

STRESSES ASSOCIATED WITH CAPILLARY SORPTION
IN MATRICES OF WET PAPER-MAKING FIBRES

A THESIS SUBMITTED TO
THE VICTORIA UNIVERSITY OF MANCHESTER

BY

G. N. CHRISTENSEN, M.Sc.

FOR THE DEGREE
OF
DOCTOR OF PHILOSOPHY

MAY 1953.

ProQuest Number: 11004401

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



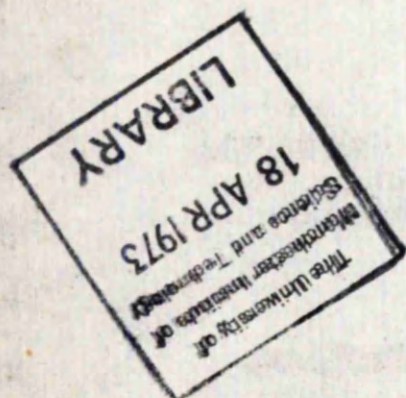
ProQuest 11004401

Published by ProQuest LLC (2018). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346



C O N T E N T S

I N T R O D U C T I O N

page

§1.	The Sorption of Water by Hygroscopic Materials.	1.
§2.	Stresses Associated with Capillary Sorption.	2.
§3.	Proposed Method of Study of Capillary Sorption.	3.
§4.	Study of Capillary Stresses.	6.
§5.	Capillary Retention and Paper Manufacture.	9.
§6.	Outline of Results.	10.

T H E O R Y

§7.	The Liquid Surface.	13.
§8.	Properties of a Curved Liquid Surface.	16.
§9.	Liquid under Stress - The Porter and Kelvin Equations.	19.
§10.	The Validity of the Kelvin Equation.	21.
§11.	Water Retention by a Single Capillary.	24.
§12.	Replacement of Air by a Liquid Phase.	27.
§13.	Liquid Retention by a Capillary Network.	29.
§14.	The Sorption Isotherm.	32.
§15.	Capillary Sorption.	33.
§16.	Saturation.	36.
§17.	Capillary Retention and the Sorption Isotherm.	38.
§18.	Sorption of Water by Cellulosic Materials.	39.
§19.	Sorption Hysteresis.	43.
§20.	Stresses Associated with Capillary Sorption.	49.
§21.	Elastic Properties of Pads of Paper-making Fibres.	55.

EXPERIMENTAL METHODS

	page
§22. Preparation of Fibre Cylinders.	61.
§23. Determination of the sorption Isotherm.	66.
§24. Measurement of Dimension Changes.	71.
§25. Application of Longitudinal Stresses.	75.
§26. Method of Procedure.	76.

RESULTS AND DISCUSSION

§27. Experiment 1.	Establishing a Reproducible Cycle.	79.
§28. Experiment 2.	Air Entry and the Effect of Beating.	84.
§29. Experiment 3.	Measurement of Volume Change.	95.
§30. Experiment 4.	Variations within the Cylinder.	101.
§31. Experiment 5.	Application of a Longitudinal Stress.	108.

CONCLUSIONS

§32. Properties of Liquids in Capillaries.	121.
§33. Principles of Elasticity applied to 'soft' Materials.	126.
§34. Properties of Paper Pulps - Application to Paper-making Technology.	128.

REFERENCES

INTRODUCTION

The work described in this Thesis concerns the retention of water by porous matrices of hygroscopic fibres and the rheological behaviour of these matrices in response to the stresses resulting from capillary sorption.

STRESSES ASSOCIATED WITH CAPILLARY SORPTION IN MATRICES OF
WET PAPER-MAKING FIBRES.

Thesis submitted by G. N. Christensen, M. Sc., for the Degree of Ph. D.
May 1953.

ABSTRACT

In this Thesis, the theoretical behaviour of liquids in capillaries is considered in detail. It is shown that application of a hydrostatic tension to a liquid retained in a capillary network may be used to control its relative vapour pressure, and this principle is employed in the porous plate technique for the study of the retention of water in matrices of wet paper-making fibres.

By means of this technique, it has been possible to determine the sorption isotherm of cylinders of these fibres in the range of humidity 0.9999 - 0.9999999. By measuring the dimension changes of the fibre cylinders during sorption and desorption, stress - strain curves also may be prepared and some of the elastic constants of the cylinders may be calculated. The Thesis is concerned primarily with the development of the technique for the making of these measurements and some of its possible applications are indicated.

The results from the experiments have yielded useful information regarding the sorptive and elastic properties of wet paper pulp over a range of moisture content from 2 - 11 g. water per g. dry fibre. At tensions smaller than that at which air is drawn into the waterlogged matrix, a reproducible sorption hysteresis loop is obtained and its importance in relation to current theories of sorption hysteresis is discussed.

The tension at which air enters the matrix may be determined and, from dimension measurements, the fraction of the volume occupied by the air at larger tensions may be calculated.

The elastic moduli of water-logged matrices of fibres have been shown to vary with moisture content and, at the highest moisture content reached, the bulk modulus was of the order 10^3 dynes/cm². The values of the moduli calculated from the stress - strain curves are apparent values only however, since plastic, as well as elastic, deformation occurs. The differences in the results from different types of pulp have indicated that the technique may possibly be used in characterising the paper-making qualities of the pulp.

§1. THE SORPTION OF WATER BY HYGROSCOPIC MATERIALS.

It is common knowledge that many materials, though insoluble in water, are capable of absorbing and retaining water at vapour pressures less than saturation to a degree which varies with the actual vapour pressure. Free liquid water on the other hand, will evaporate completely if exposed to a vapour pressure maintained at any value below saturation. That the sorbed water will not thus evaporate indicates some affinity between it and the adsorbent.

In the case of cellulosic adsorbents with which this Thesis is concerned, two main mechanisms by which water is retained are commonly recognised, namely, (i) imbibition within the cellulosic substance itself and (ii) capillary sorption in fibre cavities and inter-fibre spaces. Imbibed water is usually held by molecular and Van der Waals forces and the active centres are considered to be free hydroxyl groups on the cellulose and its associated polysaccharides. Capillary sorption is confined to liquid water held behind curved menisci in capillaries which are not so small as to modify its bulk liquid properties such as surface tension, compressibility and viscosity. Water retained by capillary sorption is sometimes called 'free water' but this is a misnomer since such water, if really free, would drain out under gravity.

No clear distinction other than by arbitrary definition is possible between capillary and imbibed water, for reasons which will be discussed in detail below. Together they comprise the total equilibrium moisture content of the material but the relative proportion of each varies with the relative vapour pressure. Thus at low humidities, imbibition is almost exclusively the adsorption mechanism, whereas near saturation vapour pressure, capillary sorption may become predominant. The range of the sorption isotherm over which capillary sorption may be considered to occur is a matter of widely divergent opinion, but the large difference in moisture content between relative humidity 0.99 and the saturated (water-logged) state is due almost entirely to changes in capillary sorption, since it may be shown thermodynamically that, under these conditions, the equivalent radius of curvature of the meniscus exceeds $0.1/\mu$ (see TABLE 1, §8).

It is with capillary sorption and associated phenomena within this range of humidity that this Thesis is primarily concerned.

§2. STRESSES ASSOCIATED WITH CAPILLARY SORPTION.

Sorption of water molecules by adsorbents is accompanied by a decrease in free energy and it is not justifiable to consider the water - adsorbent complex as a simple mixture of its separate components. In the molecular sorption range, i.e. at low relative vapour pressures, the decrease is large and may be indicated by the swelling that may occur against internal restraints or even large external stresses.

In capillary sorption at higher vapour pressures, smaller changes in differential free energy are involved, but the associated stresses, though smaller also, may be readily demonstrated. For instance, a coarse sand whose mechanical properties are not appreciably affected by molecular or surface adsorption, will run freely at all but the highest humidities. Addition of a little liquid water however, will transform the same loose sand into a coherent semi-solid whose rigidity must be derived solely from stresses initiated by the capillary water present. This is shown further by the rapid change in rheological properties as increasing proportions of water convert the sand into a slurry.

The stresses of capillary sorption may be expected to produce measurable dimension changes if the elastic moduli of the sorbent are sufficiently low. It will be shown that wet paper pulp is one of the materials which behaves thus and soft porous materials like sponge and porous rubber could be expected to do likewise.

§3. PROPOSED METHOD OF STUDY OF CAPILLARY SORPTION.

Little direct experimental study of capillary sorption has been made although the validity of some of the theoretical aspects, such as vapour pressure of liquids behind curved surfaces, have been tested by various workers. At the same time, little is known of the capillary sorption properties of many porous materials that have been studied extensively at lower humidities.

The usual method of determining the sorption isotherm consists of measuring the moisture content of the sorbent after exposure to an atmosphere of constant humidity until equilibrium is attained by evaporation or condensation but, at a relative humidity of approximately 0.99, the practical limitations appear to have been reached for reasons which are considered below (§17).

In considering an alternative approach to the practical study of capillary sorption, the possibility of transferring the water in the liquid phase was examined. From the theory of liquid surfaces, it may be shown that water held in capillaries behind curved menisci is under a hydrostatic stress, the magnitude of which is related to the double curvature of the surface. On the other hand it may be shown thermodynamically that the application of a stress to a liquid changes its vapour pressure. If the liquid surface is concave towards the vapour phase, the vapour pressure is reduced and the water is under hydrostatic tension. The quantitative relationship is such that, near saturation, very small changes in vapour pressure are produced only by quite large changes in tension (see TABLE 1, §8), which may thus be used as a sensitive control of vapour pressure. In addition, the hydrostatic tension may be used as the driving force for the transfer of liquid water to or from the porous material, so that the basic requirements for an alternative method of studying capillary sorption have been met.

An experimental method employing these principles has already been used by Haines (1) and Schofield (2) for determining the sorption

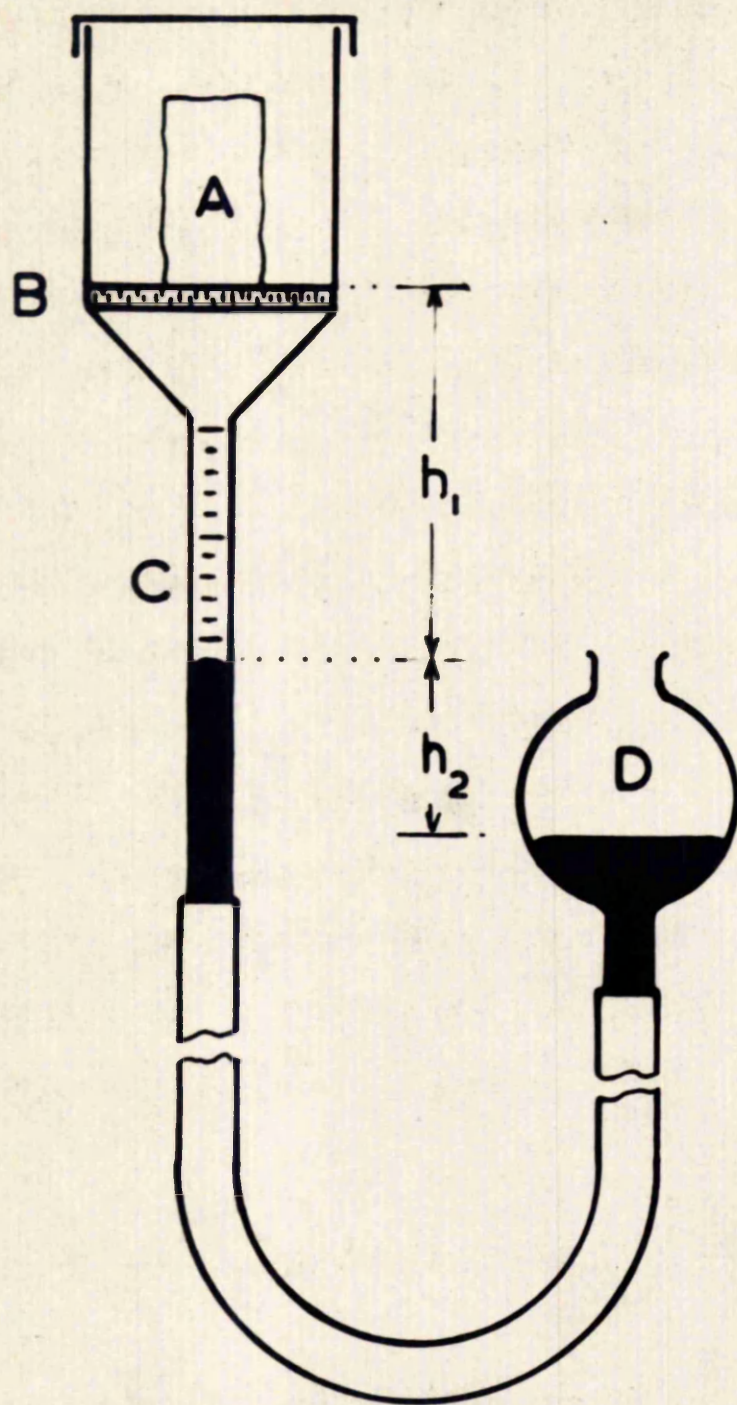


FIG. 1

of water by soils, and more recently by Preston and Nimkar (3) for following the sorption isotherms on textiles into the capillary sorption range. It consists in separating the sample to be studied from the bulk water by a rigid porous membrane, e.g. sintered glass, which is capable of transmitting hydrostatic stresses and through which liquid water may flow freely. In the form of apparatus used by Preston and Nimkar, the material to be tested (A) (see FIG. 1.) rests on a porous glass plate (B), the pores of which are maintained full of water, as also is the top of the graduated tube (C) to which it is connected. This in turn is connected flexibly to the open arm (D) to form a mercury manometer. By raising or lowering (D), the tension in the water at the plate may be varied and measured from the heights of the water and mercury columns h_1 and h_2 . With each change in tension, the volume of water taken up or withdrawn from the sample may be measured from changes in the position of the mercury surface in (C). If the initial moisture content and dry weight of the sample are known, the series of equilibrium readings so obtained may be used to construct a tension - moisture content isotherm.

This method possesses several advantages over humidity control methods.

(1) Control of tensions to small values enables extension of the sorption isotherm to vapour pressures unattainable by the direct method.

(11) Speed of transfer is very rapid so that the rate of attainment of equilibrium is determined largely by the ability of the

of the sample to adapt itself to the changed stress conditions.

(iii) The air surrounding the sample may be replaced by a non-miscible liquid thus eliminating possible errors due to evaporation and reducing gravitational effects which may be important with very soft materials.

A practical limitation of the method is that continuous films of liquid must be present throughout the sample to permit water flow. Thus substances whose capillaries are not interconnected cannot be studied with advantage by this method, though if the solid phase is permeable to water, equilibrium would be reached eventually by diffusion. Similarly at large tensions, corresponding to large meniscus curvatures, the water film between the sample and the plate may be broken and the flow of water stopped. Quantitative considerations show that the porous plate method of sorption measurement is thus complementary to the methods employing direct humidity control.

§4. STUDY OF CAPILLARY STRESSES.

One of the aims of the present study is to investigate capillary stresses in relation to the quantity of water present and the strains produced in the porous material. Although the stresses acting on the water are purely hydrostatic, the resultant stresses on the solid components will be more complex in view of the heterogeneity of the porous structure. At high moisture contents only, i.e., before air is drawn into the waterlogged sample, it may be possible to regard the stress on the sample as a whole as hydrostatic.

The elastic properties measured will be those of the matrix itself because the water, which serves merely as a means of application of the stress, is free to leave the sample by the porous plate. Since the above technique enables controlled hydrostatic stresses to be applied to the water in the sample, and the resultant strains and moisture contents to be measured, stress-strain diagrams as well as sorption isotherms may be prepared and the elastic properties studied over a wide range of moisture content.

In selecting a material for study, a number of requirements is necessary.

- (i) A large proportion of its capillaries should be sufficiently small to hold water against the largest applied tensions and form an interconnecting network.
- (ii) It should be soft enough to deform measurably under a small applied stress.
- (iii) It should possess simple elastic symmetry so that dimension changes may be measured conveniently.
- (iv) It should tend to return to its former dimensions on removal of the stress.

Had it been desired to study the sorption isotherm only, the use of rigid well-defined porous structures such as regularly packed glass spheres or rods might have been considered. Their advantage would lie in the possibility of calculation of their moisture content by geometrical methods for direct comparison with experimental results. However, to obtain reasonable retentions at the highest

tensions, very small and uniform units would be required and the regular packing of such small units would be almost impossible. Such materials would not be suitable for the study of strains as indicated above and alternative types of material were therefore considered and tested in which no simple assumptions regarding their capillary shapes and sizes could be made.

Porous materials such as delignified wood, fibrous felts, etc. were considered but found unsatisfactory. It was thought that gels might possess the necessary requirements but tests with gelatine gels showed that, following deformations resulting from desorption, there was little recovery on release of the stress. However, it had been observed that previously compressed pads of wet papermaking fibres showed very large increases in volume on being placed in water, and that the pads retained their structure unless agitated mechanically. This seemed to indicate that changes in the dimensions of these pads were controlled by the elastic properties of the fibres themselves and that, subject to preparation in suitable size and shape, aggregates of these fibres might provide suitable test materials.

Initial tests showed that large quantities of water could be transferred to and from these pads using the porous plate technique but that the quantitative results depended considerably on their method of preparation. Ultimately it was found possible to form the fibres into reasonably exact cylinders which, although markedly anisotropic, were of simple symmetry so that the resultant strains

could be measured with the desired accuracy.

§5. CAPILLARY RETENTION AND PAPER MANUFACTURE.

In the continuous manufacture of paper, a pulp suspension with a water - pulp ratio of about 200:1 flows onto a horizontal moving wire screen. During the few seconds that the pulp is on the screen the water - pulp ratio is reduced by drainage and suction to about 4 or 5 : 1, transforming the dilute suspension of pulp into a coherent mat which is capable of supporting its own weight during transfer from the wire screen to the press rolls. The water is removed as the pulp is subjected to successively increasing hydrostatic tensions, due in turn to gravity, the tube rolls, the suction boxes and the suction couch rolls. This removal is opposed by what may be termed the 'retentivity' of the pulp which depends in a complex manner on its capillary size distribution, surface area, elastic properties and possibly other factors.

At the highest tensions reached by the suction couch rolls (approx. 60 cm. mercury), only capillary sorbed water is removed, but the capillary stresses occurring in the wet pulp markedly affect the thickness of the mat and hence such properties of the final paper as its strength, permeability and absorbency. Though the mechanism of these effects is not fully understood, it is probable that the large hydrostatic tensions which develop as the last capillary water is removed, help produce the adhesion of the fibres in the dry paper.

