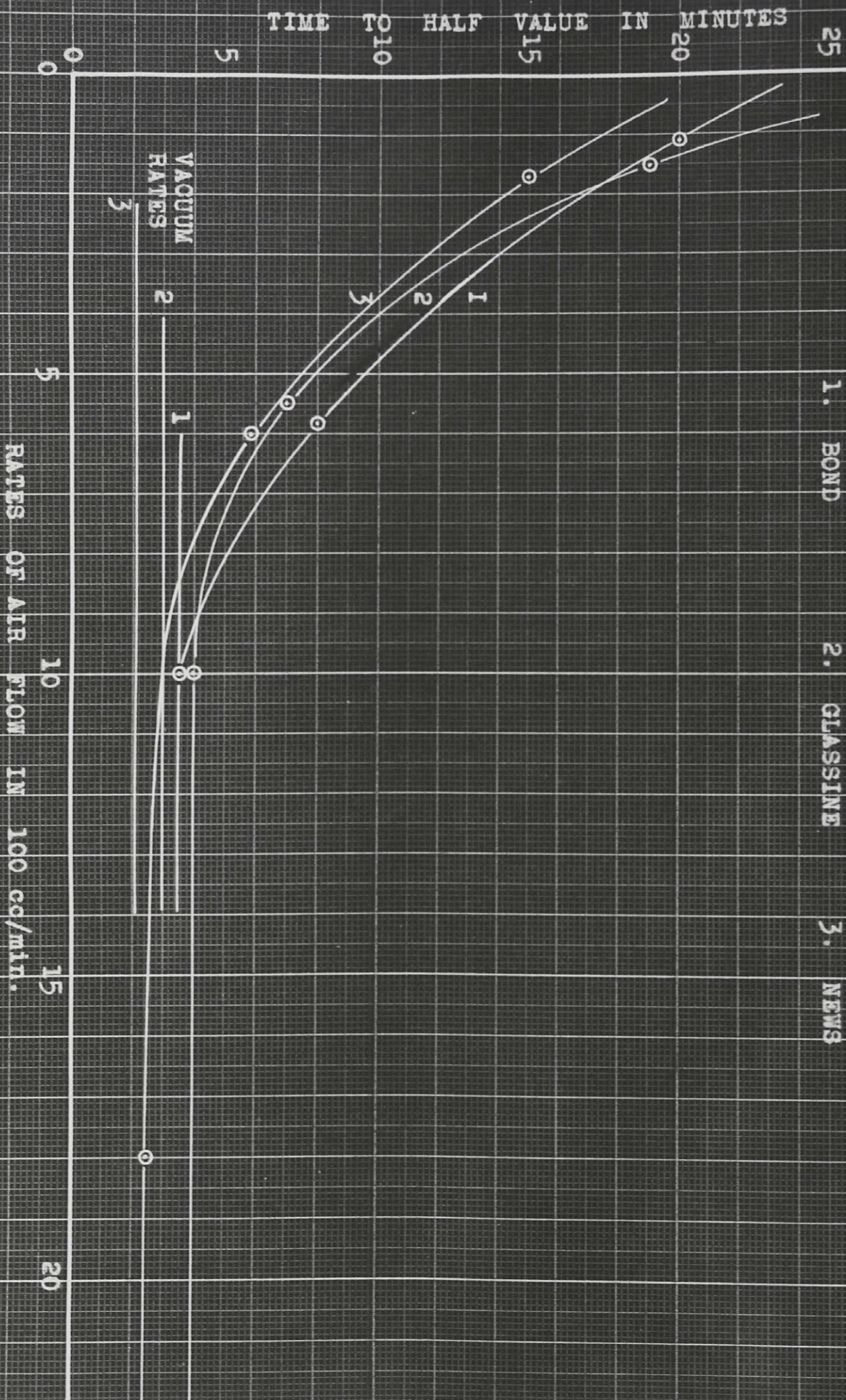
MOISTURE ADSORPTION RATE FOR NEWS IN AIR, 30° C.

- 1. 1200 cc/min.
17 to 80% R.V.P.
- 2. 600 cc/min.
2 to 98% R.V.P.
- 3. 180 cc/min.
14 to 92% R.V.P.



GRAPH NO 10

TIME TO HALF VALUE AGAINST AIRFLOW RATE
1. BOND 2. GLASSINE 3. NEWS



For purposes of reference, sorption-relative-vapor-pressure curves for the three papers are given in Graph XI.

Conclusions

The greatest differences in the moisture adsorption rates of bond, glassine and newsprint in the absence of air, occur in passing from a bone dry condition to a low moisture content which is in equilibrium with a relative humidity of about 14%.

The effect of a 10° C. increase in temperature on the adsorption rate is almost negligible.

Plotting the rates of sorption in air against the corresponding velocities of air flow shows that the rates in air approach those in vacuum at about 25 - 45 cc./min./cm² of paper.

The conclusion reached was that the adsorption rate depends on the way the fibres are held together, and measurements of the rate do not lead to information about the separate fibres.

GRAPH N^o 11

ADSORPTION ISOTHERMS FOR WATER VAPOR ON PAPER 30° C.

1. NEWS

2. GLASSINE

3. BOND

WATER ON SAMPLE, PERCENT OF DRY WEIGHT

20

15

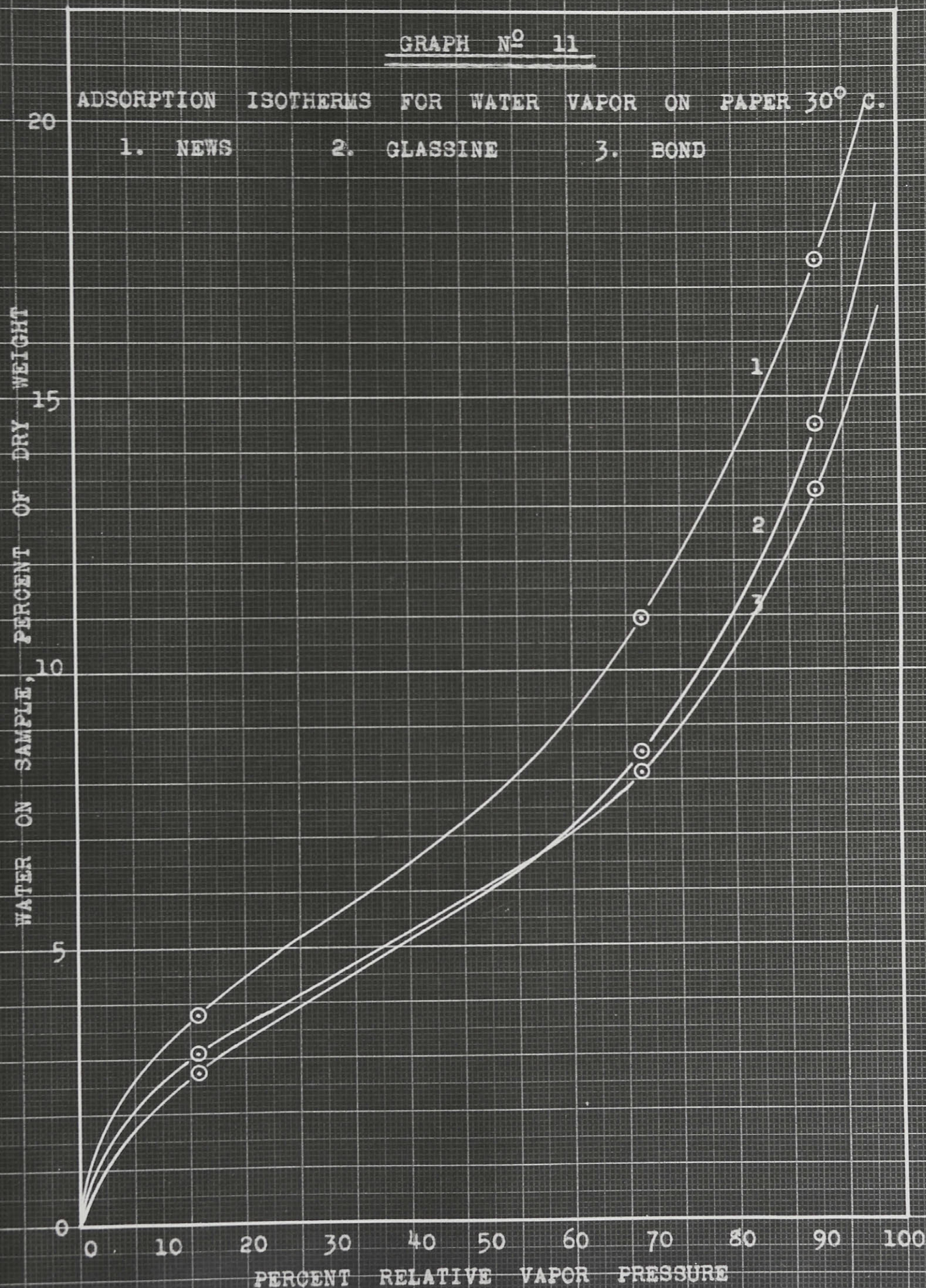
10

5

0

PERCENT RELATIVE VAPOR PRESSURE

0 10 20 30 40 50 60 70 80 90 100



SECTION IV

PART B

Hysteresis in the Extension of Paper by Moisture.

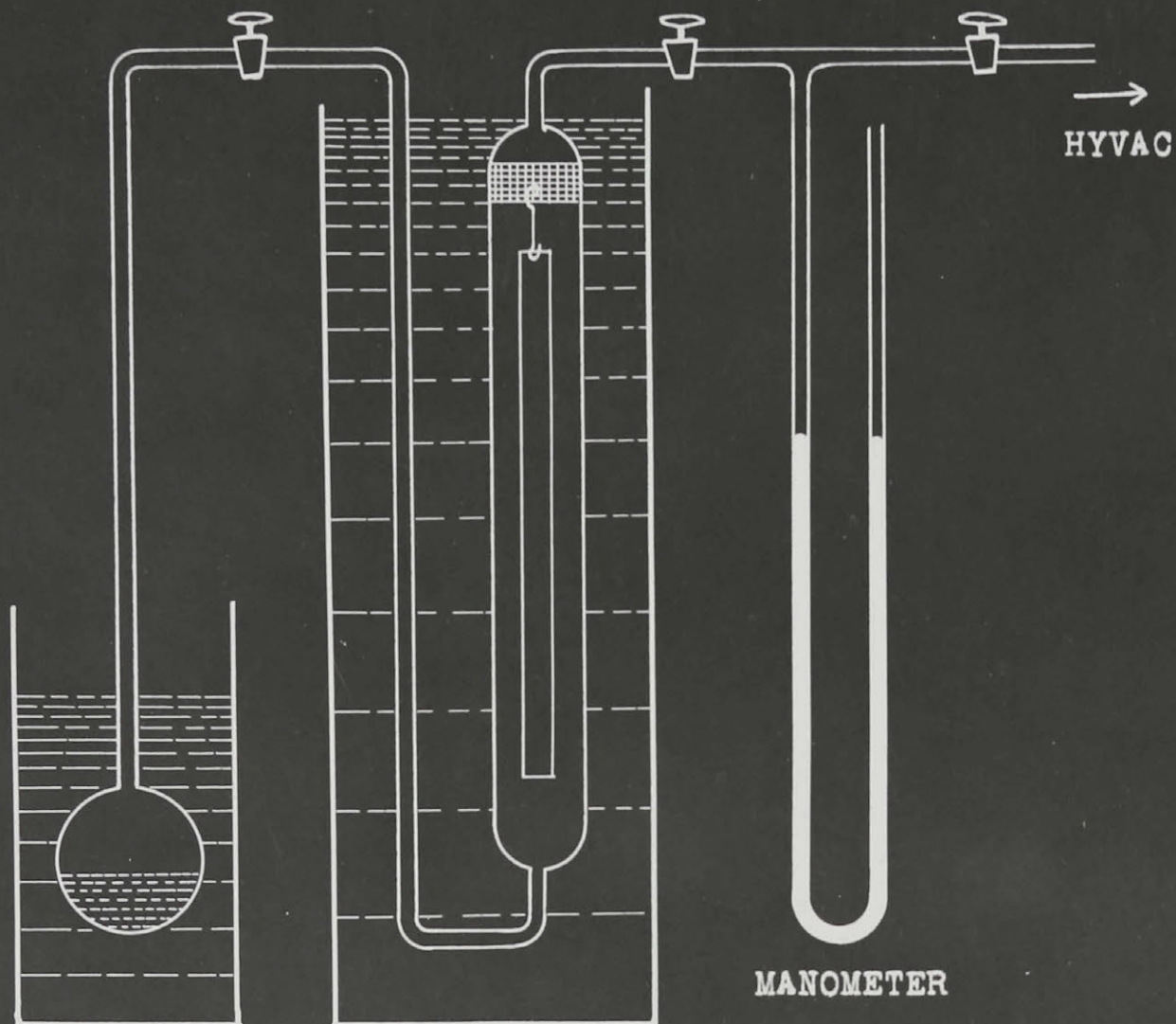
Introduction

When paper is subjected to a high humidity, the strains created in the manufacture of the sheet are to some extent released, and subsequent changes in relative humidity produce smaller changes in the dimensions of the sheet. It was the purpose of this investigation to determine the humidity necessary to release these strains and to determine the effect of temperature on the extension.

Apparatus

The apparatus consisted of a cell to contain the paper sample, a water bulb and magnetic stirrer, a manometer and hyvac pump. The apparatus and details of arrangement of the paper sample are shown in Figure VI. The temperature of the water bulb was controlled as before by surrounding it with a large Dewar flask filled with water at the desired temperature.

WATER
BULB



CONSTANT TEMPERATURE BATHS

MANOMETER

DETAIL OF
PAPER SAMPLE



FIGURE 6

APPARATUS FOR PAPER EXTENSION

In making runs, the humidity was varied in definite steps and the extension of the paper sample measured by means of a cathetometer. The equilibrium extension was reached in about one hour in the majority of cases.

Experimental Results

The results for a number of humidity cycles on a sample of unconditioned newsprint are given in Table X below:

TABLE X

Newsprint No. 10, Cross Direction.
Effective Length 36.5 cm. 25°C.
No Previous Treatment

<u>R.V.P.</u> <u>%</u>	<u>Extension</u> <u>cm.</u>	<u>Extension</u> <u>%</u>
19.42	0.122	0.334
53.89	0.195	0.532
19.42	0.110	0.301
53.89	0.203	0.556
19.42	0.116	0.317
53.89	0.192	0.525
80.96	0.324	1.128
53.89	0.277	0.757
19.42	0.124	0.338
53.89	0.221	0.604
19.42	0.129	0.353
53.89	0.223	0.610
80.96	0.317	1.153
53.89	0.240	0.657
0.00	0.000	0.000
19.42	0.106	0.290
53.89	0.223	0.610
80.96	0.317	1.153
53.89	0.245	0.670

These results are plotted in Graph XII.

The first six points show the result of the cycle 19.4% to 53.8% to 19.4% R.V.P. etc., in which the hysteresis is quite pronounced. However, after two exposures to an R.V.P. of 81%, this hysteresis is decreased.

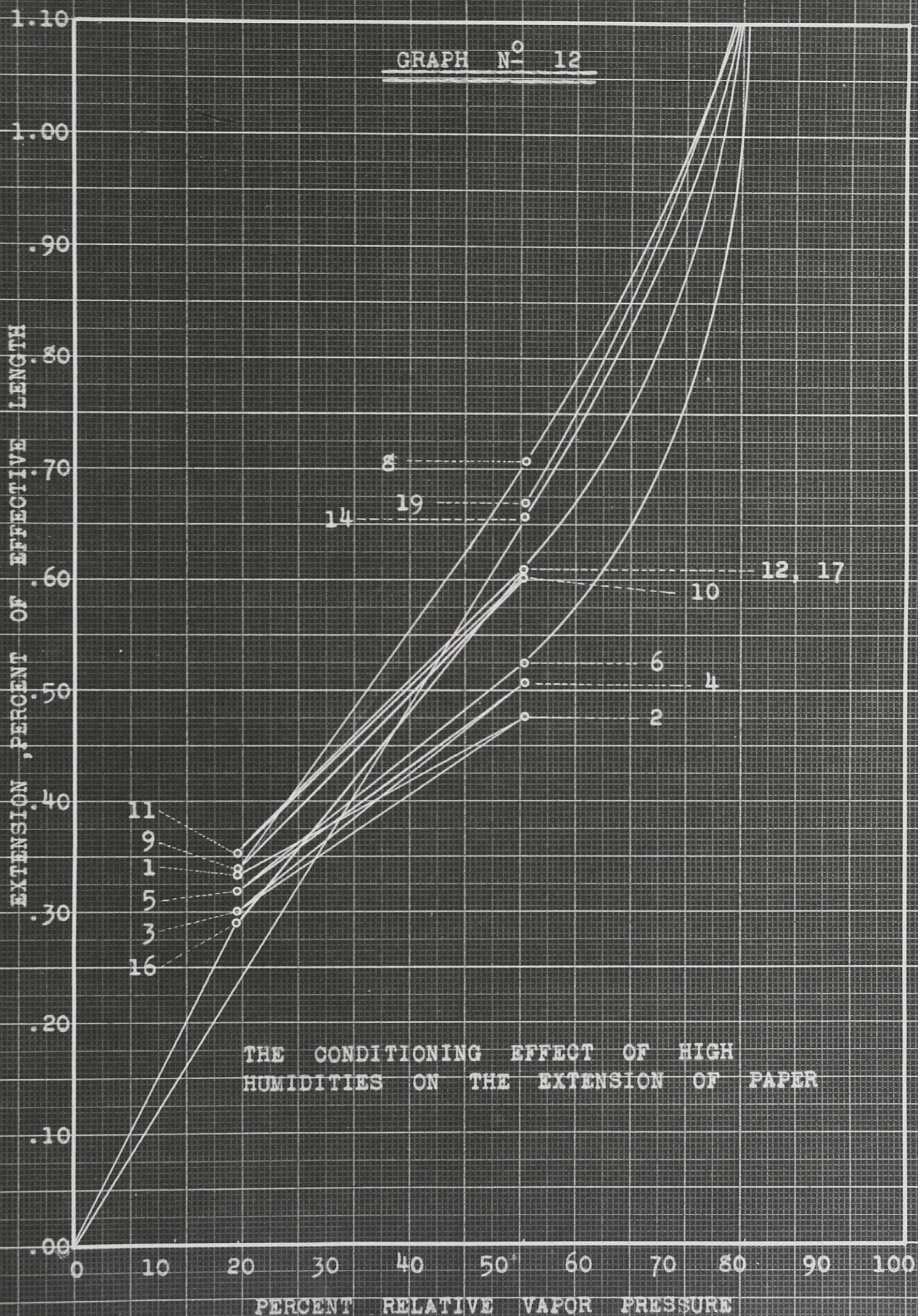
Table XI shows the data for an extension-relative vapor-pressure curve for the newsprint sample, as this was required for the purpose of obtaining a relation between water content and extension.

TABLE XI

Newsprint No. 10, Cross Direction.
Effective Length 36.5 cm.
Previously Conditioned
as in Table XII.

<u>R.V.P.</u> <u>%</u>	<u>Extension</u> <u>cm.</u>	<u>Extension</u> <u>%</u>
0.00	0.000	0.000
1.25	0.026	0.072
2.50	0.038	0.115
3.75	0.046	0.127
5.00	0.062	0.172
7.50	0.070	0.194
10.00	0.080	0.222
12.50	0.088	0.244
15.00	0.095	0.263
28.60	0.144	0.400
40.00	0.175	0.486
50.00	0.202	0.580
70.00	0.251	0.696
90.00	0.354	0.018

GRAPH N^o 12



On Graph XIII is plotted a curve for water content against extension. This was obtained by combining the data for relative humidity against extension in Table XI with the data for relative vapor-pressure against adsorption from Graph XI in Section IV A. The curve is almost linear, which means that equal extensions take place for equal amounts of water adsorbed.

Table XII is a determination of the temperature coefficient of expansion of newsprint at constant relative humidity.