In assessing their effect on the paper properties however, capillary sorption stresses cannot be considered separately from other pulp and processing variables which are closely inter-related. Unfortunately, the standard industrial measurements used for characterising the papermaking properties of the pulp, e.g. freeness and drainage measurements, are rather complex and arbitrary in nature. Also very little is known of the physical properties of the pulp such as its elasticity, pore size distribution and surface area. Since capillary stresses play such a large part during the formation of the pulp mat, their correlation with the elastic properties of the pulp was considered a convenient starting point for study.

§6. OUTLINE OF RESULTS.

The technique which was finally developed enabled tensions at the porous plate to be measured with an accuracy of 0.01 cm. mercury and this was therefore the minimum controllable tension that could be applied, corresponding to a relative humidity of 0.9999999 and an equivalent radius of meniscus curvature of 1 cm. The maximum tension applied in any test was 20 cm. mercury for which the corresponding relative humidity is 0.9998 and the radius of curvature $5.3/\mu$. It has been possible to prepare tension - moisture content isotherms over all or part of this range of tension for a number of pulp samples during both sorption and desorption of moisture. The range of corresponding moisture contents, namely 10 to 2 g. per g. dry fibres, are those found on the papermachine wire and in the press rolls where

de-watering of the pulp is effected by mechanical means.

Using a logarithmic scale for expressing the relative humidity, the corresponding sorption isotherms appear to be continuous with those of similar materials between 0 and 0.999 relative humidity as determined by vapour adsorption. The isotherms are invariably irreversible but repeated sorption - desorption cycles between the same limits of tension may produce ultimately, if the sample remains water-logged, a reproducible hysteresis loop with moisture content differences at the same tension as high as 1 g. water per g. dry fibre. Since these differences occur while the sample is still water-logged, mechanisms of hysteresis involving non-reversible emptying of the capillaries are clearly not responsible.

Measurements of dimension changes during sorption and desorption have yielded information regarding the entry of air into the water-logged fibre mats and the associated changes in stress distribution which markedly affect the formation and properties of the final paper sheet. With unbeaten stiff-fibred pulps, this may occur at tensions as low as 3 cm. mercury, corresponding to an equivalent radius (i.e., circular capillary) of 40μ which is of the same order as the fibre radius.

Measurements of strain in the fibre cylinders showed the large structural anisotropy consequent upon their method of formation, as well as the sensitive variation in elastic constants, with moisture content and method of preparation, which in some cases masked the

variations due to differences between the pulps themselves. Young's modulus in a plane parallel to the fibre orientation was approximately five times greater than that perpendicular to this plane, as a result of which the former was approximately the same value as the bulk modulus. Provided no air is present within the sample, the bulk modulus may be determined directly from the sorption isotherm if this is expressed as a (hydrostatic stress) - (volume strain) curve.

Of considerable importance is the order of magnitude of these elastic moduli, e.g. as low as 10^4 dynes/cm.². These are many times smaller than the moduli of materials such as steel (10^{12} dynes/cm.²), cellulose (10^{11} dynes/cm.²) or wood (10^{10} dynes/cm.²), demonstrating the universality of the principles of elasticity. The occurrence within these fibre mats of phenomena analogous to work-hardening and plastic deformation raises fascinating possibilities in the field of rheological study.

THEORY

BRIGHTON BORD



§7. THE LIQUID SURFACE.

If a volume of a pure liquid is introduced into an evacuated enclosed space which it does not fill completely, some of the liquid evaporates until a dynamic equilibrium is set up between the rates of evaporation and condensation. When the phase boundary formed is a plane, the pressure exerted by the vapour at the liquid surface is termed the saturated vapour pressure p_0 , at the temperature concerned. If, due to some additional factor, the vapour pressure is depressed to a value p , at the same temperature, the ratio p/p_0 , is termed the relative vapour pressure of the system.

As a result of the unsymmetrical field of forces acting on the molecules near the liquid - vapour interface, work must be done to bring a molecule from the interior of the liquid to the interface. The additional energy required to create 1 cm.^2 of new surface is the 'surface free energy' which, if measured in ergs/cm.^2 , is equivalent to the surface tension γ , expressed as dynes/cm. Either is a measure of the spontaneous tendency of the liquid surface to contract, i.e. to lower the free energy of the system. Since it was difficult to visualise a liquid in equilibrium while only part of it was under stress, the existence in reality of a surface tension has been doubted by many writers. More recently Brown (4) and Gurney (5), by considering molecular stresses and chemical potentials respectively, have suggested similar mechanisms to show that the surface of a liquid will in fact be in the state of relative tension that direct

observation and measurement indicate.

The shape of a liquid surface in equilibrium with its vapour is not determined solely by the condition that its surface area is a minimum, but that the total energy of the system including other potential energy terms such as gravitational potential energy shall be a minimum. If the liquid surface is sufficiently large, this condition is realised when the surface is a horizontal plane flat to within molecular dimensions. For a finite liquid surface bounded by solid surfaces intersecting it, additional interfacial energies are introduced which must also be included in the equilibrium condition, so that the liquid surface in the vicinity of the solid may be distorted from the original plane to form a curved meniscus. Its shape will depend on the orientation of the phase boundaries and the magnitude of the interfacial energies and the contact angle. This may be defined as the angle between the plane of the solid surface and the tangent plane at a point on the liquid surface at the smallest observable distance from the solid surface.

The physical significance of the contact angle on the molecular scale is difficult to visualise and there are many unsatisfactory features in the theoretical treatment of contact angles usually advanced. Thus, at the point of contact, equilibrium is frequently regarded as a balanced system of stresses due to the three interfacial tensions between the solid, liquid and vapour phases but the mechanism by which the solid - vapour interfacial tension may be

regarded as a directional stress on the liquid tending to cause spreading is not explained. Alternatively, if the equilibrium is considered in terms of an energy balance, it is doubtful whether any information is obtainable regarding the directional stresses on the liquid. Also, as pointed out by Bangham and Razouk (6) and Yarnold and Mason (7), the solid surface must be in equilibrium with the vapour pressure of the liquid so that it is the free energy of the interface between the adsorbed vapour and the vapour phase which determines the tendency of the liquid to spread. The phenomenon of the contact angle is thus inseparably connected with the sorption characteristics of the solid surface at or very near the saturation vapour pressure.

It is not within the scope of this Thesis to enlarge on the theory of contact angles since, for reasons to be discussed later, complete wetting will be assumed to occur under the conditions of the test. It may be noted however that Brown's theory postulates a distortion of the solid surface where it is in contact with the liquid leading to transverse stresses on the liquid at its boundaries. If so, it is possible that contact angle hysteresis (§19) may be associated with mechanical hysteresis of the solid surface.

If instead of pure vapour, air at atmospheric pressure P_0 , is present, there will be small changes in the vapour pressure and the interfacial tensions due to dissolved air and the increased total stress, but for most practical purposes these small differences may be neglected.

§8. PROPERTIES OF A CURVED LIQUID SURFACE.

(a) Difference in Hydrostatic pressure.

When a liquid surface is curved, the forces giving rise to surface tension produce a difference in hydrostatic stress P , across the interface whose magnitude may be determined from the relationship

$$P = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (1)$$

where r_1 and r_2 are the principal radii of curvature. It should be noted that where r_1 and r_2 are equal and opposite in sign (corresponding to antielastic curvature), the equivalent radius is infinite although the surface is not flat. In this case also, no difference in hydrostatic stress will occur and the surface will exert the saturated vapour pressure. For a hemispherical meniscus in a circular capillary, (1) becomes

$$P = \frac{2\gamma}{r} \quad (1a)$$

where r is the single radius of curvature of the surface. The sign of P is such that the pressure on the concave side of the curved surface is the greater. In TABLE 1 (cols. 3 and 5) are shown values of P for a pure water surface of different radii of curvature assuming a surface tension of 72 dynes/cm. This table was used for preparing graphs of the related variables from which intermediate values were read off as required.

TABLE 1.

Showing the change in equilibrium curvature of a water meniscus with change in hydrostatic tension and the corresponding relative vapour pressure determined from the Kelvin equation, assuming the surface tension of water to be 72 dynes/cm.

<u>Relative vapour pressure</u> (P/P ₀)	$\log_{10} P/P_0$	<u>Liquid tension (-P)</u>		<u>Rad. of curva- ture (r)</u> ($\mu = \text{cm.} \times 10^{-4}$)
		(cm. Hg)	(dynes/cm. ² $\times 10^6$)	
0.99900	T.9995655	101.7	1.35	1.065
05	5872	96.6	1.29	1.12
10	6090	91.5	1.22	1.18
15	6307	86.5	1.15	1.25
20	6524	81.4	1.08	1.33
25	6742	76.3	1.01	1.42
30	6959	71.2	0.948	1.52
35	7176	66.2	0.880	1.64
40	7393	61.1	0.812	1.77
45	7611	55.9	0.744	1.93
50	7828	50.8	0.676	2.13
55	8045	45.8	0.609	2.36
60	8262	40.6	0.541	2.66
65	8480	35.6	0.473	3.04
70	8679	30.5	0.406	3.54
72	8784	28.5	0.378	3.80
74	8871	26.4	0.351	4.10
76	8958	24.4	0.325	4.42
78	9044	22.4	0.298	4.83
80	9131	20.4	0.270	5.31
81	9175	19.3	0.255	5.60
82	9218	18.1	0.240	5.91
83	9262	17.3	0.230	6.26
84	9305	16.3	0.216	6.65
85	9349	15.3	0.202	7.10
86	9392	14.2	0.189	7.60
87	9435	13.2	0.176	8.18
88	9479	12.2	0.162	8.85
89	9522	11.2	0.149	9.67
90	9565	10.17	0.135	10.65
0.99999	T.9999956	1.017	0.0135	1.065×10^2
0.999999	T.9999996	0.1017	0.00135	1.065×10^3
0.9999999	T.9999999	0.01017	0.000135	1.065×10^4

(b) Capillary Rise.

One of the phenomena resulting from the difference in pressure on the two sides of a curved meniscus is capillary rise. Consider the simple case of a narrow circular capillary dipping into a water surface and surrounded by a container from which all air is removed. It may be assumed that in such a capillary the meniscus forms portion of a sphere of radius r . The water will rise in the capillary above the plane of the water surface to an equilibrium height h , at which the hydrostatic pressure in the liquid is

$$P_h = p_0 - \int_0^h \rho g dh \quad (2)$$

ρ being the density of the liquid. The hydrostatic pressure in the vapour phase at this height, i.e. the vapour pressure, is

$$P_h = p_0 - \int_0^h \rho_v g dh \quad (3)$$

where ρ_v is the vapour density.

By (1a)

$$P_h - P_h = \frac{2\gamma}{r}$$

whence

$$\int_0^h \rho g dh - \int_0^h \rho_v g dh = \frac{2\gamma}{r} \quad (4)$$

Although ρ may be assumed constant with change in h , ρ_v will vary, and in order to integrate (4), ρ_v must be expressed in terms of h .

If it is assumed that the vapour behaves as a perfect gas,

$$p_v = \frac{p}{RT}$$

whence

$$\frac{dp}{dh} = - \frac{pg}{RT}$$

i.e.

$$\frac{1}{p} \frac{dp}{dh} = - \frac{g}{RT}$$

At constant temperature, integration gives

$$\ln p = - \frac{gh}{RT} + \text{const.}$$

Since $p = p_0$ at $h = 0$

$$p = p_0 e^{-\frac{gh}{RT}}$$

and (4) may be written in the integrated form

$$p_{gh} - p_0 e^{-\frac{gh}{RT}} = \frac{2\gamma}{r} \quad (4a)$$

If the water meniscus meets the capillary wall at an angle θ , the radius of curvature r , is equal to $a/\cos \theta$, where a is the radius of the capillary. If θ is greater than 90° , the meniscus is depressed below the plane of the water surface.

§9. LIQUID UNDER STRESS - THE PORTER AND KELVIN EQUATIONS

Though determined originally from a thermo-cycle, Porter's general equation (8) showing the effect of stress on the vapour pressure of a solution may be derived thermodynamically from the following well-known equation (Glasstone (9)),

$$\left(\frac{\partial \mu}{\partial P} \right)_{n, T} = \left(\frac{\partial v}{\partial n} \right)_{P, T}$$

Thus for the vapour

$$\left(\frac{\partial \mu_{\text{vap.}}}{\partial p} \right)_{n, T} = \left(\frac{\partial v_{\text{vap.}}}{\partial n} \right)_{p, T}$$

and for the liquid

$$\left(\frac{\partial \mu_{\text{liq.}}}{\partial p} \right)_{n, T} = \left(\frac{\partial v_{\text{liq.}}}{\partial n} \right)_{p, T}$$

where μ and $(\partial v / \partial n)$ are the chemical potentials and the partial molar volumes respectively.

For a small change in pressure at equilibrium

$$\partial \mu_{\text{vap.}} = \partial \mu_{\text{liq.}}$$

so that

$$\left(\frac{\partial v_{\text{vap.}}}{\partial n} \right)_{p, T} dp = \left(\frac{\partial v_{\text{liq.}}}{\partial n} \right)_{p, T} dp \quad (5)$$

which is Porter's equation. For a single component, the partial molar volumes become the specific volumes u and v of the liquid and vapour respectively and the equation may be written in the form

$$u_p dp = v_p dp. \quad (5a)$$

It should be noted that the Porter equation is an exact equation requiring no assumptions regarding variation of u or v with pressure.

By making two assumptions, (i) that the vapour behaves as a perfect gas and (ii) that u does not vary with pressure, a simple integration is possible.

Thus by writing $v = RT/M_p$ it follows that

$$dP = \frac{RT}{M_u} \cdot \frac{dp}{p}$$

which on integration gives

$$P - p_0 = \frac{RT}{M_u} \ln \frac{P}{p_0} \quad (6)$$

By neglecting p_0 in comparison with P and on replacing P by $2\gamma/r$

$$\ln \frac{P}{p_0} = \frac{2\gamma}{r} \cdot \frac{M_u}{RT} \quad (7)$$

which is the Kelvin equation linking directly the reduction in vapour pressure with the curvature of the surface. Values thus calculated of the relative vapour pressure of pure water over menisci of different radii of curvature are given also in TABLE 1.

§10. THE VALIDITY OF THE KELVIN EQUATION

In the theory of curved liquid surfaces and capillary rise, a number of assumptions having only limited validity is involved. In equation (1a), γ is assumed to be independent of r . For large radii this is probably correct but, as r becomes very small, the number of molecules comprising the geometric surface also becomes very small and thermodynamic quantities such as γ , which depend on a statistical average behaviour of molecules, become meaningless. A theoretical analysis by Tolman (10) and Koenig (11) has shown however that, above a radius of 10^{-4} cm., the effect of curvature on γ is negligible. Tolman's approximate equation indicates that, even for $r = 10^{-6}$ cm., the reduction in γ is only 4%, but direct experimental confirmation of this relationship is difficult at these radii.

In deriving equation (4) for capillary rise, the assumption is made that the meniscus in a circular capillary forms a portion of a sphere or, if the contact angle is zero, a hemisphere. This may not be true for two reasons: (i) various portions of the meniscus will be under different stresses at different heights above the liquid plane and (ii) near the edges of the meniscus there may be wall effects affecting γ or ρ . The error due to (i) has been shown by Porter (12) to be small in small capillaries but an exact equation for any point on the meniscus is obtained by substituting the sum of the principal curvatures as in equation (1) if these are known.

In deriving the Kelvin equation two additional assumptions were made, firstly that the vapour behaves as a perfect gas and secondly that u does not vary with pressure. At vapour pressures near the critical point it is possible that the first assumption may not be justified but, under normal laboratory conditions, no appreciable variation in u is to be expected.

A number of attempts has been made to check the validity of the Kelvin equation by direct measurement of vapour pressure of curved surfaces. These may be divided into two groups, (i) those in which small droplets have been studied and (ii) those in which the liquid has been confined in narrow spaces, generally with a concave meniscus. In the former method the convex surface will have a vapour pressure greater than the saturation vapour pressure but there are advantages over the capillary methods in that the possibility of extraneous wall effects is eliminated. In a recent test by this method, La Mer and

Gruen (13) determined the equilibrium drop size of mono-disperse aerosols at controlled vapour pressures. The method was unfortunately complicated by the necessity of using multicomponent systems (e.g. di-octyl phthalate and toluene, and oleic acid and chloroform), but the Kelvin equation was found to hold for drop sizes down to 0.1μ .

Even though tests on drops show that the Kelvin equation is valid for large curvatures, its application to menisci of similar curvature in capillaries, group (11) above, may be vitiated by the proximity of solid surfaces. Several tests of the equation using liquid in capillaries have been made. Thus Shereshefsky (14) determined the rate of evaporation of water from glass and quartz capillaries at controlled vapour pressures and found evidence that the lowering of the vapour pressure was considerably greater than that calculated from the Kelvin equation. A similar though smaller effect was found for toluene. More recently Chumov (15) determined the vapour pressures of water, ethyl alcohol and benzene held between spherical and flat lenses of quartz or glass and found a similar effect. However, considerable experimental difficulties are associated with these methods including cleaning of the surfaces and the accurate control of the vapour pressures, and this evidence is now generally discounted.

Many indirect tests of the existence of long range forces from solid surfaces have been made but a comprehensive review of this evidence, such as that given by Henniker (16), is outside the scope

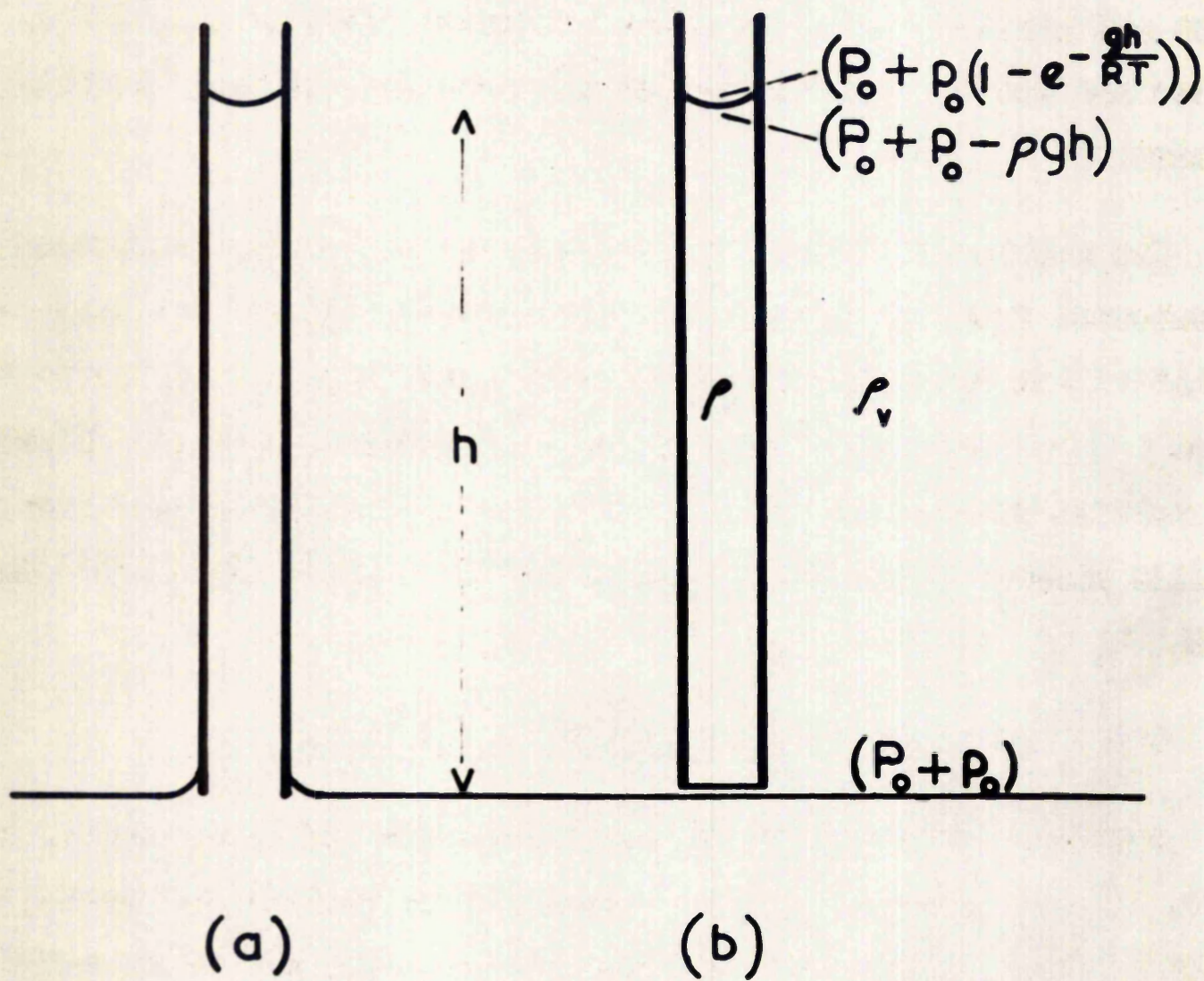


FIG. 2

of this Thesis. It is the opinion of the present author that no significant effects on the properties of water differentiating it from water in bulk are exerted beyond a distance of $0.1/\mu$ at most from the solid surface. In support of this opinion the simple, exact and critical tests by Cohan and Meyer (17), Bulkley (18), Bastow and Bowden (19) and Bowden and Throssel (20) are advanced as adequate evidence.

The Kelvin equation will be used throughout this Thesis for the calculation from the vapour pressure of curved liquid surfaces, due consideration being given to the above limitations. It should be noted however that the Porter equation implies no such limitations and relates exactly the effect of stress on the vapour pressure of liquids without reference to its method of application or the shape of the liquid surface.

§11. WATER RETENTION BY A SINGLE CAPILLARY.

Consider an open circular capillary with its lower end in the plane of a large water surface exposed to an atmospheric pressure P_0 (FIG. 2a). The water will rise in the capillary to an equilibrium height h as described previously (§8) and the hydrostatic pressures in the various parts of the system will be

at the base of the column, $P_0 + P_0$

in the liquid at its upper surface, $P_0 + P_0 - \rho gh$

and in the vapour above the meniscus, $P_0 + P_0 \left(1 - e^{-\frac{gh}{RT}}\right)$

The difference in hydrostatic pressure across the meniscus is, as before, (4a)

$$P = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) = \rho gh - p_0 e^{-\frac{gh}{RT}}.$$

The corresponding vapour pressures at the base and top of the water column are p_0 and $p_0(1 - e^{-gh/RT})$. Compared with P_0 and ρgh , p_0 and $p_0 e^{-gh/RT}$ are very small and may be neglected, so that the external hydrostatic pressure may be regarded as equal to P_0 throughout and

$$P = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) = \rho gh.$$

The capillary may now be separated by a very small amount from the plane water surface (FIG. 2b). If the small vertical displacement is neglected, there will be no change in the hydrostatic and vapour pressures of the liquid in the capillary which thus correspond to equilibrium conditions of capillary retention. The large water surface now serves merely to maintain the external vapour pressure gradient with which the water in the capillary must remain in equilibrium. Since the vapour pressure at the lower end of the capillary is p_0 , the lower meniscus will have zero curvature. As in the case of capillary rise, the length of the water column will depend on the cross-sectional shape of the capillary at the top water surface, i.e. the double curvature of the meniscus, the surface tension, the contact angle and the orientation of the capillary.

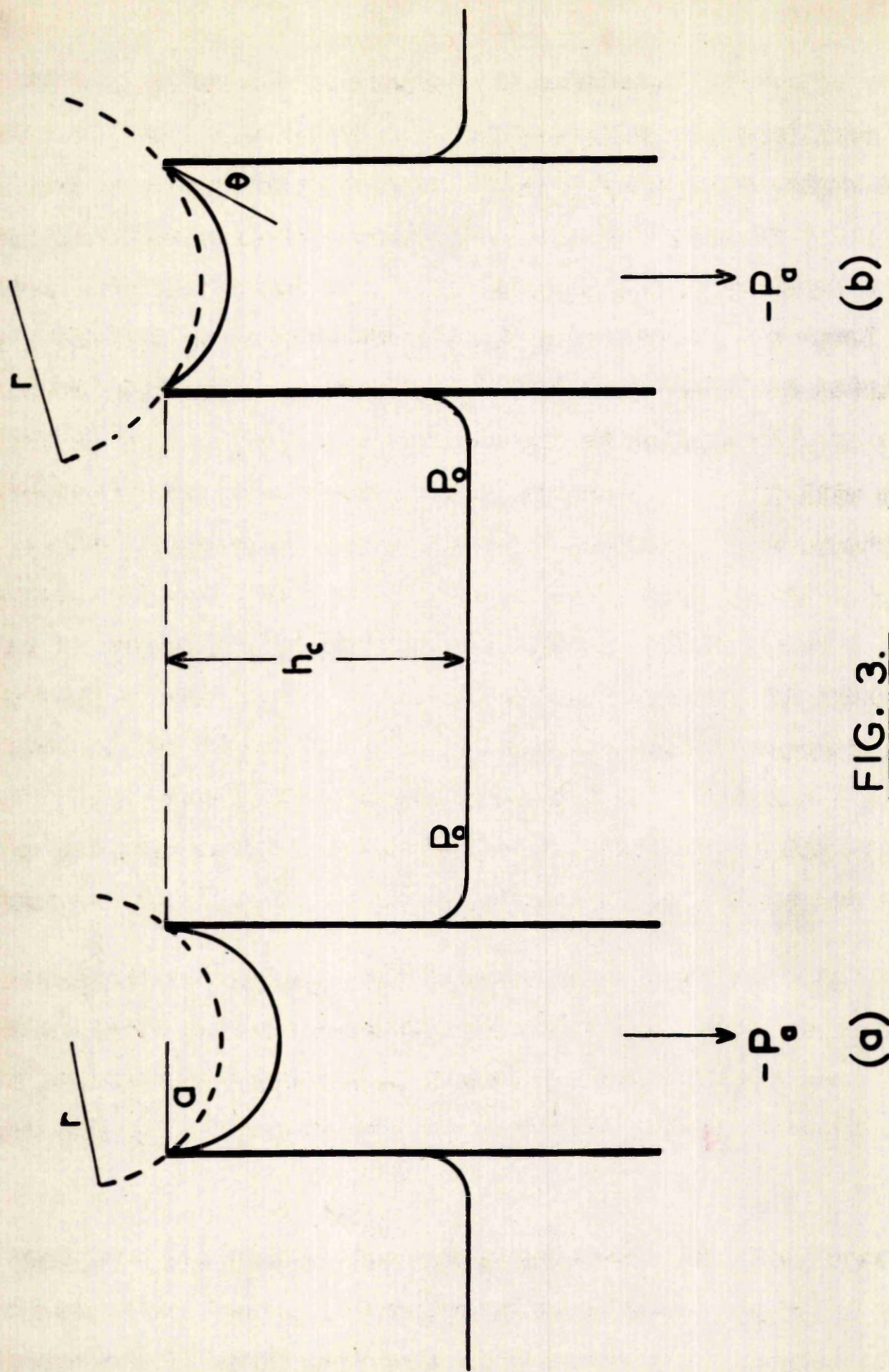


FIG. 3.

The effect of increasing the tension on the water held in a single capillary may be demonstrated as follows. Assuming zero contact angle, consider a circular capillary of radius a , such that the height h of water column it could support is considerably greater than its vertical height h_0 (FIG. 3a). If the hydrostatic pressure at its lower end is initially P_0 , the meniscus at h_0 will have an equilibrium curvature such that $\frac{2\gamma}{r} = \rho g h_0$. If a hydrostatic tension $-P_a$, is applied to the liquid column the tension at the top surface will increase to $-(\rho g h_0 + P_a)$, and the radius of curvature of the meniscus will decrease. Finally, with increasing tension, a critical point is reached at which r approaches a and the meniscus becomes a hemisphere. No further decrease in the radius of curvature is possible if this meniscus is to span the capillary, so that any further increase in tension results in a withdrawal of the meniscus down the capillary. If the capillary is sufficiently small, (see TABLE 1), the applied tension $-P_a$ may be very large compared with the tension due to the liquid column, so that $\rho g h_0$ may then be neglected.

In the above case it is assumed that the equilibrium contact angle $\theta = 0$. If $\theta > 0$ (FIG. 3b), recession of the meniscus will commence when, by increasing curvature, the angle between the profile of the meniscus and the capillary wall is reduced to θ , i.e. when $r \cos \theta = a$.

Associated with the changing applied tension and resultant curvature of the meniscus, will be corresponding changes in the equilibrium vapour pressure. The converse is also true that, if the vapour

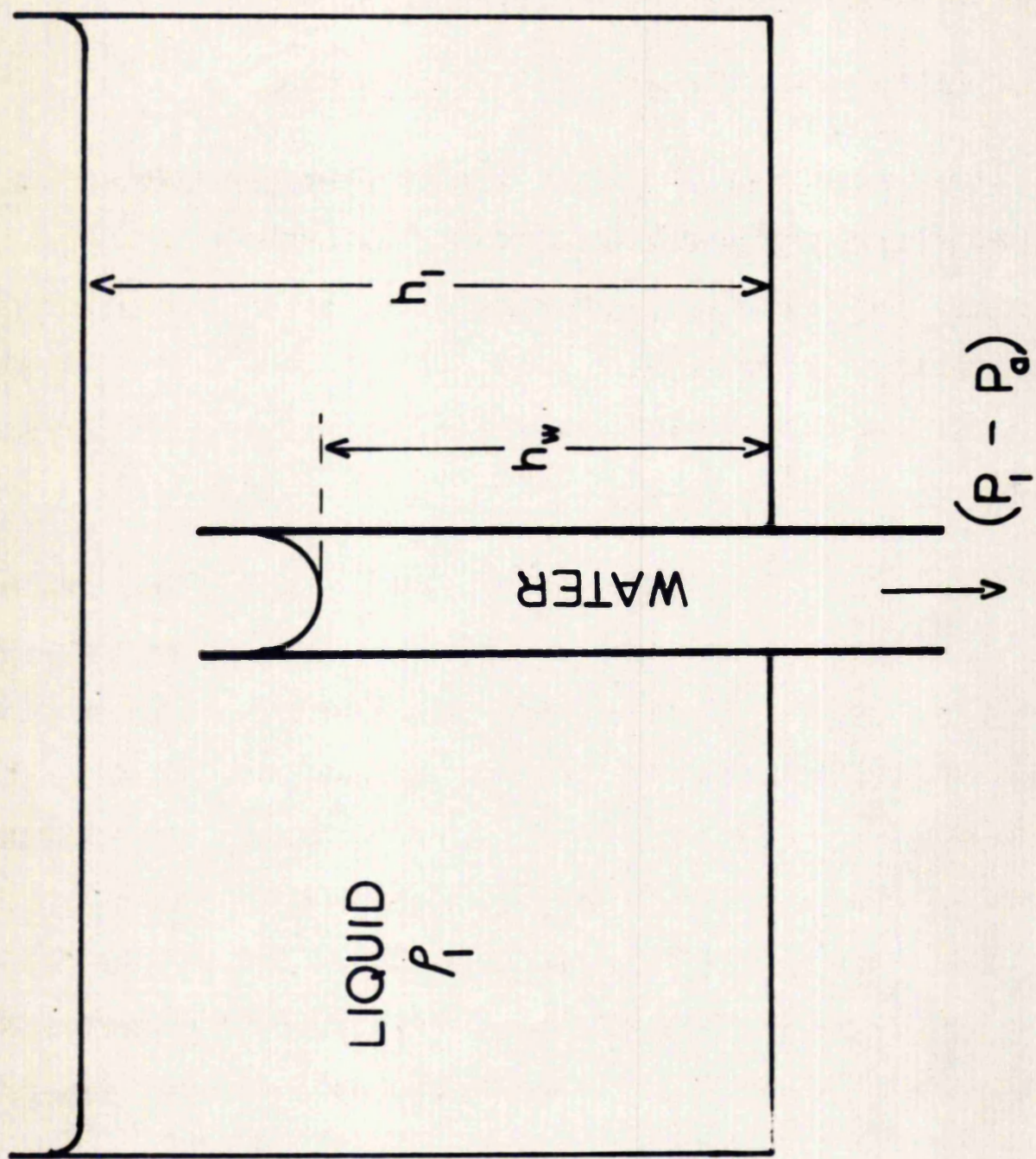


FIG. 4

pressure above the meniscus is changed, evaporation or condensation will occur until the liquid tensions, and therefore the surface curvatures, are again in equilibrium with the changed vapour pressure.

§12. REPLACEMENT OF AIR BY A LIQUID PHASE.

If, in place of air, a second liquid phase is introduced, similar principles apply but instead of the surface tension γ of water against air, the lower interfacial tension γ_1 , between water and this liquid must be used. Where curved interfaces are present in capillaries in such cases, the concave curvature will be directed towards the non-wetting phase.

Consider a capillary projecting above the base of a container filled to a height h_1 with a non-miscible liquid of specific gravity γ_1 (FIG. 4). Neglecting the constant atmospheric pressure P_0 which is present throughout, the hydrostatic pressure at the base of the container will be $\rho_1 g h_1$ and, in order to eliminate the pressure difference between the liquid and the water at this point, a pressure $P_1 = \rho_1 g h_1$ must be applied to the water. At the top of the water column h_w supported by the meniscus, the pressure difference due to curvature will be balanced by the pressure of the water column so that

$$\frac{2\gamma_1}{r} = (\rho - \rho_1) g h_w \quad (8)$$

If ρ_1 approximates to ρ , h_w will increase until, when both are equal, the water in the capillary becomes weightless and will rise to

the top of any submerged capillary irrespective of its height or the interfacial tension, provided that the column of surrounding liquid is balanced by the pressure $P_1 = \rho_1 g h_1$.

On applying a tension ($-P_a$) to the water in the capillary as before, i.e. decreasing the total pressure to $(P_1 - P_a)$, curvature of the meniscus will occur until, with increasing tension, the critical value is reached at which the meniscus will recede down the capillary as described above for the case when air is present.

The replacement of air by a liquid also affects the stress on the capillary tube. When air only surrounds the capillary supporting the water column, there is a variation in the stress acting on the capillary tube from top to bottom, the gradient of which is the same as the tension gradient in the water column, ρg per cm. i.e. neglecting the density of the air and water vapour.

In the presence of the surrounding liquid, the capillary tube has to withstand a resultant stress which is the difference in hydrostatic pressure between the water in the capillary and the surrounding liquid, and the gradient down the tube of this resultant stress is then $(\rho - \rho_1)g$ per cm. If the specific gravity of the liquid is exactly the same as that of water, this gradient will become zero since the difference between the hydrostatic pressure in the water in the capillary and that in the surrounding liquid will be the same at all points. (The actual hydrostatic pressure within either of the liquid phases will still vary with depth below the surface of the

surrounding liquid.) Under these conditions, any tension ($P_1 - P_a$) in the water in the capillary produces a stress on the capillary tube which will be uniform throughout its length. This possibility will be put to practical advantage in the experiments to be described, since, by making the water 'weightless', very low stresses may be applied uniformly to large samples as will be described in the following section.

§13. LIQUID RETENTION BY A CAPILLARY NETWORK.

If, in a non-hygroscopic material, several separate capillaries filled with water are exposed simultaneously to a constant humidity, equilibrium will be attained when, by evaporation and condensation, the menisci in all capillaries have the same double curvature and the water is under the same hydrostatic tension. If, instead, the capillaries are interconnected, equilibrium may be attained by flow of liquid water from one to the other. In a hygroscopic material water transfer may take place by molecular diffusion through the capillary walls also, but in general this will be very slow compared with the faster capillary flow.

On increasing the tension in the water, e.g. by applying suction to the base of the network, the radius of curvature of the meniscus in all capillaries will decrease uniformly until the equivalent radius of the largest capillary is reached. At this tension, called by Haines (1) the 'entry suction', the meniscus will recede down the capillary until, at some narrower cross-section, it can again span the capillary. For geometrically defined capillaries the entry

suction may be calculated and such calculations have been used by Haines (21), Fisher (22) and Smith and others (23) in studying water retention in the case of an 'ideal soil' consisting of small, uniform, regularly packed spheres.