TABLE XII

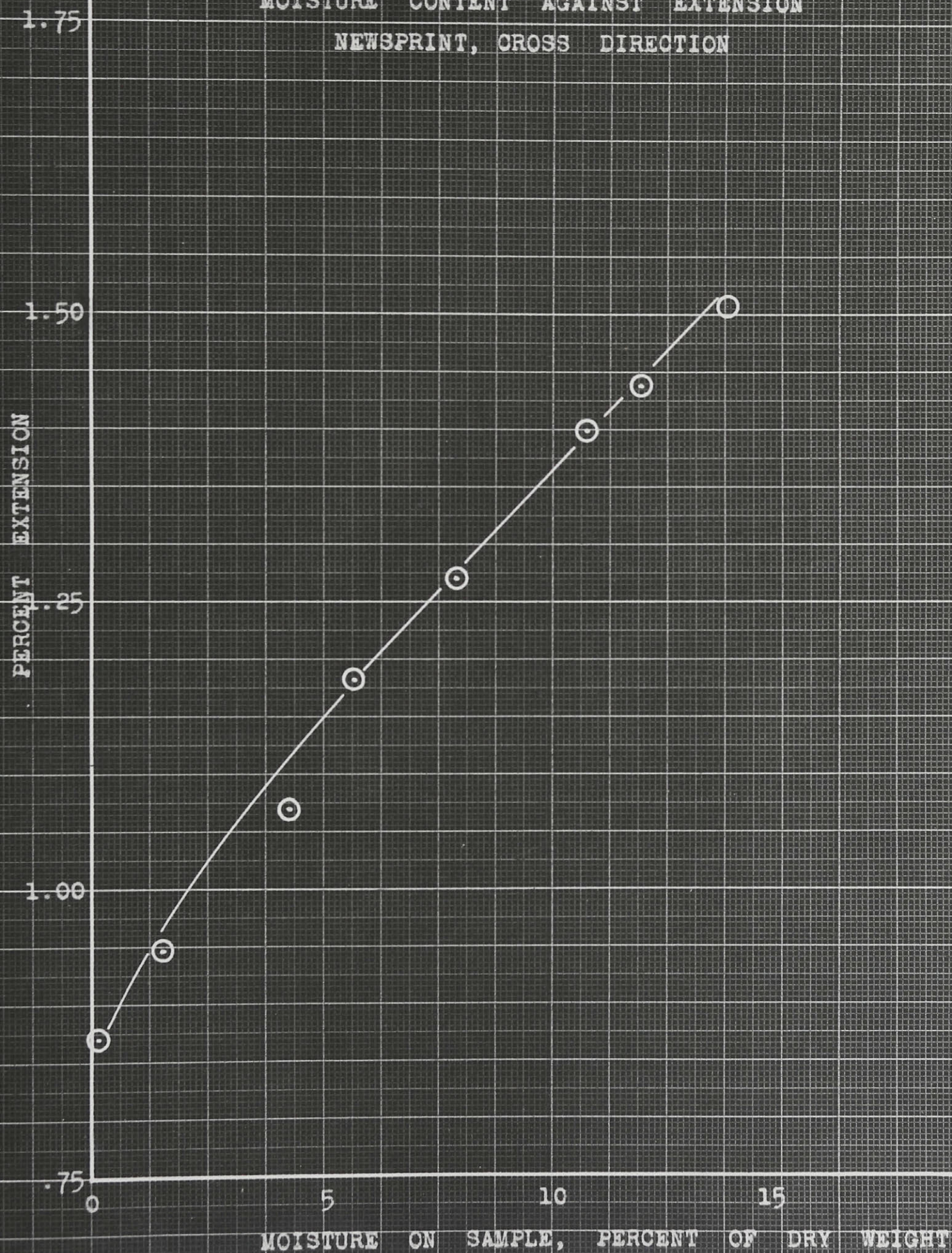
Newsprint No. 10, Cross Direction
R.V.P. 40%

Temp. °C.	Extension cm.	Corr. for wire Expansion	Corr. Extension cm.	Corr. Extension %
7.0	.000	.000	.000	.000
25.0	-.019	.009	-.010	.032
30.9	-.025	.003	-.022	.060

From this data, it can be seen that there is a very small negative temperature coefficient of extension. This agrees with the negative temperature coefficient of water adsorption by cellulosic materials in general.

GRAPH N° 13

MOISTURE CONTENT AGAINST EXTENSION
NEWSPRINT, CROSS DIRECTION



In the following table is shown the effect of conditioning on the extension of a bond paper.

TABLE XIII

Bond No. 8, Cross Direction
Effective Length 40.0 cm
Conditioned between 25 and 80% R.V.P.

<u>R.V.P.</u> <u>%</u>	<u>Extension</u> <u>cm.</u>	<u>Extension</u> <u>%</u>
0	0.000	0.000
5	0.056	0.140
35	0.230	0.575
70	0.429	1.072
90	0.660	1.650
70	0.474	1.185
35	0.268	0.670
5	0.073	0.182
0	0.000	0.000

Same sample, Unseasoned
Machine Direction

19.8	0.097	0.242
70	0.195	0.487
90	0.258	0.645
70	0.198	0.495
19.8	0.82	0.205
0.	0.000	0.000

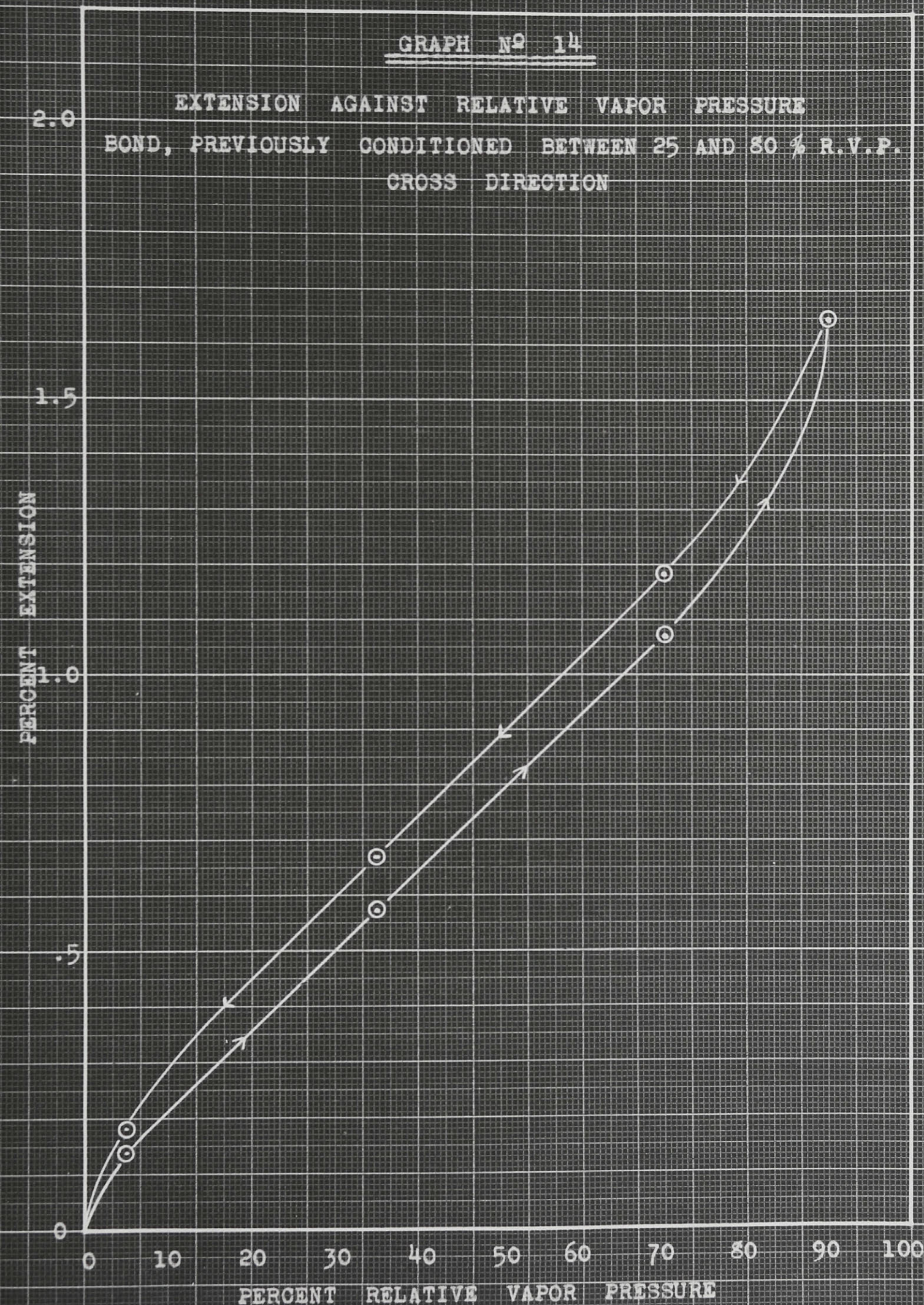
These results are plotted on Graphs XIV and XV.
The latter shows the phenomenon of negative hysteresis.

GRAPH No 14

EXTENSION AGAINST RELATIVE VAPOR PRESSURE
BOND, PREVIOUSLY CONDITIONED BETWEEN 25 AND 80 % R.V.P.
CROSS DIRECTION

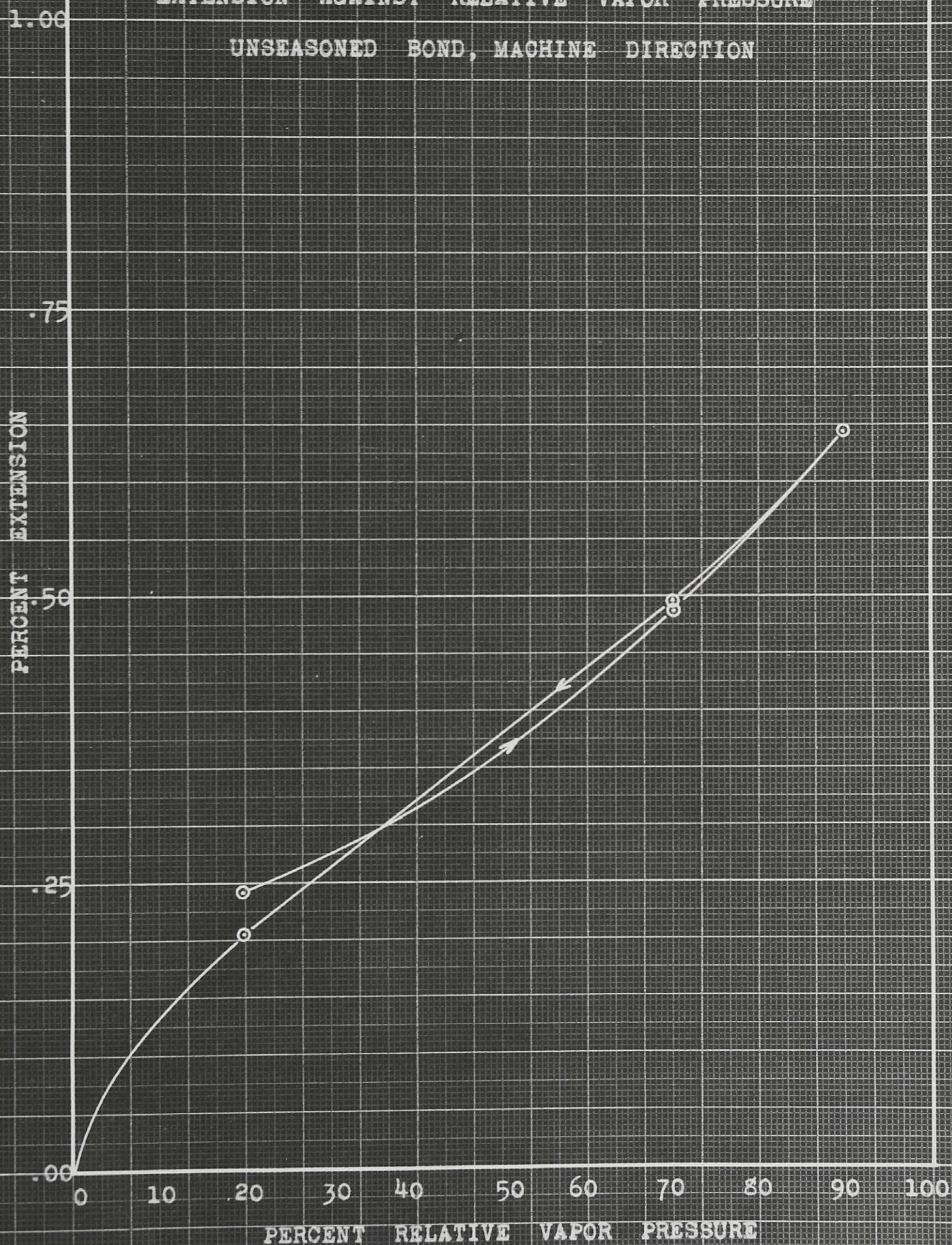
PERCENT EXTENSION

PERCENT RELATIVE VAPOR PRESSURE



GRAPH NO 15

EXTENSION AGAINST RELATIVE VAPOR PRESSURE
UNSEASONED BOND, MACHINE DIRECTION



Discussion of Results

In Graph XII are shown several humidity cycles which were carried out on a fresh sample of newsprint. Points 1 to 6 show the changes in extension for the range 19.4 to 54% relative vapor-pressure. The first cycle, points 1 to 3, resulted in a shrinkage of the paper. The second cycle showed a small extension over the first cycle. After treatment at a high humidity followed by desorption, the paper returned very nearly to its original condition at the lower humidity (point 9), although it showed a large hysteresis (point 8) at an intermediate humidity. Subsequent measurements over the same cycle as before showed that the paper had been permanently changed by exposure to the high humidity. A second treatment at the high humidity still further reduced the hysteresis.

It has been suggested that the irreversible changes which take place when paper is subjected to moisture-content changes are due to the release of strains present in the sheet as a result of the manufacturing processes. These strains may have arisen through the following mechanism: When the suspension of pulp is allowed to flow on to the moving screen of the paper machine, there is a tendency for the fibres to orientate themselves so that they lie in a direction parallel to the direction of motion, that is in the "machine direction". This orientation is of course not complete and it is merely assumed that more fibers lie in the machine direction than in any other.

When most of the water is removed from the suspension, the wet sheet is dried by application of heat; this procedure is carried out in such a way that the sheet of paper is under considerable tension in a direction parallel to its length, and it is supposed that this tension strains the fibres out of their equilibrium positions. Since this takes place while the paper is drying, the strains set up are present in the finished sheet of paper.

When the paper adsorbs moisture at a high relative humidity the strains are at least partially released, and the paper tends to contract in one or both directions. On the other hand hysteresis also takes place on desorption which results in an apparent increase in dimensions. Thus the observed change in dimensions is the result of these two opposing factors.

The results obtained from Graph XII may be explained on this basis. After treatment at a high humidity, the behaviour is quite different as far as dimensional changes with changing humidity are concerned.

The same explanation may be applied to the negative hysteresis shown in Graph XV. The contraction effect due to the releasing of strains causes a large contraction of the paper which is sufficient to outweigh the normal hysteresis effect. Thus the net effect is a contraction of the sheet.

It is noteworthy that the time required for attainment of equilibrium is longer for the extension measurements than in the adsorption measurements, indicating that there is a time lag between the adsorption of moisture and the dimensional changes

resulting from that adsorption.

The extension in the machine direction is small compared with the extension in the cross direction, because of the greater number of fibres which are more or less orientated in the machine direction. When a cellulose fibre adsorbs water, the micelles, which are more completely orientated in the direction of the fibre length, swell laterally, due to adsorption of water on their surfaces. Since the width of the micelle is very small in relation to its length, nearly all the dimensional change takes place in a direction at right angles to the length of the micelle. The same holds true of the whole fibre which is composed of a large number of micelles. Thus, expansion is greater in the machine direction than in the cross direction.

Measurements carried out on a microscopic scale indicate that cotton fibres show no appreciable increase in length when adsorption of water takes place, but that the dimensional change is nearly all due to an increase in the diameter of the fibre.

A P P E N D I X

An Attempt to use Reflected Light as a Means of Measuring Projection Areas and Coagulation of Wood-Pulps

Introduction

Previous investigation (1) by the writer had shown that it was possible to utilize, within certain limits, the intensity of light reflected from suspensions of wood-pulp as a means of measuring relative projection area; and that this method might be employed to measure the swelling or coagulating effect of electrolytes on pulps. Accordingly, a continuation of this investigation was undertaken.

However, the nature of the results obtained after several months' work indicated that further research along these lines would be of little value, so this project was abandoned; but since several interesting points were brought out, it was considered worth while to report them here.

Previous Work

In 1935, an apparatus (1) was developed to measure the projection area per gram of suspensions of wood-pulp. The characteristics of this instrument have been thoroughly in-

(1) F. Walker, M.Sc. Thesis, McGill University, 1935.

vestigated and in what follows, it will be designated "the standard area machine".

A diagram of the standard area machine is shown in Figure I and a brief description of the apparatus and its operation follows:

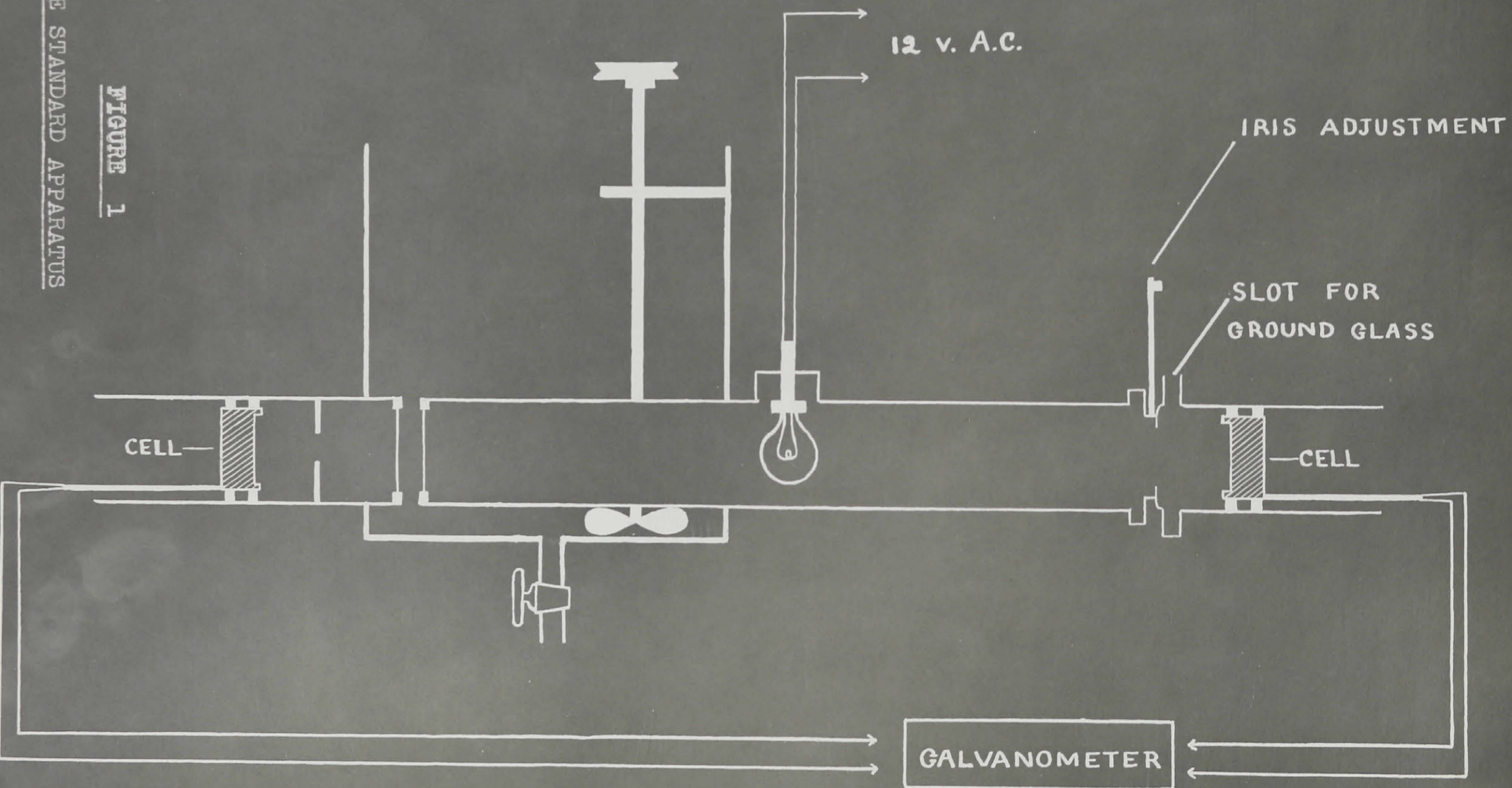
The apparatus embodies the null-point method and briefly it consists of two photo-cells on opposite sides of a common light source; the quantity of light reaching the first cell may be varied by means of an iris diaphragm, and a piece of ground glass may be interposed between the iris and the cell. Each cell is connected, in a separate electric circuit, to the coils of a differential galvanometer, arranged so that the currents are opposed to one another. In operation, the light source is turned on, the container filled with air-free water and the diaphragm adjusted so that the galvanometer reads zero i.e., is balanced. A standard piece of opal glass is placed in the slot provided, thus decreasing the intensity of light reaching one cell; the suspension of pulp is now added in sufficient quantity to decrease by an equal amount the intensity of light reaching the second cell, thereby causing the galvanometer to return to zero. After determining the concentration, a number proportional to the projection area may be obtained, as described below.

Theory

For the theory of the standard area machine, the reader is referred to the previous work (1) on that instrument.

THE STANDARD APPARATUS

FIGURE 1



In brief, the conclusion is reached that if "a" is the projection area per gram of the suspended material, and "c" is the concentration of this material required to balance the standard area machine, then

$$a \propto \frac{1}{c}$$

the above relationship holds only when $\log_{10} \frac{I_0}{I_x}$ is not greater than 0.5. By choosing a ground glass plate having a transmittancy of 40% or more, the validity of the relationship used above is assured.

Apparatus

A glass battery jar of 8 litres capacity was used as a container for the pulp suspension; the exterior of the jar was painted a matte black. Two small windows, one in the side and one in the bottom, were left, in order to measure the light intensity. The top of the jar was covered with black crepe, with a small opening for a stirrer.

A Weston Photronic photocell was placed contiguous to the glass opposite the side window, and a 250-watt projection lamp placed opposite the bottom window. A second photocell was arranged opposite the light source, for measuring the latter's intensity. The photocells were connected, through a double-pole, double-throw switch and suitable resistances, to a D'Arsonval galvanometer with lamp and scale.