The ability of the capillary network to transmit hydrostatic tensions is the basis of the porous plate method (§3) of studying capillary sorption that is used throughout this Thesis. The porous plate is itself a rigid capillary network to which, if the capillaries are sufficiently small and full of water, considerable tension may be applied before the entry suction is reached. If a porous substance, also completely filled with water, is placed on the plate so that the water is continuous between the sample and the plate, any applied hydrostatic tension will extend to the water in the sample. Thus, provided the tension is not sufficient to draw air through the plate, attention may henceforward be confined to the behaviour of the material placed upon it. If the sample is compressible, its total volume will be reduced as the tension increases, the excess water being free to flow away through the capillaries of the plate. (This aspect of the rheology of porous materials will be considered in greater detail below (§20).) So long as no air passes through the plate the sample need not cover it completely, but the greater the area covered, the more rapid will be the water transfer. On the other hand the rate of transfer of water decreases rapidly with decreasing pore size ^{of the porous plate} so that, for the rapid attainment of equilibrium, the optimum porosity will be that with an entry suction only a little greater than that ultimately required.

Although, at higher tensions, air may enter the larger pores of the sample, increased tensions may still be applied to the remaining water.

On increasing the hydrostatic tension in the water, air will first enter the larger and then progressively smaller capillaries of the sample. Provided that a continuous film of liquid water is maintained between the remaining water in the sample and in the plate, flow of liquid water will be possible. When this film is broken, transfer will be restricted to diffusion through the capillary walls, over their surface, or through the vapour phase, at rates determined by the corresponding vapour pressure gradient. This is equivalent to the usual method of studying sorption by direct humidity control as described in the following section. If a second liquid phase is used instead of air, vapour transfer will no longer be possible, although loss by solution and diffusion in the second liquid may occur to a slight extent.

Since the upper and lower surfaces of water retained in a single capillary (§11) are in equilibrium with the surrounding vapour irrespective of the height of the column, water surfaces in a capillary network must similarly be in equilibrium with the vapour phase at all heights above the base of the network. With thick samples at low applied tensions with which this Thesis is largely concerned, the change with height in hydrostatic tension through the water in the sample due to gravity may be important, but, as mentioned previously, a surrounding liquid may be used to reduce the

resultant stress gradient on the sample itself if required (see also §20).

§14. THE SORPTION ISOTHERM.

When a hygroscopic substance is allowed to reach equilibrium in an atmosphere of given relative humidity, water vapour is adsorbed to an extent depending on the nature of the adsorbent, the temperature and the stresses applied to the system as well as on the vapour pressure p . A succession of equilibrium moisture contents (m = g. water per g. dry adsorbent) plotted against p gives a sorption isotherm.

The predominant mechanism of adsorption of condensible vapours, particularly at temperatures near their liquefying points, is Van der Waals adsorption although, in the case of water, the possibility of water bridging through hydrogen bonds may increase the apparent distance over which these forces act. Nevertheless, there is direct evidence (Bowden and Throssel (20)) that the thickness of an adsorbed layer on a clean plane metal surface at humidities as high as 95 per cent. does not exceed two molecular diameters. At humidities between 99 per cent. and saturation there has been, up to the present, no comparable direct observation to show whether or not water forms a layer of greater equilibrium thickness. This is due to the difficulty of studying, over this narrow range of vapour pressure, the very rapid transition from a thin adsorbed film to a bulk liquid at saturation. Harkins and Jura (24) have suggested from indirect calculation that, during adsorption at high vapour

pressures, a uniform multilayer 9 molecules thick ('duplex film') is formed on powdered crystals such as anastase, but this estimate depends on a surface area measurement involving a sorption technique which may not be valid (see §15). There is some evidence (Bangham and Razouk (25)) that surfaces with vapour adsorbed near the saturation vapour pressure are not readily wetted by liquid adsorbate and that considerable supersaturation is necessary before vapour will condense to a liquid film on such surfaces. The existence of a finite contact angle of a liquid on an adsorbing surface seems to confirm this observation.

§15. CAPILLARY SORPTION.

If a completely water-logged porous material, i.e. one containing no entrapped air in the capillary spaces, is exposed to a slightly reduced vapour pressure, water will evaporate until stresses on the water resulting from the curvature of the meniscus formed, enable equilibrium to be established. As the remaining water cannot all be regarded as held by molecular and Van der Waals sorption, a third sorption mechanism, capillary sorption, must be recognised, which may be defined as the retention of liquid water, behind curved menisci, at reduced vapour pressures. The total sorption, i.e. the moisture content of the sample at any vapour pressure, is the resultant of all sorption mechanisms operating, but the fraction of the total contributed by each will vary throughout the sorption isotherm; thus at low humidities molecular and surface adsorption will predominate whereas at higher humidities multilayer and capillary sorption become

increasingly important. It has been shown by Barkas (26) that, during desorption of water from wood, changes in molecular sorption do occur although, at high vapour pressures, these changes are negligible in comparison with the very large changes in capillary sorption over the same range of vapour pressure.

Capillary sorption is limited to the range of vapour pressure over which the water in the capillary may be regarded as a liquid having a geometric surface and to which thermodynamic laws such as the Kelvin equation may be applied. This limit cannot be defined readily in view of the uncertainty of the transition from a thin adsorbed layer to bulk liquid. Zsigmondy's early theory (27) considered all sorption to be due to capillary condensation even in capillaries of molecular dimensions. In more recent contributions, Cohan (28) and Foster (29) consider capillary condensation of non-aqueous vapours to operate quantitatively in accord with the Kelvin equation for all molecules in excess of a double layer on the walls of the capillary i.e. above a relative vapour pressure of about 0.4 at which the radius of curvature would be only 4 or 5 molecular diameters. Although an increase in adsorption due to surface curvature in these capillaries may be expected to occur, it is doubtful whether the few molecules comprising the 'meniscus' constitute a liquid surface to which geometrical theories may be applied.

At the other extreme, in the Harkins and Jura method of measurement (30) of surface areas of crystalline powders, the effect of

capillary condensation at reduced vapour pressure has been discounted right up to saturation. This method depends on exposing the powder to the 'saturated' vapour of water or a liquid having zero contact angle as a result of which a uniform layer of adsorbate is supposedly formed whose outer surface will have the same surface free energy as liquid water and the same area as that of the powder surface. When plunged into water, the heat of immersion due to the destruction of the water surface gives a measure of the surface area of the powder. A small correction for the thickness of the 'duplex film', 8 - 10 molecular thicknesses, is usually made. For reasons discussed below (§17) it is doubtful whether, in this method, true saturation equilibrium is attained in the 24 hours allowed. The apparent success of the method probably depends on the fact that the heat of Van der Waals sorption in multilayers is only a little greater than that of the condensation of water (compare the equally successful B. E. T. theory which postulates no increase in heat of sorption beyond the first layer) and the slight excess in estimated area that this would entail is compensated by the loss in area of the very small capillaries which have been filled at the effective relative vapour pressure attained. If this did not exceed 0.98, only the fraction of capillaries with equivalent radii less than $0.05/\mu$ would be filled with water and in a loose packed crystalline powder as used by Harkins and Jura, this fraction might well be negligible.

That an increase in sorption, due to capillary structure occurs well below saturation has been indicated by Carman and Real (31) who determined the sorption isotherm of a sample of silica powder firstly

in loose form and then in the form of a compressed plug. The higher sorption by the plug was attributed to capillary condensation in the smaller capillaries although the areas of adsorbing surface were the same except for a slight reduction due to increased areas of contact in the plug.

§16. SATURATION.

Saturation in sorption is attained when the last element of adsorbed water exerts an equilibrium vapour pressure equal to the saturation vapour pressure as defined previously (§7). Under these conditions, the free energy of adsorption is equal to the free energy of condensation of water vapour on a plane liquid surface. This can only occur under the condition that, if the external surface of the adsorbed layer is physically indistinguishable from that of liquid water, it also must have zero curvature. Conversely, if at saturation vapour pressure, its surface has not zero curvature, the adsorbed water must differ physically from liquid water while possessing the same free energy of adsorption. It seems reasonable to suppose (Bangham's observations notwithstanding) that at least in some cases where the liquid adsorbate has zero contact angle, the approach to saturation is accompanied by continuous multilayer formation and capillary condensation. At saturation under these conditions, all capillaries must be filled and bridged with menisci of zero curvature which will be continuous with the external profile of the sample.

A further criterion of saturation is that there shall be no

stress other than that of its own vapour on the liquid water present. It follows that on addition of a small increment of liquid water to the saturated sample there should be no further change in the distribution of the water within it. This will not be equivalent to immersion in bulk water since, firstly, the depth of immersion will increase the total stress acting on the water and hence its distribution in the sample and secondly, immersion will destroy the external water surface of zero curvature and the tension stresses within it which, as will be shown later (§20), are capable of deforming very soft porous materials.

If the adsorbed water surface is not identical with liquid water, a possible condition for equilibrium at saturation may be deduced from the following thermodynamic equation,

$$(-\Delta F)_{\text{ads}} = (-\Delta H) - (-T \Delta S)$$

where $(-\Delta F)$, $(-\Delta H)$ and $(-\Delta S)$ represent respectively the free energy of sorption, the differential net heat of sorption and the decrease in entropy of sorption of 1 gm. of water on an infinite quantity of adsorbate at a given relative vapour pressure. If, at any stage during the formation of an adsorbed film, $(-\Delta S)$ became large, e.g. due to regular orientation, so that $(-T \Delta S)$ was greater than $(-\Delta H)$, further adsorption would lead to an increase in free energy and would not occur, so that an adsorbed layer could exert its saturation vapour pressure before a liquid surface was formed.

§17. CAPILLARY RETENTION AND THE SORPTION ISOTHERM.

The sorption isotherm is usually prepared from successive equilibrium measurements of the moisture content of the adsorbate after exposure to an atmosphere at a series of constant relative humidities. Extension of this technique above 0.99 relative humidity is difficult for practical reasons which have been referred to by Ashpole (32). These are threefold.

- (i) Exceptionally accurate and steady control of temperature is required, since a temperature change of 0.01°C . alters the humidity by 0.1 per cent.
- (ii) The vapour pressure gradients determining the rate of water transfer rapidly become smaller.
- (iii) The shape of the sorption isotherm within this range indicates that, as saturation is approached, the quantity of water to be transferred increases.

Since, at humidities below 0.99, only those capillaries of less than $0.1/\mu$ radius will have filled, it is clear that porous substances containing many capillaries larger than this will be far from saturation moisture content at this relative vapour pressure.

It has been shown that application of a stress dP , to liquid water, changes its vapour pressure by a calculable amount dp , in accordance with equation (5) (§9) which will be valid so long as the quantities u and v may be measured experimentally in very narrow capillaries (see §10). In porous materials where the void spaces are large compared to molecular dimensions, changes in stress may

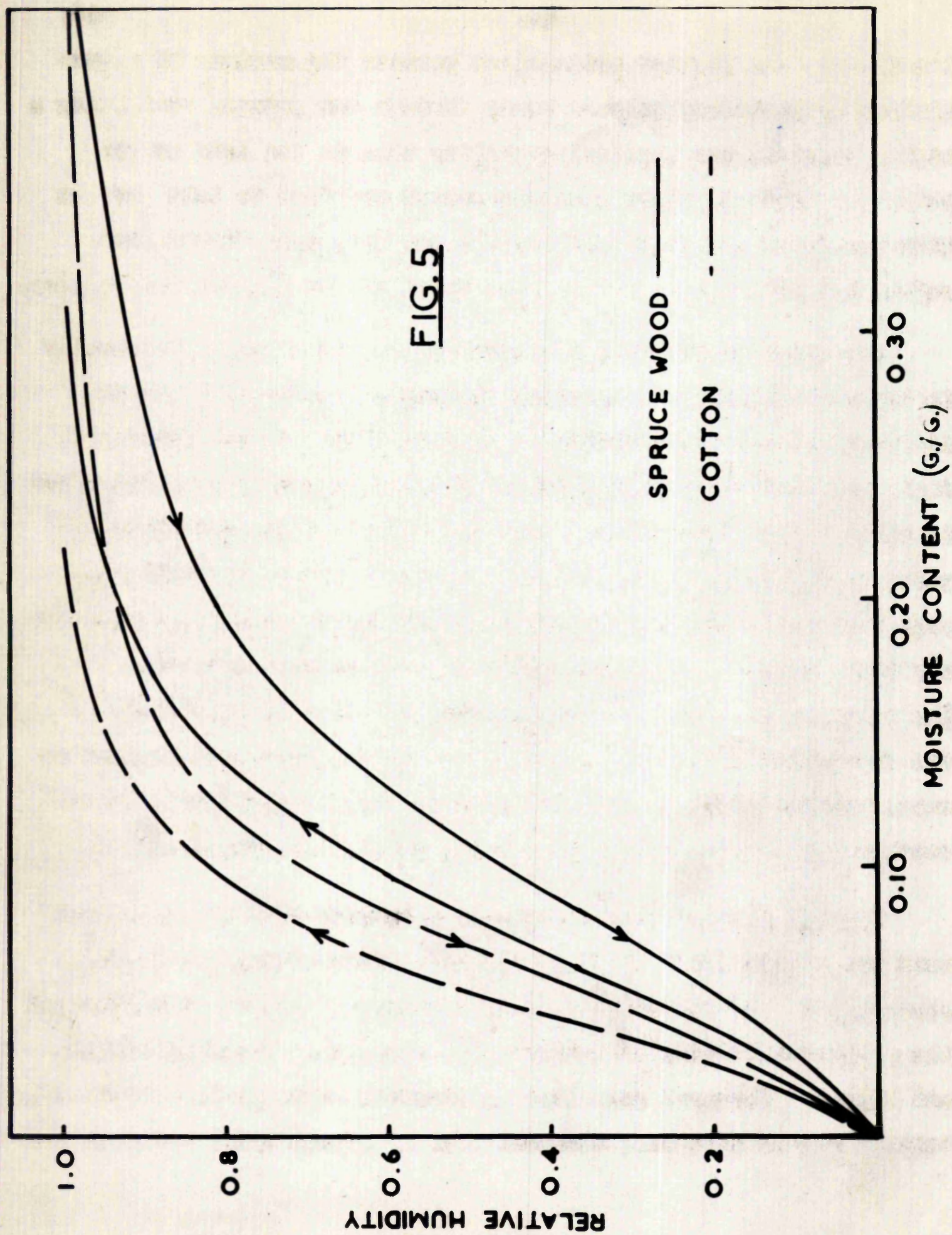
therefore be used to control the vapour pressure of water held in the voids with a high degree of sensitivity at high relative humidities. However, in order to be able to determine the relative vapour pressure equivalent to a given applied stress, integration of (5) is necessary and for convenience an approximation as in (5a) will be used. The stress - moisture content isotherm may thus be converted directly into a sorption isotherm and this is the basis of the porous plate method of determining the sorption isotherm at high humidities.

From TABLE 1 it will be seen that a tension of one atmosphere ($= 1 \text{ bar} = 10^6 \text{ dynes/cm.}^2$ approximately) reduces the relative vapour pressure from saturation to 0.999 which therefore is the lowest vapour pressure attainable by this method. It is thus complementary to the usual humidity control methods which, even with extreme precaution, cannot give a controlled humidity of higher than 0.999 ± 0.0005 .

§18. SORPTION OF WATER BY CELLULOSIC MATERIALS.

Since papermaking fibres consisting largely of cellulose are used for the present capillary sorption studies, the characteristics of water sorption by cellulosic materials are discussed briefly.

Cellulose is composed of long chain polymers of glucopyranose residues, and, for most native celluloses, X-ray and other evidence has led to the acceptance of a fringed micellar structure, i.e. a mixture of "crystalline" and "amorphous" regions with high and low degrees of orientation of the cellulose chains respectively. In



the former, the regular orientation permits the maximum of cross-linking by secondary valence bonds through -OH groups, conferring a higher chemical and physical stability than in the less ordered amorphous regions, where many -OH groups are free to take part in side reactions and whose physical properties, e.g. density and refractive index, also differ from those of the crystalline regions.

The sorption of water by cellulose may be interpreted readily in terms of its fringed micellar structure. Evidence from the differential heat of sorption at zero moisture content (Rees 33), Neale and Stringfellow 34), indicates that initially adsorbed water is held by -OH groups. The strong affinity of dry cellulose for water is indicated by the decrease in total volume of sorbed water plus cellulose (sorption compression) and by the fact that sorption may occur against very large external and internal stresses. The swelling of cellulose accompanying sorption is attributed to the separation of the cellulose chains in the amorphous regions as water bridges of lower bond energies are built up, a limit being reached owing to the stability of the crystalline regions.

Typical isotherms of cellulosic materials such as cotton and wood are reproduced in FIG. 5, the differences being due to the physical structure and macroscopic arrangement of the cellulose and the presence of extraneous materials, e.g. other polysaccharides and lignin. Several quantitative theories of molecular sorption by textile fibres have been advanced e.g. by Pierce (35), Hailwood and

Horrobin (36) and Cassie (37) but a detailed discussion of these is outside the scope of this Thesis. In general these sorption isotherms are sigmoid in shape without any discontinuity in slope up to a relative humidity of 0.98 above which most measurements become inaccurate. To determine the moisture content at saturation vapour pressure, attempts have been made to extrapolate the sorption isotherm above 0.98 relative humidity leading to values from 20 to 40 per cent. for most cellulosic materials.

Although many physical properties of cellulose, which change rapidly with increasing moisture content, approach a limiting value at these moisture contents due to the inability of the intermolecular spaces of the amorphous regions to expand further, these moisture contents are clearly not identical with saturation defined above (§16) nor do they represent the maximum attainable moisture content, since complete immersion in water followed by draining leads to considerably higher values in most cases. This has led to the statement that, above a humidity of 0.99 there is a discontinuity in the slope of the isotherm as capillary condensation commences (38). In measurements by Barkas (39) and Ashpole (32), adsorption has been continued to humidities as high as 0.999 with considerable increase in the quantity of water adsorbed. Nevertheless, the change in slope of the isotherm is gradual as saturation is approached and the apparent discontinuity is due to the comparatively compressed scale on which this part of the sorption isotherm is plotted.