Since the deflection as measured on the scale was not quite linear in its relation to the light intensity, a

potentiometer was hooked up in such a way that each scale reading could be obtained in millivolts.

A diagram of the apparatus is shown in Fig. 2.

To prevent light reaching the lateral cell directly, a bakelite cylinder was suspended inside the battery jar and a circular aperture cut so as to come directly opposite the cell. In this way, the only light reaching the cell was that scattered at about 90° from the suspension.

Initially it was found that stray currents were obtained from the photocells even when in total darkness; these were due to electrolytic effects from the acid soldering flux, and were rapidly eliminated.

Experimental Method

The light source was turned on and its intensity adjusted to the value to be used during the run. The cells were allowed to fatigue for 15 minutes, water poured into the jar, and then sufficient pulp added to produce the desired consistency. Then a reading of the galvanometer was taken, corresponding to the intensity of light reflected from a suspension of this particular concentration. One or two litres of the suspension were filtered, the pulp dried at 105° C. for an hour, and the concentration calculated. More pulp was added, enough to give a slightly lower concentration, and the measurements repeated. In this way was obtained a curve, concentration against intensity of light scattered at about 90° .

FIGURE 2
THE REFLECTION APPARATUS

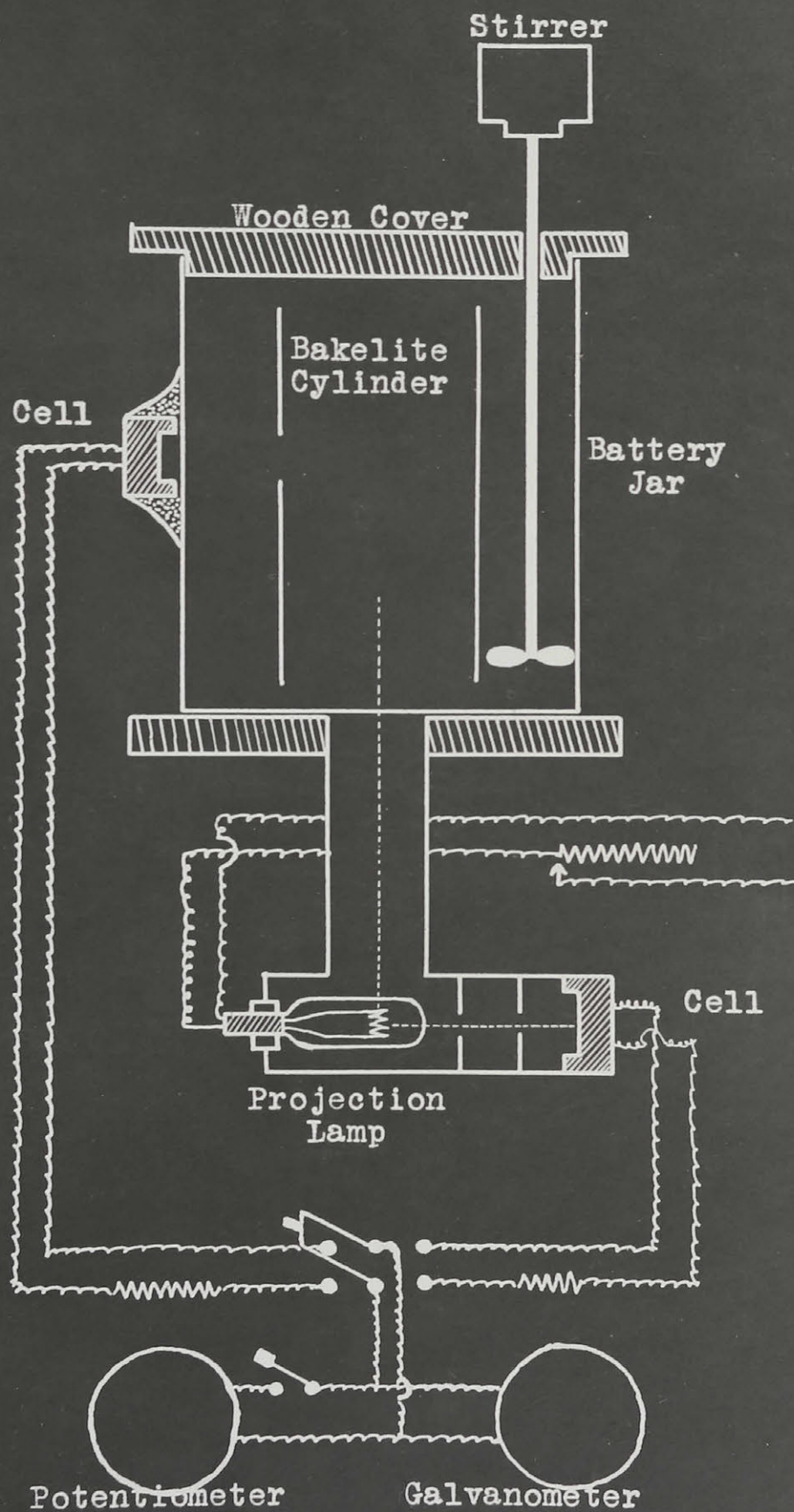


FIGURE 2

Experimental Results

1. Comparison of Reflection Apparatus with Standard Apparatus

Two pulps were obtained, a groundwood and a sulphite, and their relative projection areas determined by transmitted light on the standard area machine; then the same pulps were used in the reflection apparatus, and an attempt was made to obtain the same ratio between the areas from both instruments by an analysis of the results from the reflection apparatus.

Table I shows the areas of the sulphite and groundwood as measured on the standard apparatus.

TABLE I

<u>Run No.</u>	<u>Pulp</u>	<u>Calculated Concentration, g. per 100 ml.</u>	<u>Reciprocal of Concentration, Area</u>
1	Groundwood A	0.0453	22.08
2	Sulphite A	0.1078	9.27
3	Groundwood A	0.0475	21.02
4	Sulphite A	0.1076	9.29

Table 2 is a dilution run, using the same groundwood in the reflection apparatus and measuring the concentrations which give various intensities of reflected light.

TABLE II

<u>Run No.</u>	<u>Pulp</u>	<u>Cal. Conc. g./100 ml.</u>	<u>Rel. Intens. of Reflected Light</u>	<u>Reciprocal of Conc.</u>
5	Gwd. A	0.1257	0.0868	7.95
6	Gwd. A	0.0829	0.2207	12.06
7	Gwd. A	0.0636	0.3313	15.74
8	Gwd. A	0.0476	0.4675	21.00
9	Gwd. A	0.0359	0.5618	27.89
10	Gwd. A	0.0187	0.6655	53.65
11	Gwd. A	0.0097	0.5268	103.3
12	Gwd. A	0.0027	0.3127	370.2

The data of Table II is plotted on Plate I. There is obviously no simple relation between intensity of reflected light and the concentration.

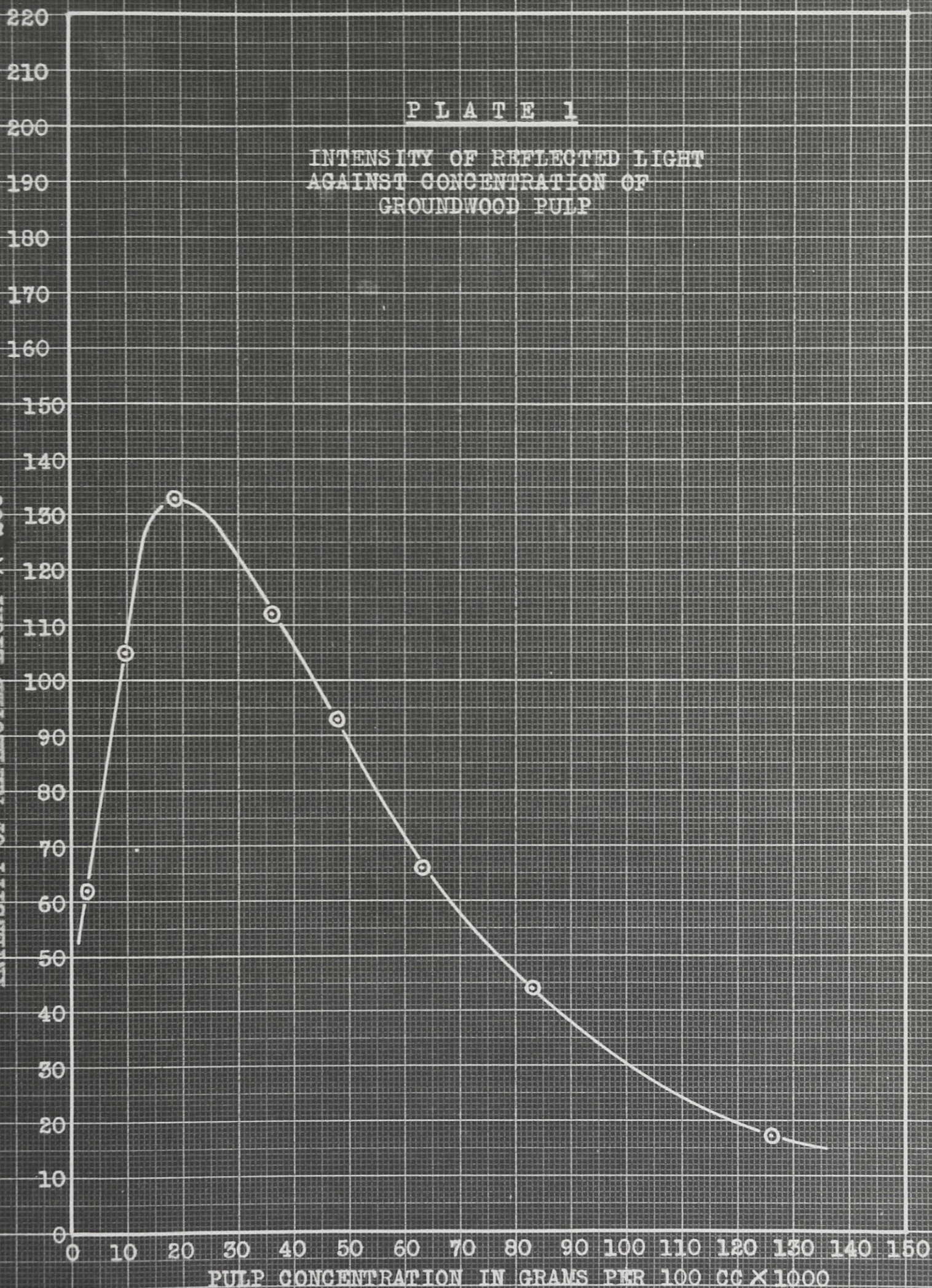
The occurrence of a maximum point is inherent in the nature of the apparatus: as the pulp concentration increases from zero, the intensity of light reaching the photocell increases rapidly because of the great amount of light reflected from the pulp particles; but as the concentration increases still further, the transmittance of that part of the suspension which is between the photocell and the center of the bakelite cylinder, begins to decrease, thus decreasing the intensity of light reaching the cell.