An expansion of the upper end of the humidity scale may be

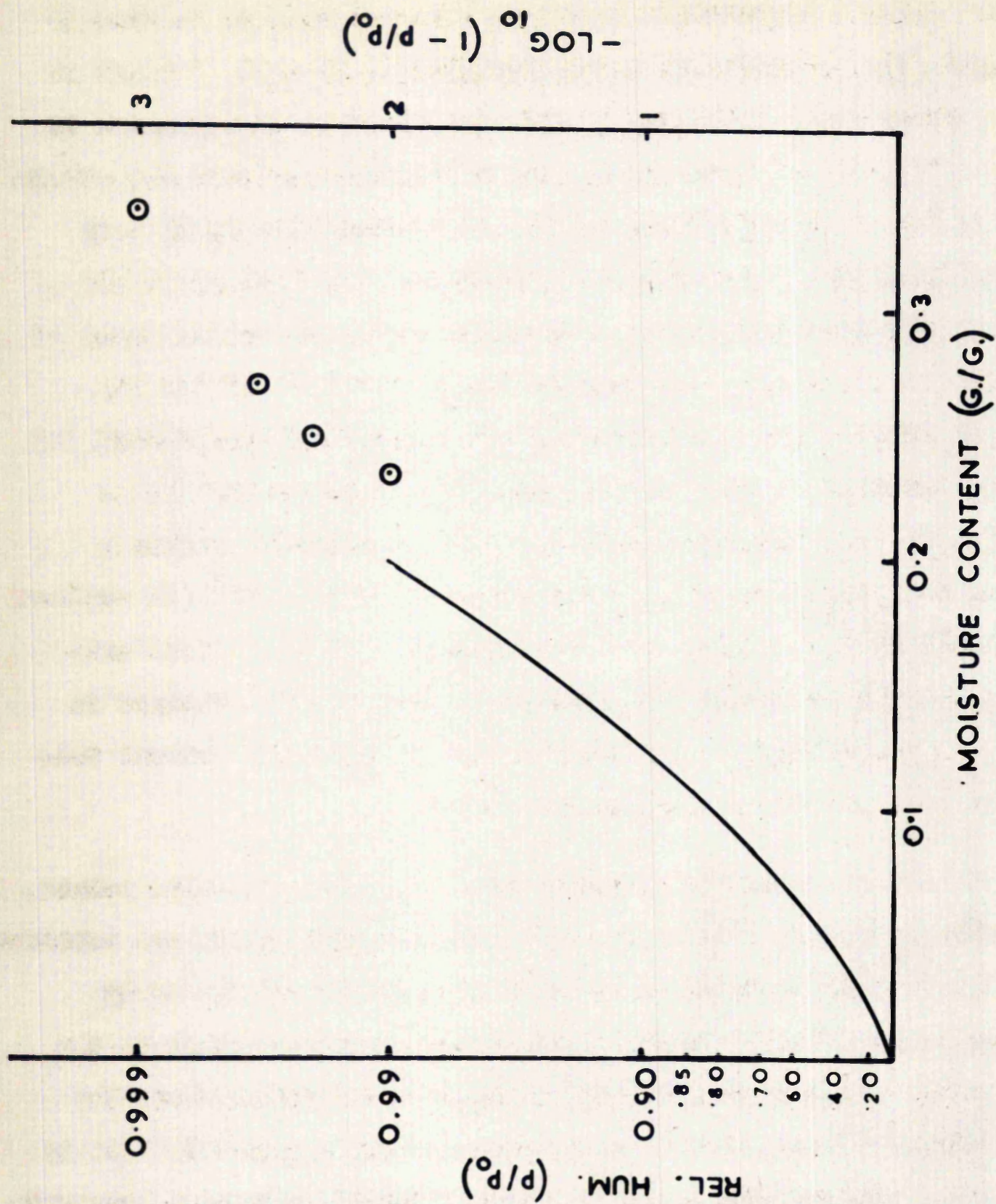


FIG. 6

obtained using a logarithmic basis in a manner similar to that of Schofield (2). Instead of using Schofield's pF unit (defined as $\log_{10} H$ where $H = - (RT/Mg) \ln p/p_0$), the humidity is expressed as $-\log_{10} (1 - p/p_0)$. In FIG. 6, the adsorption isotherm for cotton shown in FIG. 5 is re-plotted as the continuous line up to 0.99 relative humidity. The separate points between 0.99 and 0.999 are Ashpole's data for cotton and, allowing for the differences in material and technique, the continuity of the slope of the two curves is reasonable. A feature of this method of presenting the sorption isotherm is that the saturation vapour pressure is at infinity, so that the sorption isotherm of a material having a limiting moisture content at saturation vapour pressure (in contrast with a salt solution) will become asymptotic to a vertical axis passing through this moisture content. There is no evidence in FIG. 6 to suggest that cotton at the highest moisture content thus attained is approaching a saturation value.

A condition, commonly referred to as "fibre saturation point", is held to represent the moisture content at which cellulose substance is "saturated" while the capillary spaces are completely empty. From theoretical considerations, it is clear that no point on the experimental isotherm can correspond to this condition since the distribution of water between the cellulose and its capillaries is an equilibrium condition in which neither can be saturated independently of the other. Alternatively, it may be suggested that fibre saturation represents, in the saturated sample, the water held within the cellulose molecular structure only. To make this distinction

however, a definition of the cellulose surface is required which distinguishes between the largest intermolecular spaces within the amorphous regions and the smallest fissures or cracks on the defined cellulose surface. Since there is no corresponding discontinuity in the sorption isotherm, it is doubtful whether any but an arbitrary distinction can be drawn. "Fibre saturation" must therefore be regarded merely as an approximation to the amount of water held at saturation vapour pressure in close association with the cellulose substance (i.e. Van der Waals and surface adsorption) as distinct from that held by predominantly capillary sorption.

§19. SORPTION HYSTERESIS.

(a) General

Over at least part of the sorption isotherms of many systems, the phenomenon of sorption hysteresis is observed in which the equilibrium moisture contents during desorption differ reproducibly from those during adsorption. In the sorption of vapours on the so-called rigid adsorbents (e.g. silica gel) the differences were first attributed to the presence of incompletely removed permanent gases or alternatively to non-attainment of equilibrium even over long periods until careful measurements by Rao (40) and Higuti (41) showed that the equilibria did represent final states and further that the adsorption and desorption isotherms were reproducible between the same limits.

Although it is now generally accepted that there may be more than one moisture content in equilibrium with a given vapour pressure,

it is still a matter of opinion whether or not the equilibrium is a metastable state. In a recent interpretation of hysteresis in general, Everett and Whitton (42) suggest that each small scale working unit (domain) of which the system is composed passes through a metastable state with each reversal of trend of conditions, and although the transition in each unit from metastable to stable state is not necessarily reproducible (cf. supersaturation), hysteresis, which is the statistical resultant of all these transitions, will be reproducible if the number of such units is sufficiently large.

The characteristics of true sorption hysteresis are that

- (i) the hysteresis loop is reproducible exactly between the same limits of vapour pressure and that the desorption moisture content is greater than the adsorption moisture content at the same vapour pressure,
- (ii) 'scanning loops' between intermediate vapour pressures are similarly reproducible and lie within the limiting loop between zero and saturation vapour pressure,
- (iii) work is expended in completing any hysteresis cycle isothermally.

In considering theories of hysteresis it is clear that no system of purely reversible mechanisms actuated solely by the relative vapour pressure can explain irreversible hysteresis without the intervention of an external force. Since, apart from non-reproducible phase changes, water itself behaves reversibly, the non-reversibility must reside within the properties of the sorbent or its surface.

Following Zsigmondy's theory of sorption in terms of capillary condensation, it was suggested that hysteresis was due to the differences in advancing and receding contact angles as the capillaries filled and emptied, but this served merely to transfer the problem of hysteresis from capillary sorption to surface wetting. An alternative explanation based on capillary theory, the 'ink bottle' effect, was advanced by McBain (43) but it may be shown that this mechanism depends on the existence of an unstable, or at least metastable, state during desorption. Also it was shown by Cohan (28) that hysteresis occurred in systems where pores of this shape were not likely to be present at all.

Foster (44) suggested that the initial portion of the isotherm, corresponding to monolayer formation over the capillary surface, was reversible and that the beginning of the hysteresis loop marked the onset of capillary condensation and from this attempts were made to deduce the equivalent capillary radii by means of the Kelvin equation. Cohan (45) extended the quantitative considerations and suggested that hysteresis could occur in open capillaries as a result of the 'cylindrical meniscus effect', but again the mechanism may be shown to include an unstable state as in the case of the 'ink bottle' theory. Even if these mechanisms, i.e. contact angle, ink bottle and cylindrical meniscus effects, are accepted as part explanations of hysteresis in capillary sorption, it is certain that the behaviour of liquid surfaces in capillaries cannot account for hysteresis in molecular sorption which has been observed by Barkas on wood (26).

However, not all theories of sorption hysteresis depend on capillary phenomena. Thus Gregg (47) has associated hysteresis with delayed phase changes in the adsorbed monolayer. Bangham and Fakhoury (48) had plotted πA against π for numerous adsorbents on charcoal (π is the surface pressure of the adsorbed film, assumed mobile, and A the area occupied per molecule) and observed a similarity to pV against p curves of an imperfect gas or vapour below its critical point. Gregg showed that when πA is plotted against πS where S is the adsorbing surface per gm. of sorbent, there is a marked similarity to the behaviour of films adsorbed on water surfaces. By plotting data from many adsorption isotherms on this basis, Gregg was led to suggest that the range of vapour pressure over which hysteresis occurred corresponded to unimolecular adsorption and not capillary sorption since the shape of the $\pi A - \pi S$ curve over this region corresponded to the transition from the 'liquid-expanded' to the 'liquid-condensed' state of adsorbed monolayers on a water surface.

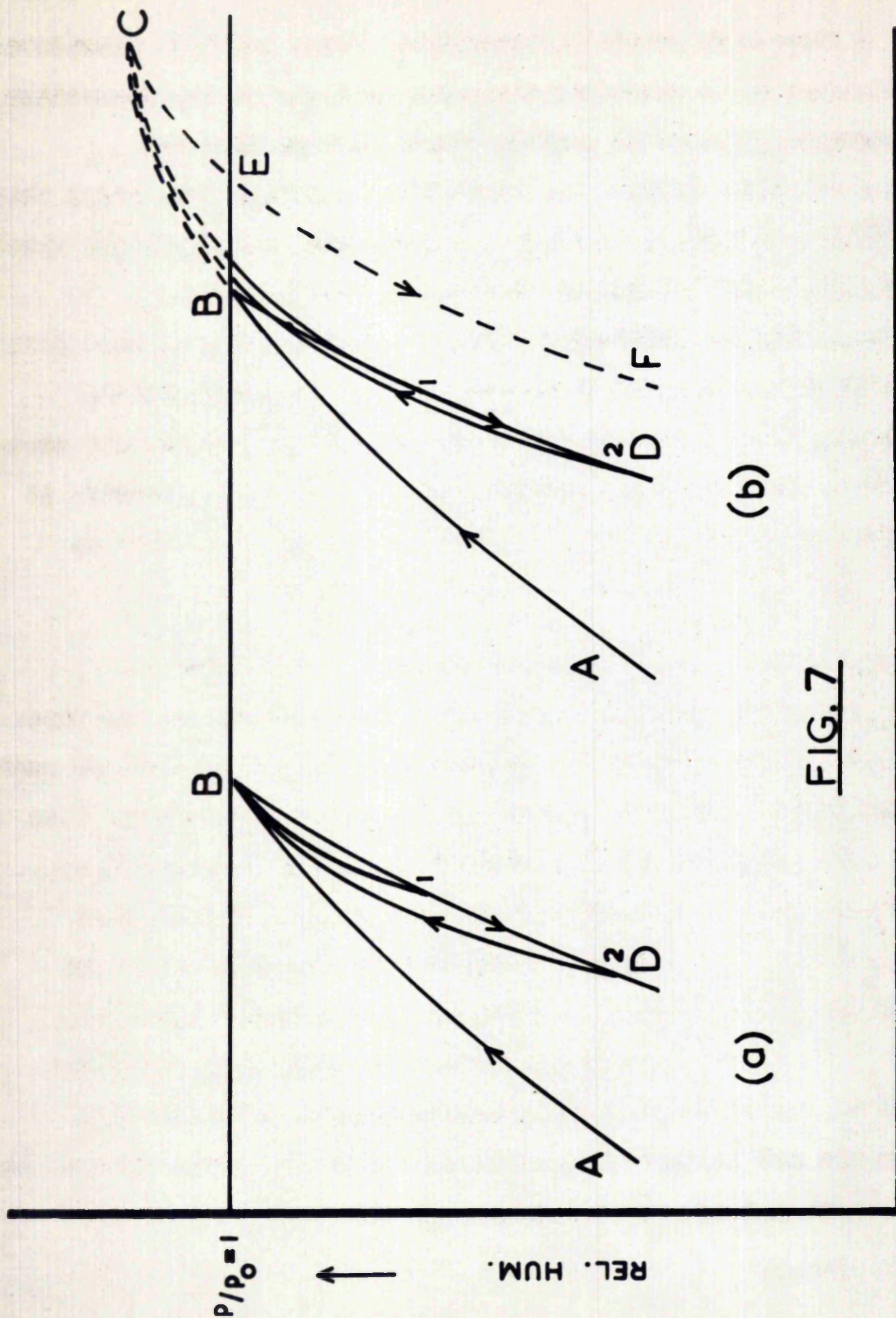
(b) Cellulosic materials.

Whatever the validity of Gregg's theory of hysteresis for rigid adsorbents, it is not the complete explanation for cellulosic materials in which hysteresis is observed over the full range of the sorption isotherm, nor is it likely that capillary phenomena will be solely responsible. Many of the quantitative theories of sorption of water by cellulose and other fibrous materials do not account adequately for the phenomenon of hysteresis in spite of its universal

occurrence. That it is not to be attributed to delayed equilibrium has been shown by Urquhart (49) who observed its persistence after exposure of cotton to a steady vapour pressure for several years without any drift towards a unique moisture content. Urquhart (50) has suggested that hysteresis may be due to the rupturing of hydrogen bonds between adjacent -OH groups in amorphous cellulose during adsorption with a lag in their re-formation during desorption. Again the concept of metastable states of Everett and Whitton might well apply even if the behaviour of any individual hydrogen bond was not reproducible.

An alternative approach to sorption hysteresis has been developed by Barkas (51) by treating cellulose as a swelling gel. By showing thermodynamically that sorption by such a gel is influenced by the internal and external stresses present, it has been possible to relate sorption hysteresis with mechanical hysteresis (plasticity) in a thermodynamically rigorous and quantitative manner. No assumptions regarding the mechanisms of plastic flow are necessary, but this too may be dependent on non-reversible hydrogen bonding. It is possible that sorption hysteresis of the so-called rigid adsorbents may depend on mechanical hysteresis of their surfaces and Brown's theory of contact angles (4) involving distortion of the solid surface at the point of contact suggests a possible mechanism.

In view of the practical difficulty of determining the sorption



(b)

(a)

FIG. 7

MOISTURE CONTENT →

isotherm at very high relative humidities, there has been considerable speculation as to whether hysteresis persists at the saturation vapour pressure, i.e. as to whether there is more than one equilibrium moisture content at saturation. It has been shown that for zero contact angle, saturation requires that all capillary spaces should be filled and bridged by menisci of zero curvature. It follows that, for the saturation moisture content to have more than one value in this case, the dimensions of the saturated sample itself should be able to vary, i.e. mechanical hysteresis must occur. Although this may not be appreciable with the rigid adsorbents, it may possibly occur in the case of porous gel structures such as cellulose.

If it were possible to perform a series of reproducible sorption - desorption cycles between zero and true saturation vapour pressures, a unique value of the moisture content at saturation must be obtained since this forms the limit of a closed hysteresis loop (point B, FIG. 7a), but this is no proof that other equilibrium moisture contents cannot exist also at saturation. If it were possible to extend the sorption isotherm into the supersaturated state (point C, FIG. 7b), any hysteresis loop extended into this region would enclose a range of moisture contents (B to E) at the saturation vapour pressure. That higher vapour pressures than saturation are not in fact attainable is due to the properties of the water adsorbate and not to the adsorbing cellulose in which the hysteresis arises.

A possible method of determining whether a single moisture content only exists at saturation vapour pressure may be seen from FIG. 7. In case (a), ABD represents portion of the hysteresis loop between zero and saturation vapour pressure. If adsorption is commenced from any of a series of points 1, 2, ... on the desorption isotherm, all adsorption isotherms must converge to the unique value at saturation. In case (b), where ABD is again portion of the same hysteresis loop, adsorption from the series of points, 1, 2, ... will yield adsorption curves converging on some point C in the super-saturated state and falling within the envelope of the larger hysteresis loop ACF. In practice, no decision between these two alternatives is possible at present due to the impossibility of extrapolating through the unknown curvature of the isotherm above 0.99 relative humidity. An indication of the answer to this problem may be found using the techniques described in this Thesis extending the controllable upper limits of vapour pressure.

§20. STRESSES ASSOCIATED WITH CAPILLARY SORPTION

Although, for convenience, the following discussion on stresses will deal directly with matrices of papermaking fibres containing water, the principles involved apply equally well to any capillary structures containing any liquid.

In a water-logged bundle, all the fibres but a few in the surface, are immersed completely in the water. These surface fibres together with the water menisci between them form the external surface of the sample. When the liquid is under a hydrostatic

tension, these menisci become concave but, unless the capillary is large and air entry occurs, the line of contact of the meniscus on the external surface may be assumed to remain unaltered. Each meniscus exerts a stress on the surface fibres at this line of contact in the direction of the water surface, and since the menisci are concave, these stresses will have a resultant component directed towards the interior of the sample. The surface fibres will thus tend to be displaced inwards, but since they form part of an entangled fibre network, a stress on any one surface fibre is converted to a stress on the sample as a whole at a relatively short distance in from the surface of the sample. In the following theory, the assumption is made that, if the number of surface fibres, i.e. in contact with the menisci, is sufficiently large, the resultant stress on the fibre matrix as a whole may be regarded as uniform and normal to its external surface, i.e. a hydrostatic compression.

It has been shown already however, that water behind concave menisci is under hydrostatic tension. If the tension is applied by means of the porous plate, removal of the water from the matrix is opposed only by the surface tension stresses and the limited compressibility of the matrix. To a first approximation therefore, the hydrostatic compression on the matrix may be regarded as equivalent to the hydrostatic tension on the water in it, since both act over the same external surface area of the sample. It should

be noted that the water, which is free to flow away as the matrix is compressed, serves merely as a means of applying the stress. Similar results would follow, though much more slowly, if the removal of water occurred by evaporation.

On considering the stresses on the individual components of the matrix, two limitations of this approximation may be seen.

- (i) Since the liquid water does not completely cover the surface fibres, the exact area of application and direction of the resultant stress are uncertain and both will vary as the shape of the meniscus is changed.
- (ii) The surfaces of the interior fibres in contact with the water are subject to the hydrostatic tension tending to produce in them a volume dilatation which would be absent if an external compression alone were applied to the matrix. This effect can probably be neglected in most cases where the bulk modulus of the fibre substance is much higher than that of the matrix.

If, following each change in applied tension, the external dimensions of the matrix are measured, stress - strain curves may be constructed and elastic moduli of the matrix calculated, e.g. measurements of changes in volume with tension will yield the bulk modulus of the matrix at any particular moisture content. Although the stress applied to the matrix as a whole may be regarded as a hydrostatic compression the resultant stress on the individual fibres will be much more complicated due to strain conversion, and the final

dimensional changes of the matrix will involve bending of the fibres and sliding at points of contact. The resultant strains in the matrix, which may be highly anisotropic, are thus due to a reorientation of its fibres involving all elastic moduli and not to a volume change in the fibres themselves which, as indicated previously would be a dilatation.

At higher tensions, after air has entered the matrix, the hydrostatic tension acts only on areas where liquid water is in contact with the fibre surfaces. Directional stresses are thus applied directly to the internal fibres and the equivalence to a uniform external hydrostatic compression can no longer apply. Unless a simple geometric regularity is assumed for the fibre matrix, an analysis of these stresses is impossible. In spite of the fact that the hydrostatic tension in the remaining water will be increased, the resultant average stress on the matrix as a whole may well decrease.

It has been shown previously that the hydrostatic compression acting on the matrix may be regarded as uniform throughout the matrix only if the variation due to gravity has been eliminated by a surrounding liquid. Even assuming such a zero stress difference everywhere between the water and the surrounding liquid, there will still be stresses present in the matrix itself. These may be shown to be equivalent to small compressive stresses which will restrict the uptake of water by the matrix even at saturation vapour pressure.

- (a) The lower fibres in the matrix will be under compression by the upper ones to an extent depending on the difference

between the specific gravities of the fibre substance and water.

- (b) Even though there is no difference in hydrostatic stress between the phases on opposite sides of the meniscus, the surface tension in the meniscus will still produce stresses on the surface fibres at the point of contact. Since for a sample of finite size, these stresses must have a resultant component normal to the surface of the sample, the matrix will be under a residual compressive stress.

As described later (§22), the paper fibres were formed into regular cylinders for which the magnitude of both these residual stresses may be estimated approximately, and shown to be comparable with the smallest tension applied in the present series of experiments. The equivalent relative humidity corresponding to this tension is therefore the theoretical upper limit that may be reached by means of the porous plate technique.

- (a) If the weight of the dry fibre in a cylinder is m gms., and its specific gravity s , its weight in water will be $m(s - 1)/s$ gms. This weight is supported on its base of area πd^2 where d is the diameter in cms. and this may be regarded as a stress at its base of

$$s_1 = \frac{m(s - 1)}{s} \cdot \frac{980}{\pi d^2} \quad \text{dynes/cm.}^2$$

$$\text{i.e.} \quad s_1 = \frac{980 m(s - 1)}{\pi d^2 s} \cdot \frac{10^{-4}}{1.33} \quad \text{cm. mercury.} \quad (2)$$

- (b) In the case of a perfect cylinder of fibres, there will be a stress due to surface tension acting parallel to the axis on the end circumference of the cylinder. If the end surface of the cylinder is regarded as rigid,* this may be considered as a compressive stress over the entire area of the end surface and its magnitude will be given by

$$\begin{aligned}
 s_2 &= \frac{4\pi d \gamma}{\pi d^2} = \frac{4\gamma}{d} \quad \text{dynes/cm.}^2, \\
 &= \frac{4\gamma}{d} \cdot \frac{10^{-4}}{1.33} \quad \text{cm. mercury.} \quad (10)
 \end{aligned}$$

In addition there will be a radial stress directed towards the axis of the cylinder over its entire curved surface of

$$s_3 = \frac{2\gamma}{d} \cdot \frac{10^{-4}}{1.33} \quad \text{cm. mercury.} \quad (11)$$

If the volume dilatations of the fibres and water under a hydrostatic tension are neglected, the reduction in the external volume of the matrix ΔV_m , is the same as the change in inter-fibre volume, which, in the water-logged state, will correspond to the change in volume of the water present ΔV_w .

* This assumption is valid in view of the rigid restraints applied to the ends of the cylinder during measurements.

§21. ELASTIC PROPERTIES OF PADS OF PAPER-MAKING FIBRES.

It is necessary now to consider the elastic properties of the pads of papermaking fibres used in the present series of investigations. The elastic properties of the fibre matrix will not be identical with those of the fibres of which it is composed, since their concentration and orientation within the matrix will also be important. This may be illustrated for instance by comparing the elastic properties of natural wood with those of the cellulose gel of which it is composed. It is not easy to determine elastic constants of single wood fibres since the practical difficulty of direct measurement on single fibres does not yet appear to have been overcome. Nor are they readily predictable from the elastic constants of cellulose itself, since the orientation of the cellulose within the fibre cell wall is complex and varies considerably with different types of fibre. Nevertheless, the elastic properties of an ideal wood fibre, in which this inhomogeneity has been taken into account, have been described by Barkas (51) and, by means of this model, from measurements on spruce wood blocks, the elastic moduli of the cellulose gel forming the secondary wall of the wood fibre have been estimated. In TABLE 2 are shown these moduli together with those of the corresponding wood, the former at a moisture content of 10.4 per cent. and the latter at a moisture content of 12 per cent.

TABLE 2.(Unit of stress = 10^{10} dynes/cm.²)

	cellulose gel	wood blocks
Young's modulus, longitudinal (E_l)	36	12.3
" " , transverse (E_t)	0.9	0.6
bulk modulus (k)	8.4	0.73
rigidity modulus, transverse (G_{tr})	0.23	0.03

Clayton and Pierce (52), Collins (53) and Brown, Mann and Pierce (54) have found the longitudinal Young's modulus of dry cotton fibres to be of the same order of magnitude as wood falling to approximately 1/10th when they are wet.

The size and shape of the individual fibres comprising paper pulp vary with their source and method of preparation. Throughout the present series of tests however, unbeaten softwood pulp was used in which the fibres are usually 2 to 7 mm. in length with tapered ends and approximately 1/100th of this in cross-section. Although they are not always straight, the fibres are not excessively convoluted or twisted. In the present series of experiments, the papermaking fibres were formed into cylinders on which capillary sorption was studied. The method of preparing these cylinders will be described in detail elsewhere (§22) but for the following theoretical outline of their properties, it is necessary to indicate here the type of structure that is built up.

A very dilute suspension of fibres in water flows continuously down a vertical cylindrical tube and the water passes through a horizontal wire screen on which the fibres are trapped, until a pad of the required height or weight is built up. The resultant cylinder may be considered, to a first approximation, to consist of fibres orientated at random in the transverse plane, so that the cylinder possesses axial symmetry. A number of secondary factors (e.g. velocity gradient from the centre to the wall of the tube, segregation of fibre sizes, changes in the differential and total vertical pressure and rate of flow) probably cause radial and axial variations in the pad structure but these will be discussed subsequently (§22). In the following theory however, the cylinder will be considered to have a modified rhombic symmetry with isotropic properties in one principal plane.

For a rhombic system of symmetry, the basic equations for strains parallel to the three perpendicular principal axes, x , y , and z , are as follows:

$$\frac{dx}{x} = - \frac{1}{E_x} (X - \sigma_{xy} Y - \sigma_{xz} Z) \quad (12)$$

$$\frac{dy}{y} = - \frac{1}{E_y} (-\sigma_{yx} X + Y - \sigma_{yz} Z) \quad (13)$$

$$\frac{dz}{z} = - \frac{1}{E_z} (-\sigma_{zx} X - \sigma_{zy} Y + Z) \quad (14)$$

where X , Y , and Z are the stress parallel to these axes, E_x , E_y and E_z the corresponding Young's moduli, and σ the Poisson ratio, in which the suffix xy for instance, indicates the ratio of the strain

in the x direction to that in the y direction on application of a stress Y, X and Z being zero.

In the case of transverse isotropy, the elastic properties are isotropic over one of the principal planes e.g. xy. If any direction in this transverse plane is denoted by t and the longitudinal axis by l, equations (12) to (14) may be re-written.

$$\frac{dl}{l} = -\frac{1}{E_l} (L - 2\sigma_{lt} T) \quad (15)$$

$$\frac{dt}{t} = -\frac{1}{E_t} [-\sigma_{tl} L + T(1 - \sigma_{tt})] \quad (16)$$

The elastic properties of a material possessing rhombic symmetry of this type may be represented by the following seven elastic constants:

$$E_l, E_t, G_{lt}, G_{tt}, \sigma_{lt}, \sigma_{tl}, \sigma_{tt},$$

where G is the shear modulus. It may be shown that these constants are related by the following equations

$$\frac{\sigma_{lt}}{E_l} = \frac{\sigma_{tl}}{E_t} \quad (17)$$

$$G_{tt} = \frac{E_t}{2(1 + \sigma_{tt})} \quad (18)$$

so that five independent observations are required for the calculation of all seven constants. A typical scheme of measurements capable of yielding the required data is presented below. Only a portion of this scheme will be completed in the present Thesis.

Experiment 1.

Consider the application, to a cylinder of fibres, of a hydrostatic pressure P_1 . Substituting $L_1 = T_1 = P_1$ in the above equations (15) and (16) gives

$$\frac{dl_1}{l} = - \frac{P_1}{E_1} (1 - 2\sigma_{1t}) \quad (19)$$

$$\frac{dt_1}{t} = - \frac{P_1}{E_t} (1 - \sigma_{t1} - \sigma_{tt}) \quad (20)$$

Substitution of σ_{t1} from (17) in (20) gives

$$\frac{dt_1}{t} = - \frac{P_1}{E_t} (1 - \sigma_{tt}) + \frac{P_1 \sigma_{1t}}{E_1} \quad (21)$$

It should be noted that the volumetric strain is given by

$$\frac{dv_1}{v} = \frac{dl_1}{l} + 2 \frac{dt_1}{t}$$

Since this is equal to $-P_1/k$ where k is the bulk modulus,

$$\frac{1}{k} = \frac{1}{E_1} (1 - 4\sigma_{1t}) + \frac{2}{E_t} (1 - \sigma_{tt}) \quad (22)$$

(For an isotropic system in which $E_1 = E_t$ and $\sigma_{t1} = \sigma_{tt}$, (22) simplifies to the usual equation

$$\frac{1}{k} = \frac{3}{E} (1 - 2\sigma). \quad)$$

Experiment 2.

Consider the application of a hydrostatic pressure P_2 combined with a longitudinal compressive stress L_2 . Substitution in equations (15) and (16) gives

$$\frac{dl_2}{l} = - \frac{1}{E_1} (P_2 + L_2) - 2P_2\sigma_{lt} \quad (23)$$

$$\begin{aligned} \frac{dt_2}{t} &= - \frac{1}{E_t} - (P_2 + L_2)\sigma_{tl} - P_2(1 - \sigma_{tt}) \\ &= \frac{(P_2 + L_2)}{E_1} \sigma_{lt} - \frac{P_2}{E_t} (1 - \sigma_{tt}) \end{aligned} \quad (24)$$

Thus by measuring the stresses P_1 , P_2 and L_2 , and the corresponding axial and transverse strains in equations (19) and (23), the two unknowns, E_1 and σ_{lt} may be determined. Substitution of these values in equations (21) and (24) then enables E_t and σ_{tt} to be found, and from these and equations (17) and (18) σ_{tl} and G_{tt} . Of the seven constants, there remains only G_{lt} , and a separate experiment involving this shear modulus directly would be necessary for its determination. For instance, measurement of torsion about the longitudinal axis of the fibre cylinder would give the required data.

The theory outlined in the preceding paragraphs applies strictly to bodies which are purely elastic and whose moduli do not change with the degree of strain. However, the effects of small deviations from the simplifying assumptions will be considered when discussing the results of the final experiment, §30.

EXPERIMENTAL METHODS

BRITISH BORD



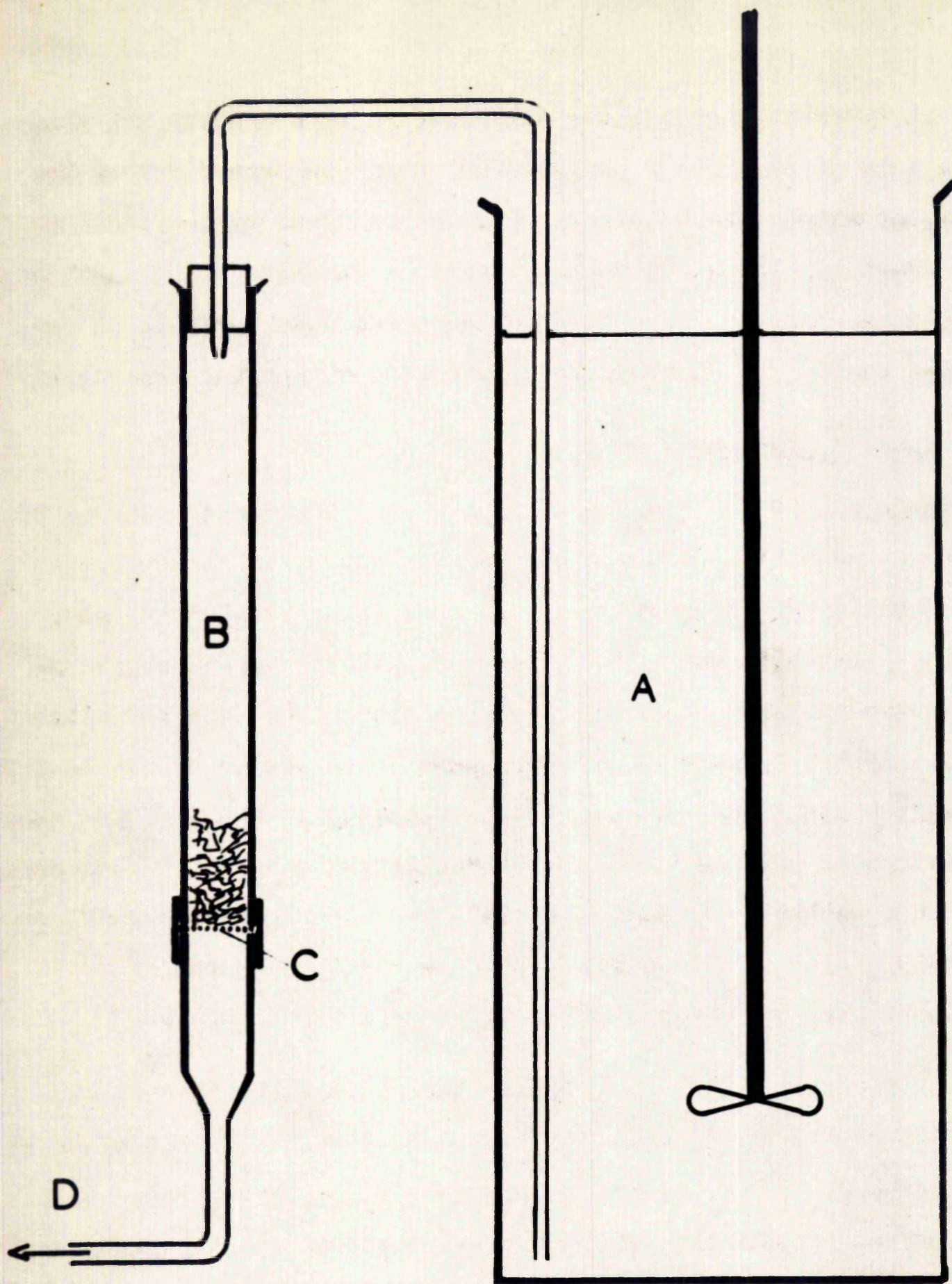


FIG. 8

The experimental methods described in this section are those ultimately adopted after considerable trial and error during the course of which many important observations were made. However, this completed technique was used only in the final experiment in the series. Any important deviations from these methods in the earlier experiments will be described when discussing their results.

§22. PREPARATION OF FIBRE CYLINDERS.

Brief reference has already been made (§21) to the method by which the papermaking fibres are formed into cylinders on which both sorption and dimension changes were observed with changing applied tension. Prior to adopting this technique, a slurry of fibres was merely placed on the porous plate under a small tension and desorption commenced, but considerable variation in the tension - moisture content isotherm was found depending on the size and shape of the sample and the technique of handling it. It was also obvious that this method would not be satisfactory for the measurement of dimension changes. Finally by trial and error the method of preparing the fibres in the form of cylinders was evolved.

In this method a dilute suspension of 0.2 g. of fibres in 2 litres of distilled water (A) (see FIG. 8) is drawn through a fine wire screen held in position by a rubber sleeve at the base of a tube 1.2 cm. in diameter which is that required for the final pad. The fibres are trapped by the screen and a pad is slowly built up to a thickness of from 2 - 4 cm. During the final stages of preparation

of the pad in the tube, air - free distilled water is allowed to percolate slowly through to dissolve any air bubbles that may have been formed in the interior of the cylinder. The pad formed in this way is too soft for convenient handling and its moisture content has to be reduced before it may be transferred without deformation to the plate of the sorption apparatus. To do this a plunger fitting closely to the inside of the tube is pressed onto the top of the pad (while a water column is still present) and the excess water squeezed out mechanically until the water - pulp ratio is reduced to about 6 : 1. On removing the sleeve and the wire base, the pad can be pushed out by the same plunger and handled fairly easily.

This method of formation resembles the formation of a sheet of paper on the wire of a paper machine or in a laboratory sheet making apparatus, although the consistency of the pulp suspension used here is considerably less. This was found to be necessary to prevent flocculation of the fibres during their passage down the tube. As a result each fibre settles individually leading to greater uniformity in pad structure.

An 'ideal' pad prepared by this method would be expected to form a cylinder which, though anisotropic as a result of fibre orientation, should be uniform in any diametral plane and along its axis. For a number of practical reasons this ideal cylinder was not attainable as variation in both consistency and orientation occurred both axially and transversely, although an assumption of

axial symmetry seemed quite justified. The reasons for these deviations from ideal structure will be considered in detail, in view of their probable effect on the elastic properties of the cylinder.

(a) Variation in consistency from centre to circumference.

From direct observation it was seen that the flow of the suspension in the tube by the time the surface of the pad was reached was approximately laminar, as a result of which the faster flow in the centre of the tube tended to increase the thickness of the pad at this point. This non-uniformity may be limited however by the flow then tending to increase relatively through the thinner peripheral regions, but no deviation from axial flow could be detected as the suspension neared the surface of the pad.