If the light source and the cell could occupy exactly the same position, the maximum would not be observed. This condition was approached in later work by placing both cell and light source side by side against the bottom of the jar.

PLATE 1

INTENSITY OF REFLECTED LIGHT
AGAINST CONCENTRATION OF
GROUNDWOOD PULP

INTENSITY OF REFLECTED LIGHT X 200



PULP CONCENTRATION IN GRAMS PER 100 CC X 1000

Since this curve showed a maximum point, the determination was repeated with a view to increasing the accuracy and extending the limits of concentration. The results of this second set of runs are summarized in Table III and graphed on Plate II.

TABLE III

<u>Run No.</u>	<u>Pulp</u>	<u>Rel. Intens. of Reflected Light</u>	<u>Concentration g/100 ml.</u>
13	Gwd. A	0.0044	0.7110
14	Gwd. A	0.0193	0.2124
15	Gwd. A	0.0532	0.1528
16	Gwd. A	0.1002	0.1150
17	Gwd. A	0.1580	0.0933
18	Gwd. A	0.2350	0.0734
19	Gwd. A	0.2741	0.0719
20	Gwd. A	0.3309	0.0631
21	Gwd. A	0.4309	0.0515
22	Gwd. A	0.5381	0.0376
23	Gwd. A	0.6085	0.0291
24	Gwd. A	0.6161	0.0121
25	Gwd. A	0.5500	0.0115
26	Gwd. A	0.4590	0.0075
27	Gwd. A	0.3718	0.0028
28	Gwd. A	0.2543	0.0010

The area measurements on the standard machine were also repeated, as the apparatus is capable of greater reproducibility than is apparent from Table I. The resulting data is shown in Table IV.

PLATE NO. 2

INTENSITY OF REFLECTED LIGHT
AGAINST CONCENTRATION OF
GROUNDWOOD PULP

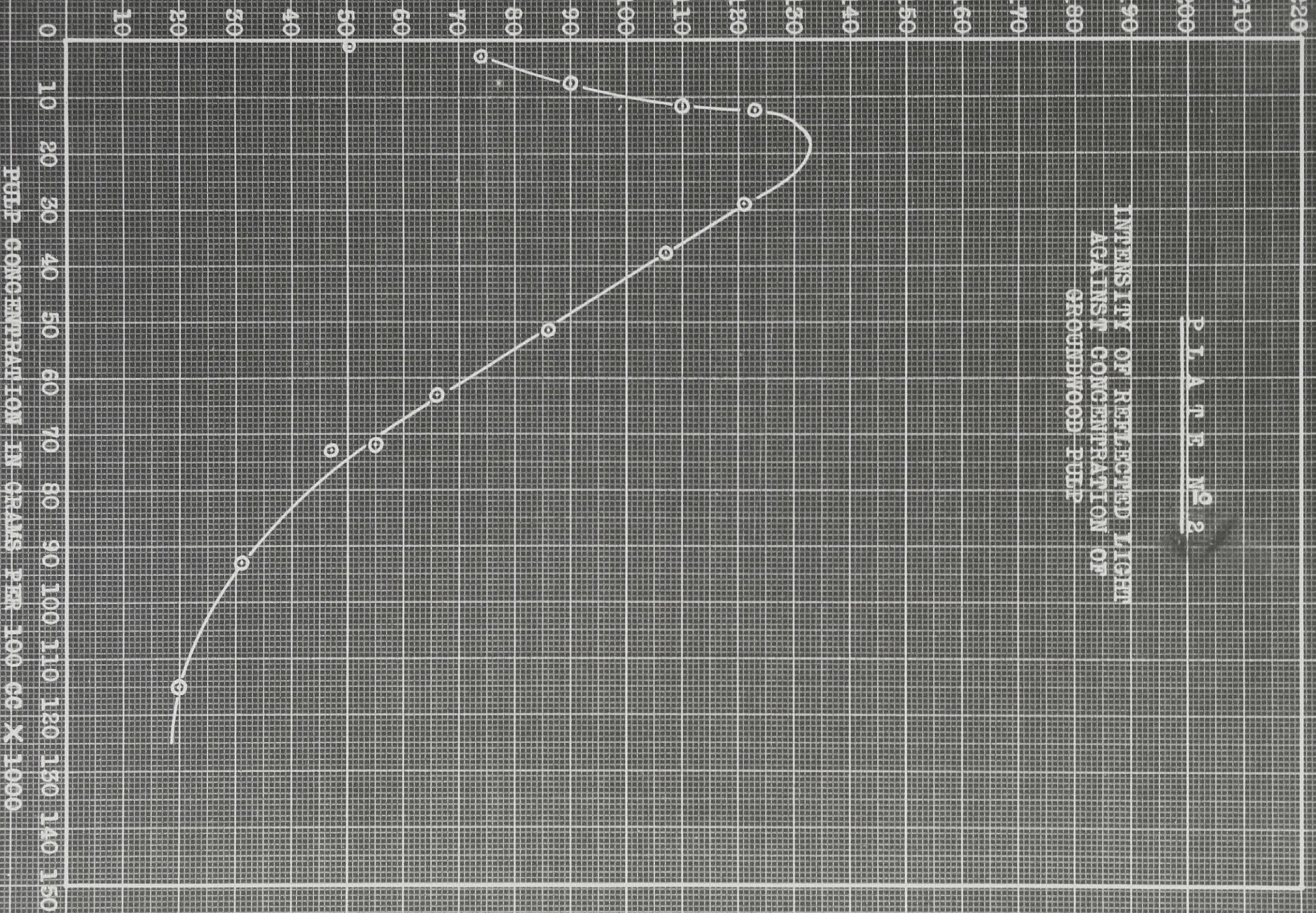


TABLE IV

<u>Run No.</u>	<u>Pulp</u>	<u>Calculated Concentration, g./100 ml.</u>	<u>Reciprocal Concentration, Area</u>
29	Gwd. A	0.0473	21.17
30	Gwd. A	0.0471	21.26
31	Sul. A	0.1084	9.22
32	Sul. A	0.1094	9.14

Average ratio of the areas, 1:2.297

A corresponding run was made on the reflecting apparatus with the sulphite A pulp, the results being shown in Table V and plotted on Plate III.

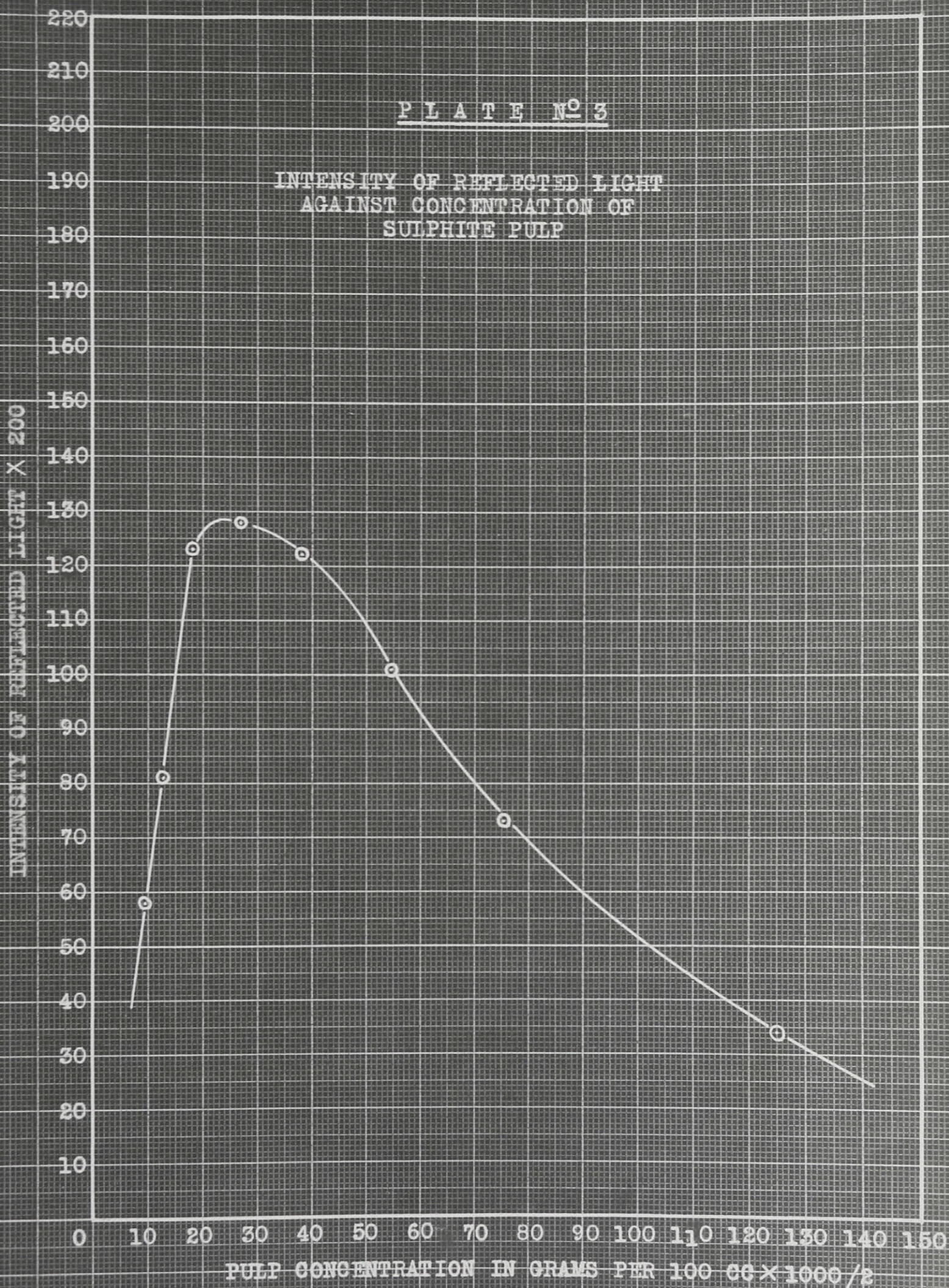
TABLE V

<u>Run No.</u>	<u>Pulp</u>	<u>Calculated Concentration, g./100 ml.</u>	<u>Rel. Intens. of Reflected Light</u>
33	Sul. A	0.4069	0.0412
34	Sul. A	0.2499	0.1720
35	Sul. A	0.1493	0.2901
36	Sul. A	0.1505	0.3677
37	Sul. A	0.1094	0.5091
38	Sul. A	0.0767	0.6117
39	Sul. A	0.0541	0.6436
40	Sul. A	0.0363	0.6178
41	Sul. A	0.0531	0.5549
42	Sul. A	0.0254	0.4057
43	Sul. A	0.0190	0.2923

PLATE N° 3

INTENSITY OF REFLECTED LIGHT
AGAINST CONCENTRATION OF
SULPHITE PULP

INTENSITY OF REFLECTED LIGHT X 200



For purposes of comparison, the graphs of Plates II and III were plotted together on the same scale in Plate IV.