(b) Variation in orientation from centre to circumference.

Although during the flow of the suspension down the tube, the velocity gradient would tend to align the fibres parallel to the axis, on striking the surface of the pad the fibres generally settled in a transverse direction. The subsequent vertical compression of the pad tended to increase this horizontal orientation. Nevertheless some variation in final orientation probably resulted from the velocity gradient. Of greater effect than this however, was the wall of the tube which restricted the freedom of the fibres near it to settle horizontally leading to a hollow profile of the pad surface at all stages of its growth. This was found to persist in the final pad as shown by its cleavage across

the axis into layers which were saucer-shaped.

(c) Variation in consistency and orientation along the axis.

It would have been desirable that, as the pad was built up, each increment in thickness should have been made under identical hydrodynamic conditions. This would require constancy of both hydrostatic pressure gradient through the pad and rate of flow, which could be obtained only by steadily increasing the total pressure difference through the pad as it thickened. This, however, would lead to increasing pressure being applied to the fibres first laid down at the base of the cylinder whereas the last fibre increment would not be affected. Further, the theory of filtration suggests that there would be a tendency towards segregation of particle sizes in successive layers following each increment. Both of these effects would lead to changes in density along the axis of the cylinder and to a smaller degree, variations in orientation.

Attempts were made to overcome some of these irregularities. The saucer-like shape of the surface due to the walls was evident even at the base of the cylinder which became rounded when removed from the tube and led to instability when it stood on this end on the porous plate. The flat wire screen at the base of the tube was therefore made dome-shaped to counteract this curvature and a reasonably flat base was obtained although the correction did not persist any distance up the sample.

An attempt was made to keep the rate of flow approximately constant (at 30 cm.³/min.) and as a result the total head of flow across the sample was gradually increased from a few cm. mercury at the start to approximately 70 towards the end. The vertical stress on the base of the pad thus resulting was many times greater than was applied subsequently during the course of the elasticity determinations, but in an attempt to render this preliminary compression more uniform the whole cylinder was compressed strongly by the plunger and then released while still in the presence of excess water in the tube.

Unfortunately, the effect of these structural variations on the elastic properties of the cylinder cannot be predicted with certainty. Consequently the assumption of a rhombic system of elastic symmetry represents an approximation from which the deviations will be apparent only in the results. The greatest changes in dimensions accompanying changes in capillary sorption would be expected to occur in the axial direction, i.e. normal to the plane in which most of the fibres are lying. If in fact the fibres were to lie completely horizontally it is hard to see that any changes in dimensions in this plane could occur at all without considerable slipping of the fibres over one another. In practice small transverse dimension changes do occur.

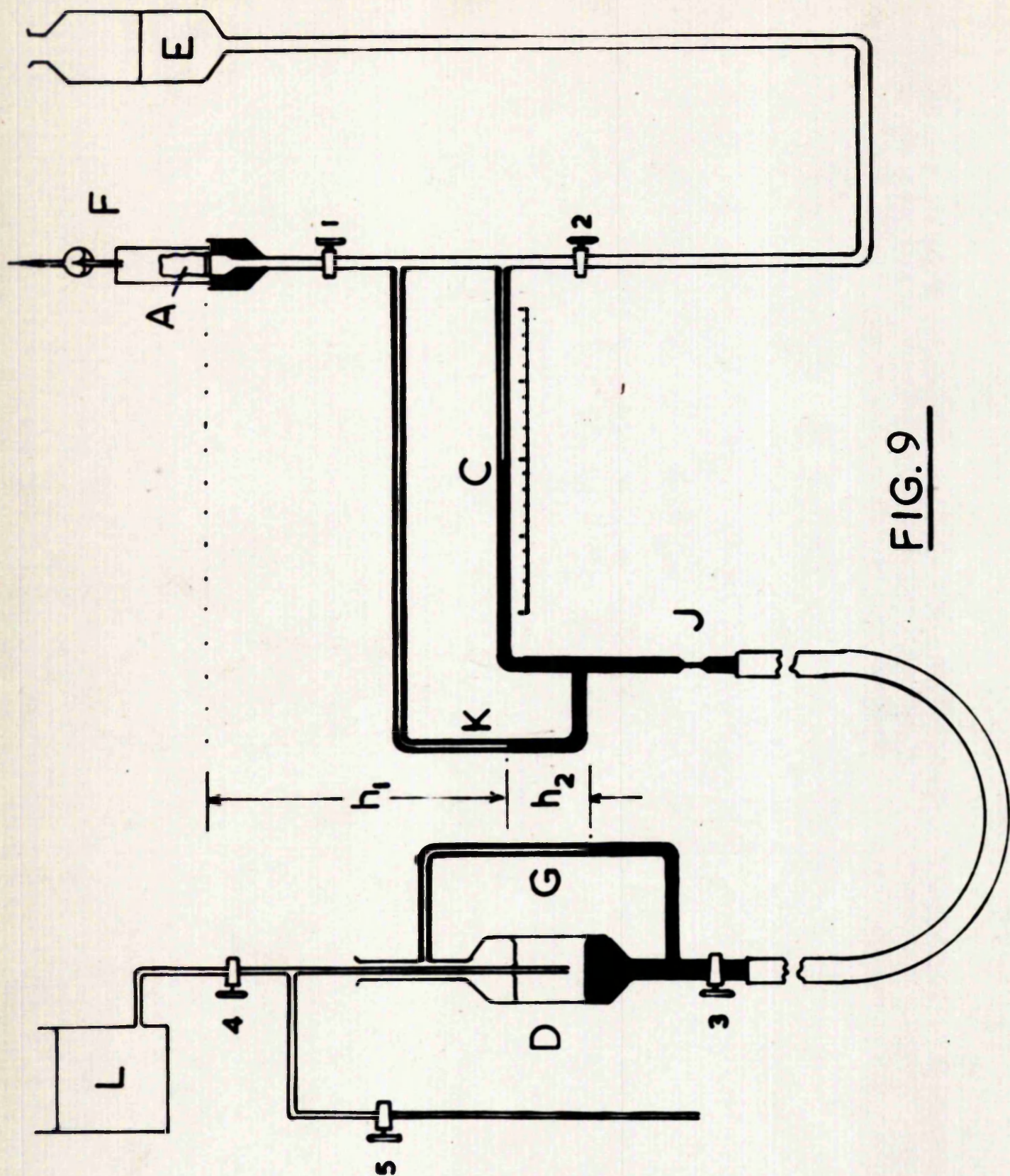


FIG. 9

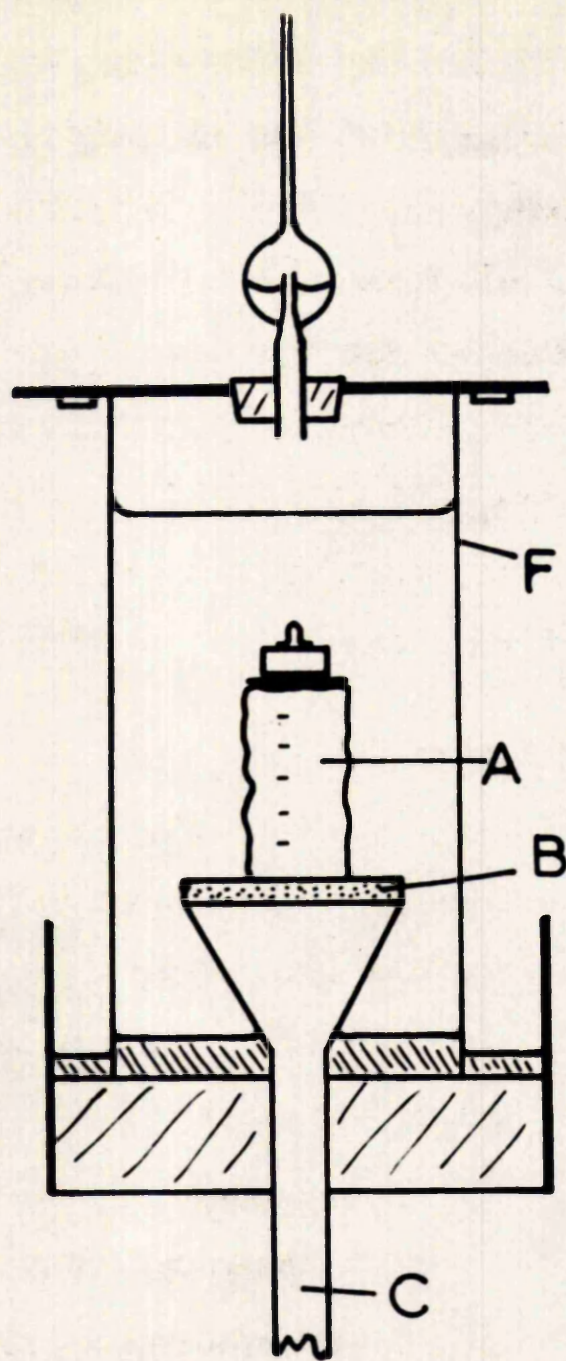


FIG. 10

§23. DETERMINATION OF THE SORPTION ISOTHERM.

The experimental technique for determining the capillary sorption isotherm which was adopted has already been indicated briefly in the Introduction (§3). While suitable for making approximate measurements, the apparatus in the simple form described possessed several disadvantages for the measurements it was desired to make on cylinders of paper fibres. Several modifications were therefore necessary and these are described in turn below. The assembly of the complete apparatus as used in the present series of investigations is shown in FIG. 9.

(a) The porous plate.

As the maximum tension required in the present series of tests did not exceed 20 cm. mercury, a porous plate containing capillaries less than 5μ in equivalent radius (see TABLE 1) was necessary and these requirements were met by a Grade 4 Pyrex sintered glass disc. In order to keep the total volume of water in the apparatus to a minimum (reducing errors due to temperature changes), the porous plate was made just slightly larger than the diameter of the sample (see §13). Instead of having the sample surrounded by a cylindrical tube attached to the plate as in FIG. 1., the arrangement shown in detail in FIG. 10 was adopted, in which the tube ending in the porous plate (B) projects into a rectangular chamber (F), to permit optical measurements to be made.

(b) Reduction of evaporation.

Since the changes in moisture content of the sample are determined solely from the volume of liquid water withdrawn through the porous

plate, it is necessary to eliminate if possible any changes in moisture content by evaporation or condensation. Theoretically this requires that the vapour pressure in the surrounding air should be at all times in exact equilibrium with the hydrostatic tension to which the sample is subjected, but the practical difficulty of doing this has already been discussed and an approximate control of humidity is all that can be expected. If the sample were completely enclosed, no evaporation from the system could occur although some transfer from the sample to the surrounding wall might take place depending on the size and shape of the cover and the temperature gradients occurring. If a free liquid surface was enclosed the air would be virtually saturated (except for gravitational effects). The vapour pressure gradients and thence the rate of vapour diffusion from the sample to the walls would be sufficiently small to be neglected in experiments of short duration. Provision of a capillary leak would be necessary to eliminate total pressure changes as the sample changed in size.

The form of cover and method of support actually used in the final experiments are shown in detail in FIG. 10. The porous plate (B) is surrounded by a cup sealed at its base with its rim just below the level of the porous plate. This cup contains a seal (initially mercury was used, later, a setting resin) for the rectangular glass chamber (F) over the top of which is a glass cover provided with a capillary air leak. This has an intermediate bulb containing water so that any air entering the cover becomes

virtually saturated. It was found however, that, over a period of several days, water gradually misted over the inside surfaces of the glass cover and the mercury. The amount of this condensate, though small, was unknown but, since water would be withdrawn from the tube (C) to take its place in the sample, its effect would be to produce an apparent gradual increase in the moisture content of the sample.

(c) Use of a non-miscible liquid.

Early tests showed that the quantity of water, which these fibre cylinders could absorb when no tension was applied at the base, was limited by the height of the sample itself (see §§12, 13). The possibility of using a non-miscible liquid in place of air was therefore considered as described previously. In addition to eliminating the stress gradient on the fibre matrix, the surrounding liquid would also reduce evaporation provided very little water dissolved in the second phase. To be ideal the liquid should possess the following properties:

- (i) it should be highly insoluble in water and vice versa,
- (ii) it should have the same specific gravity as water at 20°C.,
- (iii) it should be non-volatile and chemically stable,
- (iv) it should have no effect on the physical or chemical properties of the fibres in the water - swollen state,
- (v) it should be colourless and clear,
- (vi) its interfacial tension with water should be as high as possible.

Of several organic compounds possessing most of the required characteristics three readily available compounds, anisole, indene and iso-butyl benzoate, were tested and the last named finally selected. Its density when saturated with water relative to water at 20°C. was found by direct weighing to be a little too high and exact adjustment was made by adding a few parts of paraffin oil.

(d) Changes in moisture content at constant tension.

One of the disadvantages in the simple apparatus shown in FIG. 1 is that, as equilibrium is approached, there is a gradual change in the tension acting on the sample due to the change in the level of the mercury surface in (C). This has two disadvantages. It is difficult to pre-select the final tension at which the equilibrium moisture content is measured. Secondly, following the initial rapid change in moisture content with each tension change, different portions of the sample may be adsorbing and desorbing simultaneously as equilibrium is approached and, where hysteresis is present, inappropriate moisture contents would be obtained. In the modified apparatus this was overcome by placing the graduated tube (C) in a horizontal position so that changes in volume of water in the sample could occur without affecting the height of the water column h_1 . By making the bore of the tube sufficiently small, approximately 2 mm, there was no tendency for the mercury ~~water~~ column to break and allow water to pass. At the same time by making the cross-section of the bulb (D) sufficiently large, e.g. 5 cm. diameter, the mercury level within this arm did not change appreciably with change in moisture

content of the sample. To enable accurate measurements of the mercury levels to be made, two identical side tubes (G) and (K) were added in which the difference in mercury levels gave the height h_2 . If the height of the mercury level in (G) giving zero tension at the plate (B) was known, differences only in the height of this surface were then needed to determine the applied tension provided (C) was exactly horizontal.

During increases in the moisture content of the sample, it was necessary to reduce the rate of advance of the mercury column in (C) to less than 1 mm./sec. to avoid trapping water against the walls of the tube. This was achieved by including the fine constriction (J).

(e) Sensitivity and the lowest applicable tension.

The difference in mercury levels in the tubes (G) and (K) were measured with a cathetometer having a sensitivity of 0.005 cm. This was therefore the maximum sensitivity in measuring the applied tensions that could be expected assuming that all other errors, in levelling the apparatus etc., could be reduced to this value. Similarly the minimum measurable tension that it was possible to apply at the base of the sample was 0.005 cm. Hg (unless another liquid were used in place of mercury) which may be seen from TABLE 1 to be equivalent to a relative humidity of 0.99999995 and a radius of meniscus curvature of 1 cm. In practice, due to combined errors, it is doubtful whether the position of the mercury surface in G corresponding to zero tension could be determined with an accuracy

exceeding ± 0.01 cm. Hg, although differences in tension may be adjusted and measured with the higher accuracy. It may be shown that this order of magnitude represents the lower theoretical limit of tension (and therefore highest equivalent humidity) that may be attained using the porous plate method. In §20 it was shown that, even under a condition of zero pressure difference between the capillary water and the external medium, there were residual stresses on the matrix arising from its weight and also from the surface tension of the water surface. Numerical calculation of the vertical compressive stresses by means of equations (9) and (10) for the fibre cylinders used shows that together these may reach the same order of magnitude as the sensitivity of the apparatus. For example, for a cylinder in which $s = 1.5$, $m = 0.2$ and $d = 1.2$, the stress on its base due to the weight of the fibre matrix itself is given approximately by

$$S_1 = \frac{0.2 \times 980}{3\pi \times (1.2)^2} \cdot \frac{10^{-4}}{1.33} = 0.0011 \text{ cm. Hg,}$$

and the stress due to surface tension ($\gamma = 35$),

$$S_2 = \frac{4 \times 35}{1.2} \cdot \frac{10^{-4}}{1.33} = 0.0088 \text{ cm. Hg,}$$

so that together $S_1 + S_2 = 0.01$ cm. Hg.

§24. MEASUREMENT OF DIMENSION CHANGES.

Although the theoretical analysis of the elastic behaviour of the sample (§21) assumes an ideal cylinder with rhombic elastic symmetry, this was not likely to be realised in practice.

Preliminary measurement showed that in many cases variations within the cylinder were too large to justify the use of mean values representing strains in the cylinder as a whole. Apart from the inherent structural variations within the cylinder previously discussed, end restraints due to the method of support were also evident. It could be expected therefore that only those portions of the cylinder far removed from these restraints could be expected to behave in a normal manner, and to give results to which the above theories of elasticity could be applied. Since the moisture content could be measured only for the cylinder as a whole, it was necessary to measure its dimension changes at numerous points and to integrate the results in order to compare its total volume change (ΔV_m) with the change in moisture content (ΔV_c). The length of the cylinder was therefore divided into horizontal segments whose behaviour within the cylinder as a whole was studied individually. In practice it was not convenient to use the same subdivision of its length when measuring both axial and transverse strains, so that graphical methods were found necessary to enable appropriate strains to be determined for any given segment.