Now, separate abscissae were taken, each denoting a definite concentration of pulp, and the ratio of each pair of corresponding ordinates calculated. The results are given in Table VI.

TABLE VI

<u>Abscissae</u>	<u>Corresponding Concentration g/100 ml.</u>	<u>Ratio of Gwd. Ordinate t o Sul. Ordinate</u>	<u>Ratio of Sul. Abscissa t o Gwd. Abscissa</u>
120	.240	0.0384	2.47
110	.220	0.0612	2.71
100	.200	0.0819	2.70
90	.180	0.1069	2.68
80	.160	0.1209	2.70
70	.140	0.1645	2.62
60	.120	0.1989	2.59
50	.100	0.2647	2.59
40	.080	0.3747	2.68
30	.060	0.5370	2.79
20	.040	0.6400	2.77
10	.020	2.14	2.53

True ratio of groundwood area/sulphite area = 2.297

Both the ratio $\frac{\text{groundwood ordinate}}{\text{sulphite ordinate}}$ and the ratio $\frac{\text{sulphite abscissa}}{\text{groundwood abscissa}}$ were calculated: the former shows no signs of being constant, but the latter is roughly constant in the range of concentration from .220 to .040 g. per 100 ml. This means that the ratio of the concentrations of the two pulps

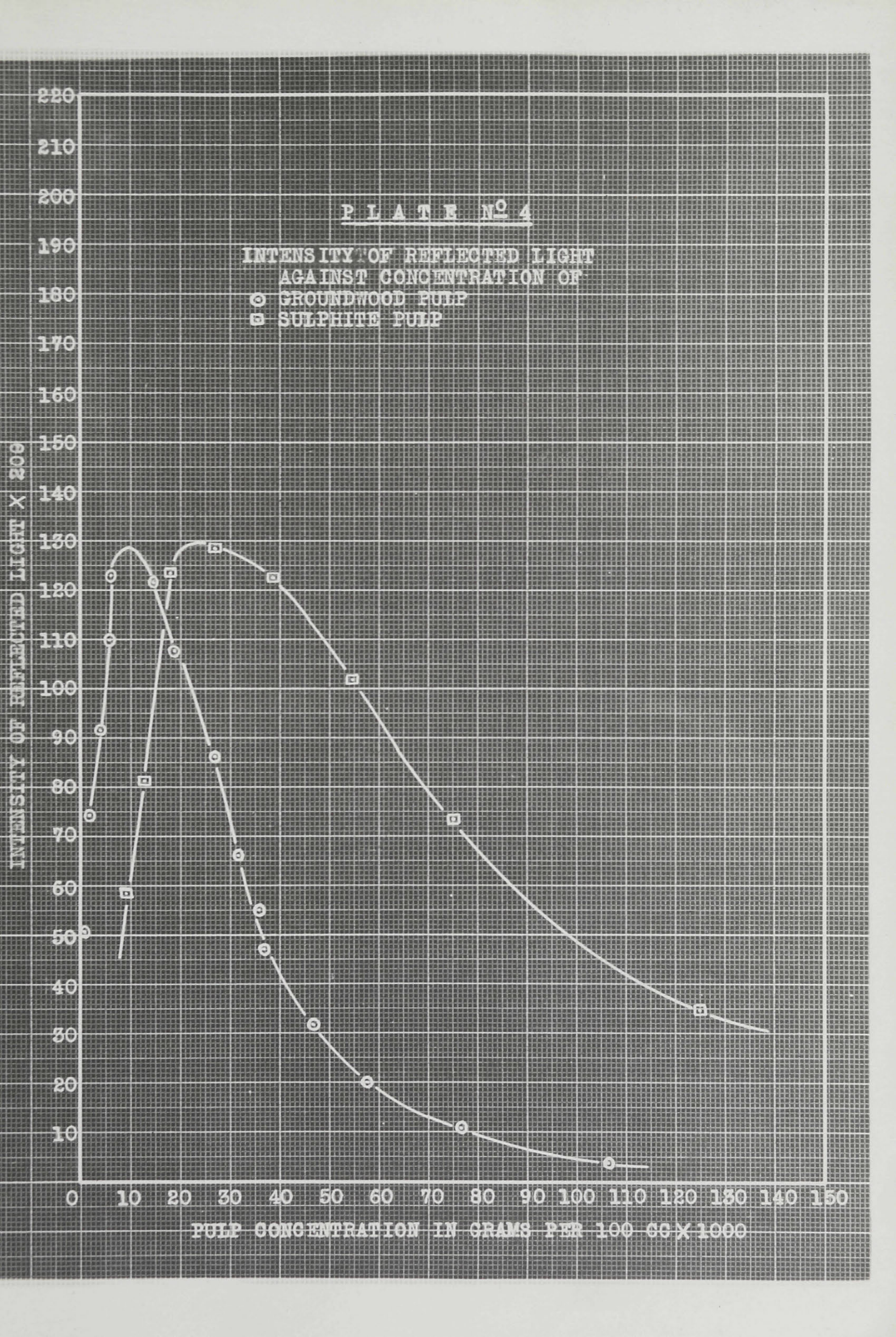
PLATE No 4

INTENSITY OF REFLECTED LIGHT
AGAINST CONCENTRATION OF

- GROUNDWOOD PULP
- SULPHITE PULP

INTENSITY OF REFLECTED LIGHT X 200

PULP CONCENTRATION IN GRAMS PER 100 CC X 1000



required to reflect equal intensities of light, is approximately constant over the above concentration range.

Since, from Table IV, the true ratio of the areas is 1 : 2.297, we may conclude that the ratio of the intensities of reflected light at equal concentrations is not proportional to the ratio of the projection areas, at least as determined in the above apparatus; and that the ratio of the concentrations necessary to reflect equal light intensities is approximately constant.

In a previous set-up (1) a relationship had been noted, but only in a low concentration range. This may be explained as follows: In Plate IV and Table VI, the ratio of the ordinates approaches the "true" ratio of the areas as the concentration decreases and becomes equal to it at about 0.02 g./100 ml. Another fact which shows that the apparatus is not suited to measuring relative areas is brought out by considering a concentration of $\frac{60}{500}$ g. per 100 ml. on Plate IV: Although present in equal concentrations, the sulphite reflects 5 times as much light, despite the fact that its projection area per gram is half that of the groundwood.

Because the foregoing results seemed more interesting at lower concentrations, it was decided to investigate the ends of the curves in Plate IV, using much lower concentrations.

Two new pulps, Groundwood B and Sulphite B were calibrated on the standard machine, and their relative projection areas found to be 2.89 : 1.

Table VII shows the data for lower concentrations and a graph is given on Plate V.

TABLE VII

<u>Run No.</u>	<u>Pulp</u>	<u>Calculated Concentration, g./100 ml.</u>	<u>Intensity of Reflected Light</u>
51	Gwd. B	0.0073	0.4023
52	Gwd. B	0.0125	0.5425
53	Gwd. B	0.0178	0.6356
54	Gwd. B	0.0099	0.4800
55	Gwd. B	0.0155	0.5836
56	Sul. B	0.0143	0.3478
57	Sul. B	0.0164	0.4269
58	Sul. B	0.0205	0.5005
59	Sul. B	0.0285	0.6142
60	Sul. B	0.0135	0.3763

The dotted line extrapolation is not fully justified because of the position of the zero reading with water alone, but it serves to show that, at low concentrations, the two curves become almost parallel, and in the region of concentration about .008, the ratio of concentrations required to reflect an intensity of .35 is $\frac{.004}{.012}$, or as 1 : 3. This explains previous results where the ratio of the areas was found proportional to the concentrations required to reflect equal intensities of light.

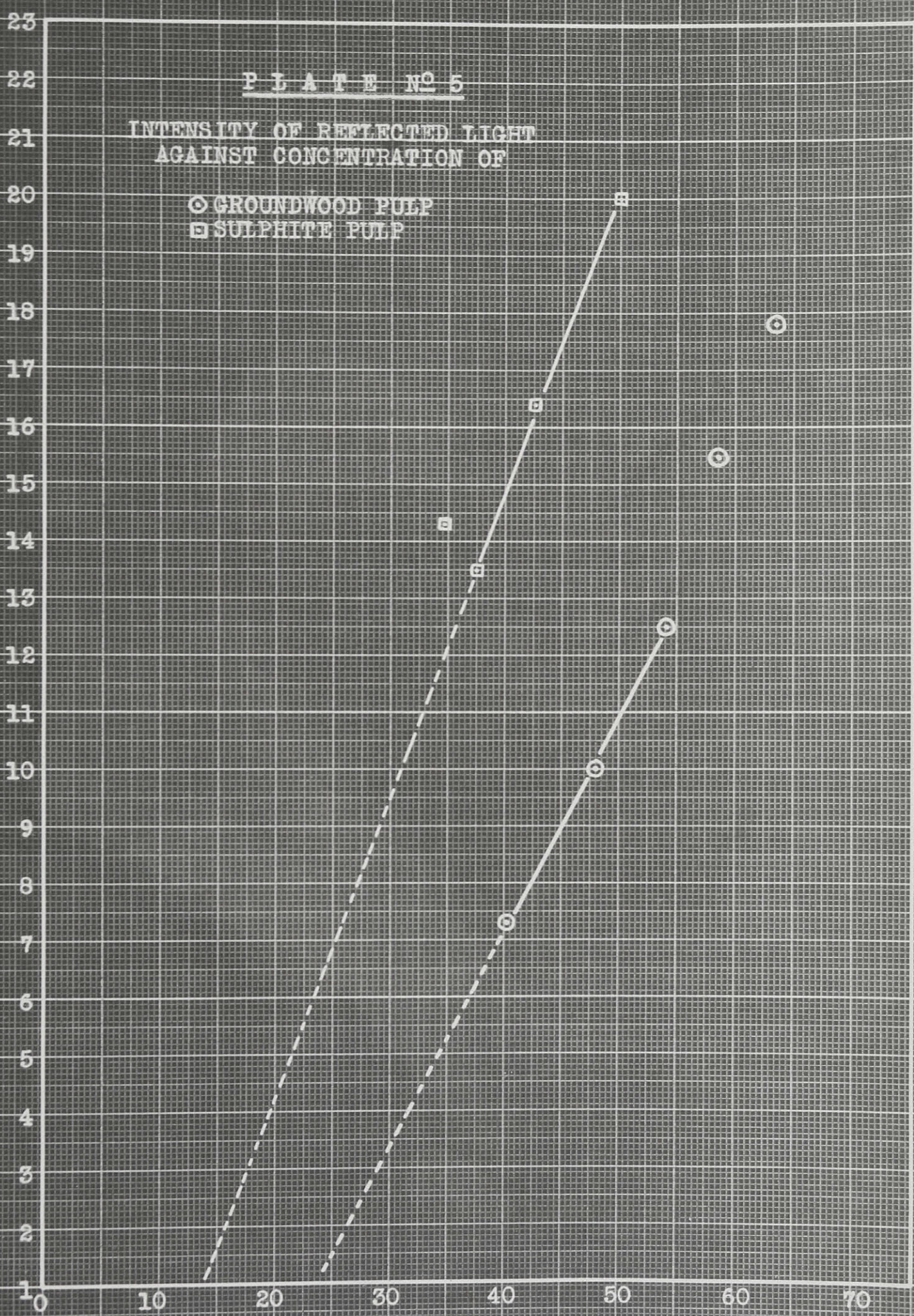
PLATE No 5

INTENSITY OF REFLECTED LIGHT
AGAINST CONCENTRATION OF

○ GROUNDWOOD PULP
□ SULPHITE PULP

INTENSITY OF REFLECTED LIGHT

INTENSITY OF REFLECTED LIGHT $\times 100$



Experimental Results

2. Effect of Electrolytes on Pulp Suspensions

In continuation of the previous work (1) on swelling of pulps by alkalies, it was thought that it would be of interest to make use of reflected light to follow the effect of various electrolytes on pulps. The apparatus used was identical with that used above, except for the fact that the photo-cell for measuring reflected light was placed at the bottom of the glass jar, side by side with the light source. In general, the experimental method was also the same except for the following: Addition of electrolyte would change the pulp concentration and intensity of reflected light apart from any chemical action, so a volume of distilled water was added, equal to the total volume of alkali to be used during a run, and the resulting deflection of the galvanometer noted; during a run, the same total volume of electrolyte was added in small portions and each reading corrected for the concentration change.

Five electrolytes were used, sodium hydroxide, hydrochloric acid, sodium chloride, magnesium sulphate and aluminium sulphate in hydrochloric acid.

Table VIII gives a representative run with hydrochloric acid. Groundwood C was used in all these runs.

(Table VIII on Page 13.)

TABLE VIII

Additions of 10 n. HCl	Time, Mins.	Galvanometer Reading	Correction for Conc. Change	Corrected Galvanometer Deflection
0	5	40.6		40.6
10 ml.	6			
	13	40.4		
	15	40.0	0.15	40.15
10 ml.	16			
	20	38.3		
	25	36.5	0.30	36.80
10 ml.	26			
	28	36.4	0.45	36.85
10 ml.	28			
	34	35.4	0.60	36.0
10 ml.	36			
	43	35.4	0.75	36.15
50 ml.	44			
	50	35.2	1.3	36.5
150 ml.	51			
	52	31.1	3.8	35.0

Table IX summarizes the results obtained with the five electrolytes.

TABLE IX

Volume Added	NaOH		HCl		NaCl		MgSO ₄		Al ₂ (SO ₄) ₃	
	Deflec.	n.	Deflec.	n.	Deflec.	n.	Deflec.	n.	Deflec.	n.
0	38.8	0	40.6	0	40.7	0	39.3	0	40.3	0
10 ml.	33.6	.035	40.1	.035	40.1	.018	38.0	.020	40.7	.015
10 "	30.3	.066	36.8	.066	39.1	.033	36.7	.035	39.4	.030
10 "	28.4	.099	36.8	.099	37.1	.050	35.6	.055	39.0	.045
10 "	27.7	.131	36.0	.131	36.6	.066	35.6	.072	39.0	.060
10 "	28.1	.164	36.1	.164	36.3	.082	35.7	.090	39.6	.075
50 "	27.3	.322	36.5	.322	35.6	.161	35.1	.170	39.1	.145
150 "	26.0	.77	35.0	.77	35.4	.385	34.5	.400	39.9	.350

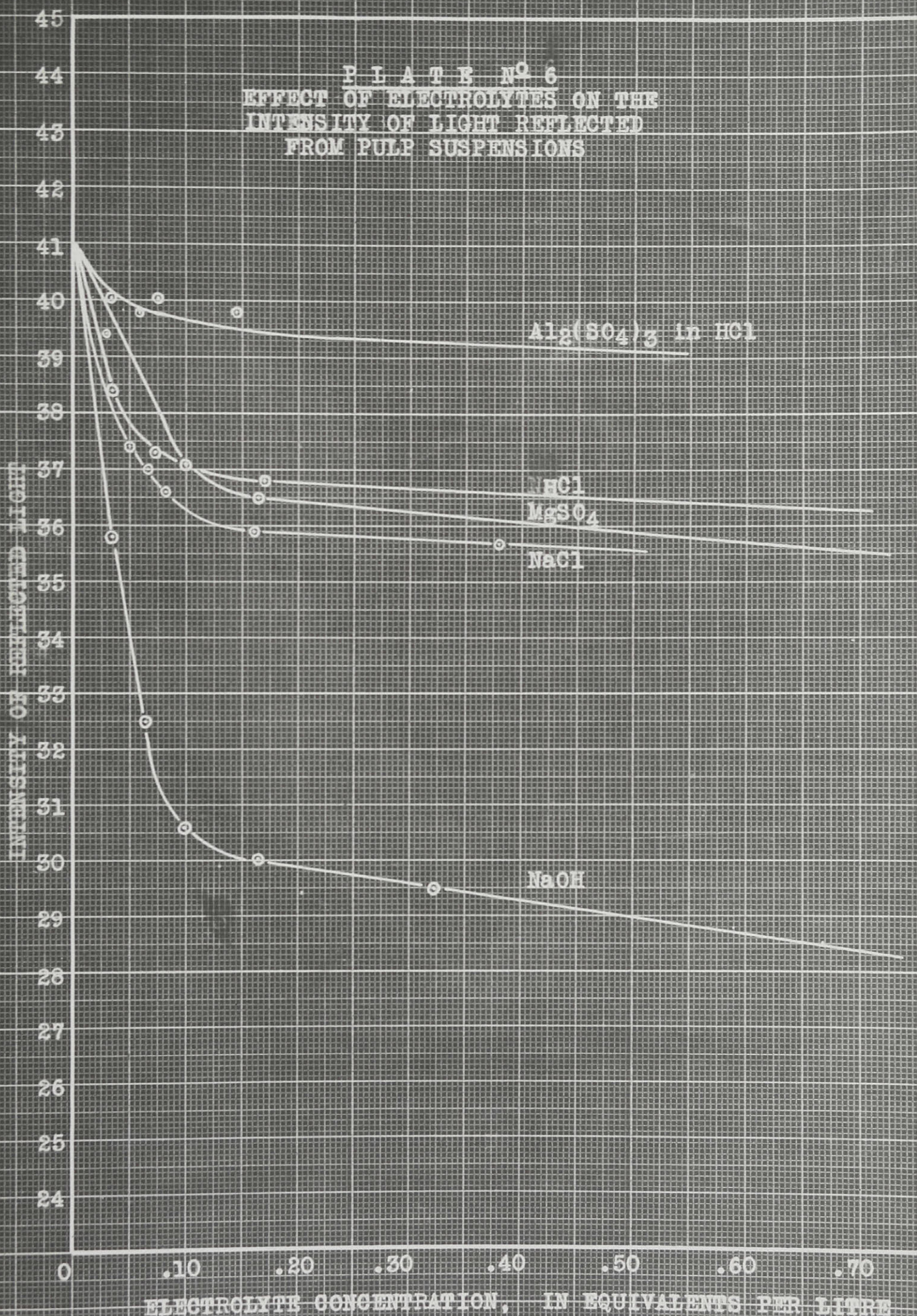
Because the pulps were all obtained from runs on the standard area machine, their initial and final concentrations were the same in each case, and therefore in plotting the results on Plate VI, all the initial readings were taken as being equal.

The curve for aluminium sulphate has been corrected for the addition of hydrochloric acid.

Discussion of Results

All the electrolytes cause a decrease in the amount of light reflected from the suspension, but by far the greatest effect is seen in the case of sodium hydroxide. It is also noteworthy that the trivalent ion Al^{+++} shows very little effect. It is known that the iso-electric point is meaningless, because of the fact that it would be in solutions so acid that normal cellulose could not exist. Thus the apparent coagulation observed above is more probably due to the alkali as such, rather than to any electrokinetic effects of ionic charge.

PLATE № 6
EFFECT OF ELECTROLYTES ON THE
INTENSITY OF LIGHT REFLECTED
FROM PULP SUSPENSIONS



S U M M A R Y

Adsorption and desorption isotherms for water on standard cellulose were measured at two different temperatures, the heats of adsorption and desorption calculated and found to be in qualitative agreement with previously measured heats of wetting as determined in an adiabatic calorimeter.

It was definitely proved that the hysteresis which occurs in the adsorption and desorption of water by cellulose is not affected by the pressure of residual permanent gases.

The apparent density of water adsorbed on standard cellulose at various concentrations was determined with a higher degree of accuracy than had been previously obtained, by employing a modification of the apparatus used by other investigators.

The rate of moisture adsorption by paper under various conditions of relative vapor-pressure and temperature was measured both in the presence and absence of air. The method used was more sensitive than any previously employed.

The conditioning effect of a high humidity on the dimensional changes of paper with relative vapor-pressure was investigated, as well as the effect of temperature on these changes.

CLAIMS TO ORIGINAL RESEARCH

Heats of adsorption and desorption for water on standard cellulose were calculated from experimentally measured isotherms and compared with heats of wetting data obtained by other investigators. These measurements were made with sufficient precision to confirm that the heat of wetting of cellulose containing desorbed water is greater than the heat of wetting of cellulose containing an equal amount of adsorbed water.

The apparent density of water adsorbed on standard cellulose was measured with the greater degree of accuracy made possible by a modification of the apparatus employed by previous workers. As a result it was found that the change in the apparent density of the water with increasing water adsorption was not as great as had been previously obtained. These results are more in conformity with the accepted hypothesis of the structure of the cellulose-water system.

The hysteresis which occurs in the adsorption and desorption of water by standard cellulose was found to be unchanged when the pressure of residual permanent gases was reduced to 10^{-5} mm. of mercury. If the claim to the contrary made by Patrick had been confirmed, it would mean that the hypothesis now generally accepted in regard to the structure of the cellulose-water system would have to be completely changed.

The rate of adsorption of moisture by papers under various conditions of relative humidity, temperature, and presence of inert gases was measured with a greater precision than had been previously employed.

The conditioning effect of a high relative humidity on the dimensional changes of paper was investigated and shown to be explainable on the basis of the known properties of cellulose fibres when subjected to a varying relative vapor-pressure of water.

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