For convenience, the cylinder was allowed to stand on its end on the porous plate so that the axial strain was determined from changes in height of the cylinder. These were large enough to be measured directly with the cathetometer (sensitivity 0.005 cm.). In the earlier experiments, strains in the total height only of the cylinder were measured. In order to determine the relative

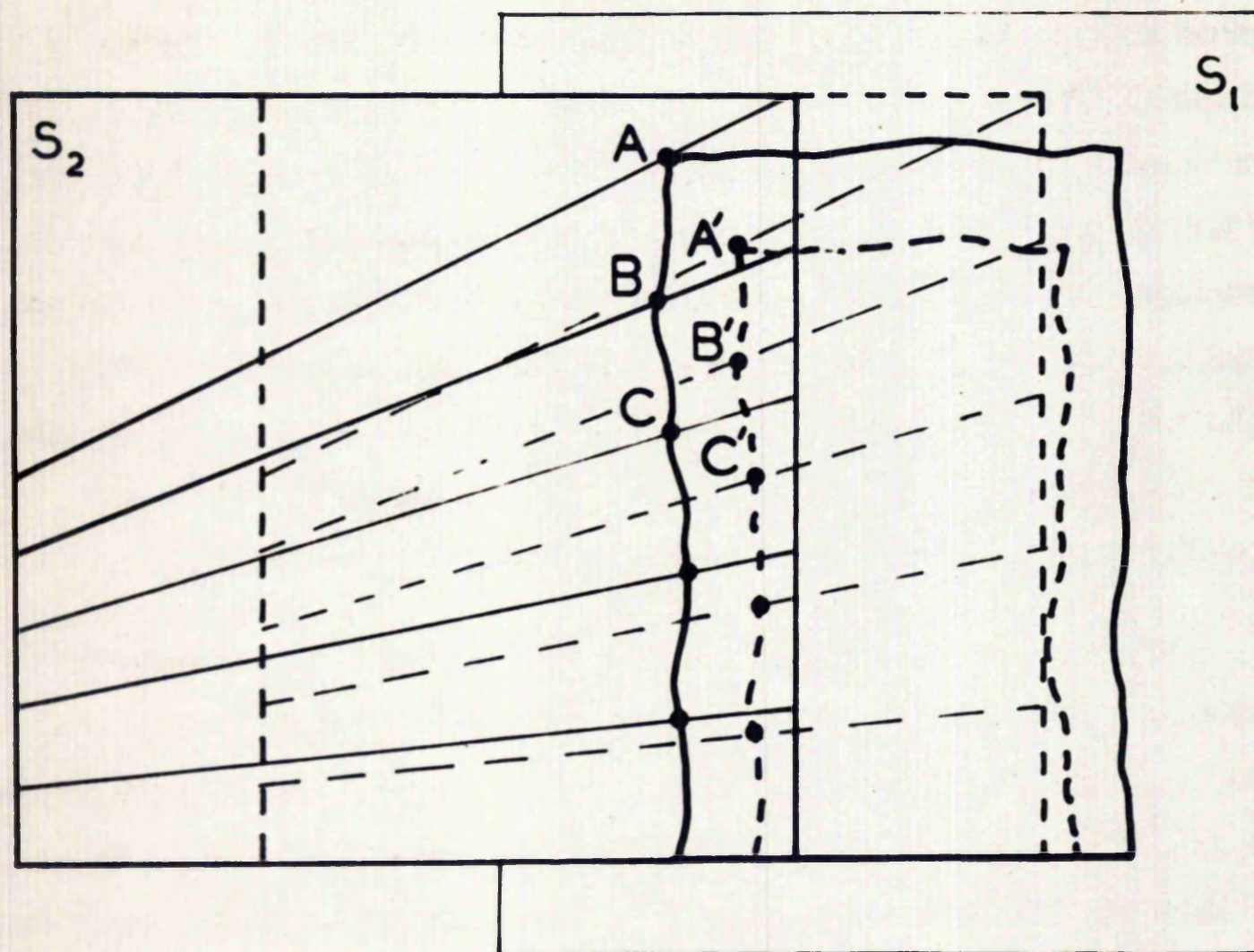
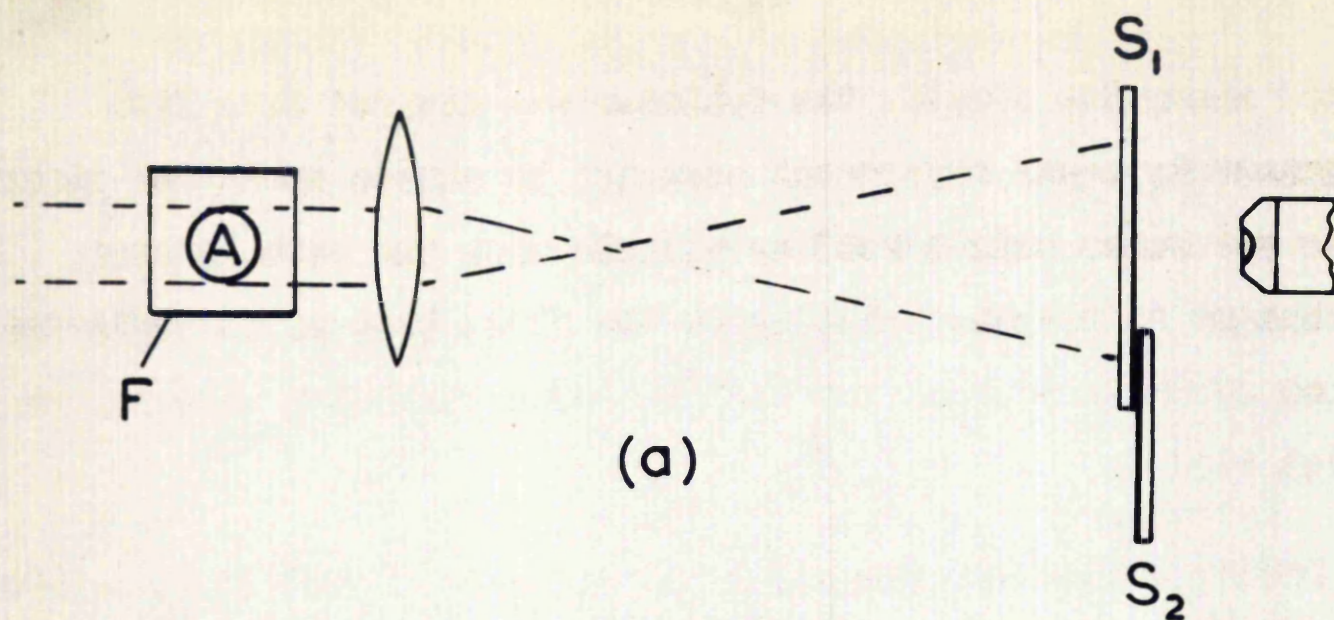


FIG. 11

strains along its length, the cylinder was divided into five approximately equal horizontal segments by minute specks of black ash as reference points readily visible with the cathetometer. The changes in height, relative to the fixed base of the cylinder, of each of these points were then observed following each change in applied stress.

Before transverse strains could be measured with the required accuracy, magnification was necessary. Mechanical levers were impracticable for this in view of the isolation of the sample and the small stresses involved, so an optical method was used. This consisted in placing the cylinder (A) in a beam of parallel light (FIG. 11a) normal to the flat sides of the glass cover (F) and focussing the image of its profile (magnification $\times 5$) on a ground glass screen (S_1). The diameter of the cylinder at any height could be determined from the width of the image measured from behind the screen with a horizontal travelling microscope, the exact magnification of the image being determined independently.

The cylinder was divided vertically into equal segments by horizontal lines ruled on (S_1). To measure the diameter of any segment, the vertical hair line of the microscope was brought up to one side of the image so that the area of the shadow from overlap on one side of the line was balanced by the area of light on the other side resulting from depressions of the profile. From differences in readings taken thus on each side of the segment, its mean width was obtained. Since irregularities in the profile were usually

small within any one segment, errors in visually locating the hair line were not very large. From a knowledge of the magnification of the image, determined independently, the mean diameter of the segment was obtained.

With each change in tension, it was desirable to measure the strain in each of these original segments, but as these changed their position on the screen due to longitudinal shrinkage of the cylinder, a special method of following them was required. This is shown schematically in FIG. 11b, using five segments for simplicity. In the plane immediately behind (S_1) and overlapping it slightly, was placed a transparent second screen (S_2) having sloping lines ruled in such a way that any vertical line drawn through them was divided into equal parts. The top line was made to coincide with the top corner (A) of the image by sliding (S_2) horizontally behind (S_1). The intercepts of the profile AB, BC, etc. then marked the equal segments whose mean diameters were measured. At the next equilibrium moisture content when the sample had shrunk (e.g. forming the dotted profile,) the screen (S_2) was moved further across (S_1) until the top line again coincided with the corner of the image now in the position (A'). The intercepts (A'B'), (B'C'), etc. then formed the same number of equal segments which, provided the shrinkage was uniform, would be the same as the initial segments though reduced in size. The new diameters were then measured as before.

In addition to the measurement of the volume strains in separate segments of the cylinder, it was desirable also to calculate its

total volume (V_m) for comparison with its volume (V_w) calculated from its oven-dry weight, specific gravity and moisture content, thus affording a mutual check of both sets of measurements i.e. while the sample was still in the water-logged state. However an uncertain correction was rendered necessary occasionally by the fact that some cylinders had an irregular top and the volume of this portion had to be added to that of the segments. An approximate estimate only of this could be made and this constituted the largest source of error in calculating the volume. Generally, however, the agreement was good (within a few percent) and even better agreement was obtained in the volume changes ΔV_m and ΔV_w where this correction was not involved.

§25. APPLICATION OF LONGITUDINAL STRESSES.

In the final experiment to be described in the present series, small vertical stresses were applied to the cylinder by means of a brass weight placed on its upper end. In order to distribute this stress evenly over the end of the cylinder, a small, wire mesh disc of the same diameter as the cylinder was placed on its top end at the time of its formation. This served two additional purposes.

- (i) It ensured that the top end of the cylinder was flat thereby increasing the accuracy of the volume calculations.
- (ii) It applied a dimensional restraint on this end of the cylinder similar to that at the base due to its contact with the porous plate.

To apply the stress, the flat glass cover (see FIG. 10) was temporarily removed. The brass weight was lowered on a hook through the surrounding liquid, by means of a small windlass, and located as nearly as possible on the centre of the end, to avoid uneven compression of the cylinder. The cover was then replaced.

§26. METHOD OF PROCEDURE.

Following is the sequence of operations involved in making a typical series of measurements on a single fibre cylinder.

The apparatus was carefully cleaned, filled with air-free distilled water and assembled as shown in FIG. 9 without the sample or the surrounding liquid. The tube (C) was carefully levelled by means of the cathetometer, and the mercury level in (C), corresponding to zero tension at the plate, was determined when a continuous film of water appeared at the surface of the porous plate. The position of the mercury surface in (C) was noted since this corresponded to the initial moisture content of the cylinder when placed on the plate and could be adjusted by running water in or out of (E). By raising (D) a small pool of water was formed on the top of the porous plate onto which the sample was placed forming an air-free contact between the base of the cylinder and the plate.

In preparing the cylinder, a known weight of air-dry conditioned fibres was used and their initial moisture content determined by oven drying matched samples which had been conditioned at the same time. The freshly prepared cylinder of fibres was removed from the tube in

which it was formed by means of a plunger and the fine black marks placed in appropriate positions along one side. It was then weighed together with the wire screen disc on its top end and transferred as rapidly as possible to the porous plate of the apparatus. A small tension was applied immediately to the plate and the sample on it by lowering (D) and the non-miscible liquid was then added.

The liquid used in the final experiment in this series consisted of freshly distilled iso-butyl benzoate. Its specific gravity which was slightly greater than one, was reduced to 1 ± 0.001 by adding a small quantity of paraffin oil and then saturated by shaking with water and allowing to stand. After checking the specific gravity by a direct weighing method, the saturated liquid was run carefully into the rectangular container until its level was approximately 1 cm. above the top of the cylinder, and the flat glass cover placed in position. The hydrostatic head of this liquid above the porous plate was added to the tension applied at the plate as indicated in §12 and changes in its level during the course of the sorption cycles were recorded.

In the final experiment the series of sorption - desorption cycles was commenced from the desorbed condition, and accordingly an initial tension of approximately 1 cm. mercury was applied. This was found from previous tests to be the maximum tension that could be applied to the fibres under test without entry of the surrounding liquid. The sample was then taken through a series of cycles between this and zero tension until after 7 or 8 such cycles the

moisture contents at these limits of tension were found to be reproducible. The time required for equilibrium to be established following each change in tension was from 12 to 24 hours although 95 per cent. of the change occurred in the first hour. The experiment proper, involving small changes in tension (with and without additional stresses) together with dimension and moisture content measurements, was then commenced.

Several additional measurements were also necessary to complete the data. It was necessary to measure the weight of the wire screen disc on the top of the sample both in air and in the surrounding iso-butyl benzoate and also the effective stress of the added weights in the iso-butyl benzoate. From the assembled data it was then possible to measure changes in moisture content, changes in dimensions and volume and all applied stresses.

BRITISH BORD

RESULTS AND DISCUSSION.



In the following portion of the Thesis, results from each of five separate experiments will be discussed. These were selected from the total experimental work done as best illustrating the development of technique and at the same time demonstrating between them all the phenomena that have been observed during the course of experimentation. Lack of time prevented a more complete presentation of experimental data which, however, would serve merely to confirm the observations described. Since this Thesis is concerned primarily with the development of a principle and its experimental application, the quantitative results should not be regarded necessarily as typical of the pulp from which test samples were prepared. In order to employ these methods for the characterisation of paper pulps, further study of the effects of variation in experimental technique would be necessary.

§27. EXPERIMENT 1. ESTABLISHING A REPRODUCIBLE CYCLE.

Before finally attempting to apply the porous plate technique to measurements on fibre cylinders, it was considered desirable to determine some of the sorption characteristics, particularly that of cyclic reproducibility at very low tensions, of small samples of papermaking fibres to which a minimum of stress had been applied and in which the initial desorption was as far as possible an extension of the de-watering process in forming the pad.

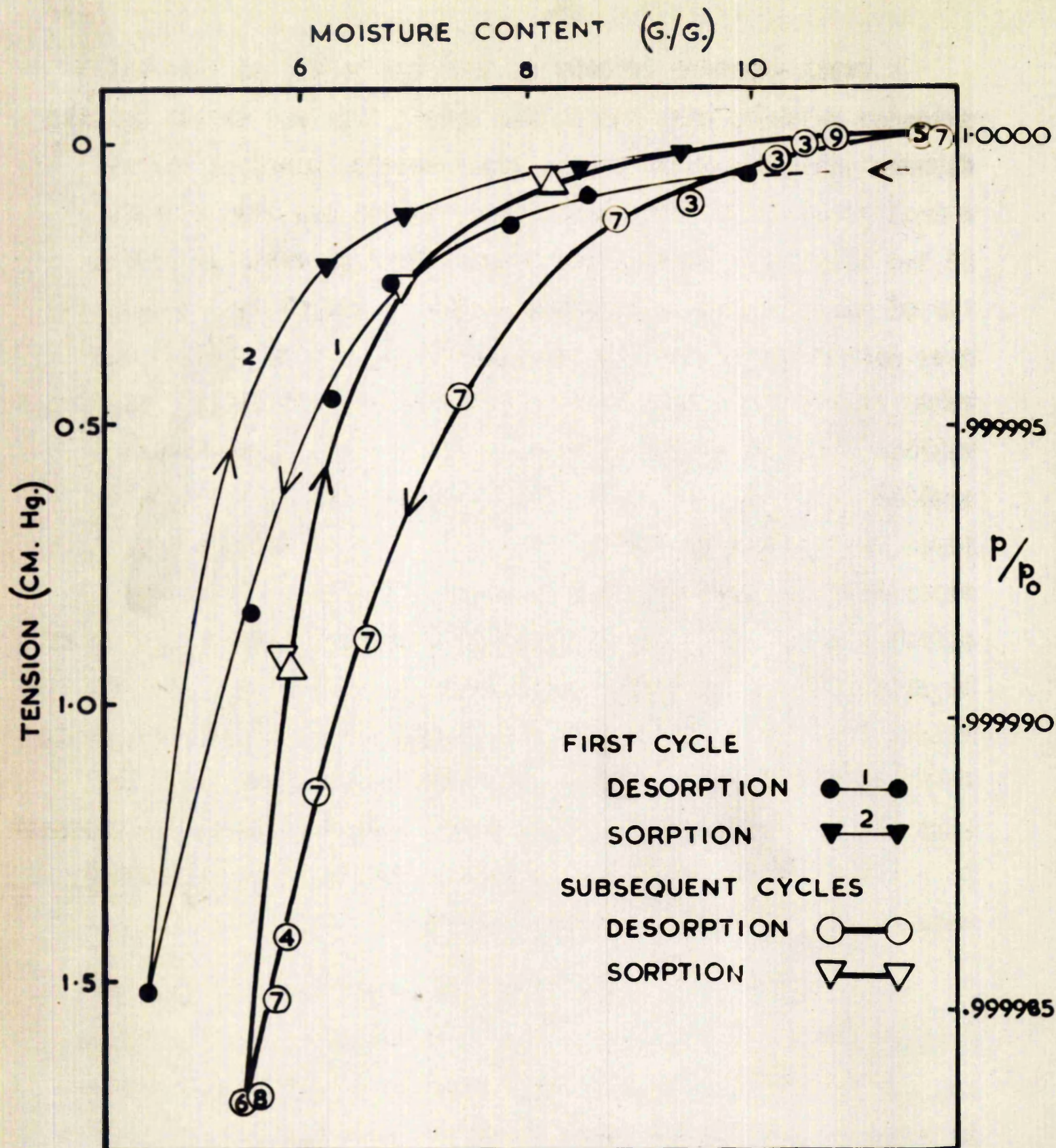


FIG.12

A small quantity (0.0190 g. oven dry basis) of bleached unbeaten sulphite pulp was formed into a thin mat in the cylinder-forming apparatus under a very small tension gradient and no manual compression was applied when the mat had been formed. It was allowed to drain under a small head of water and transferred as carefully as possible to the porous plate. Since some distortion of the mat was inevitable, it was flooded with water through the plate in an attempt to relieve these distortions without breaking up its formation, and a small tension then applied. No second liquid phase was used for this experiment since the maximum height of the sample did not introduce an error due to stress gradient greatly in excess of the other errors present. No measurements of dimension changes were made in this experiment. The actual moisture content and oven dry weight were determined at the end of the series of sorption cycles which are shown in FIG. 12. The total period over which the sorption cycles were studied was only seven days since the approach to equilibrium was considerably more rapid for this thin sample than for the cylinders described elsewhere.

The initial desorption (black dots) was measured from a moisture content of approximately 10 g. water per g. dry fibre (g./g.) falling to 4.6 g./g. at a tension of 1.515 cm. mercury. In order to prevent air entry which had been found independently to occur with this pulp at approximately 3 cm. mercury, tensions of 1.75 cm. mercury were not exceeded. The following adsorption

(black triangles) was taken to nominally zero tension (± 0.01 cm. Hg.) at the point 3 from which the second desorption was followed to point 4 then adsorption to 5 and so on to 9, completing four cycles. The data from this single experiment is valuable in demonstrating a number of important phenomena.

1 (a) Reproducibility.

It may be seen that, after the first desorption and adsorption, the sorption cycle between approximately the same tension limits became reproducible within experimental error. The explanation offered for the difference between the first and subsequent cycles is that, during the first cycle, some relative displacement of the fibres occurred in the loosely formed pad and this displacement became permanent due to entanglement and possibly bonding between the fibres. Following the second desorption, no further permanent changes occurred.

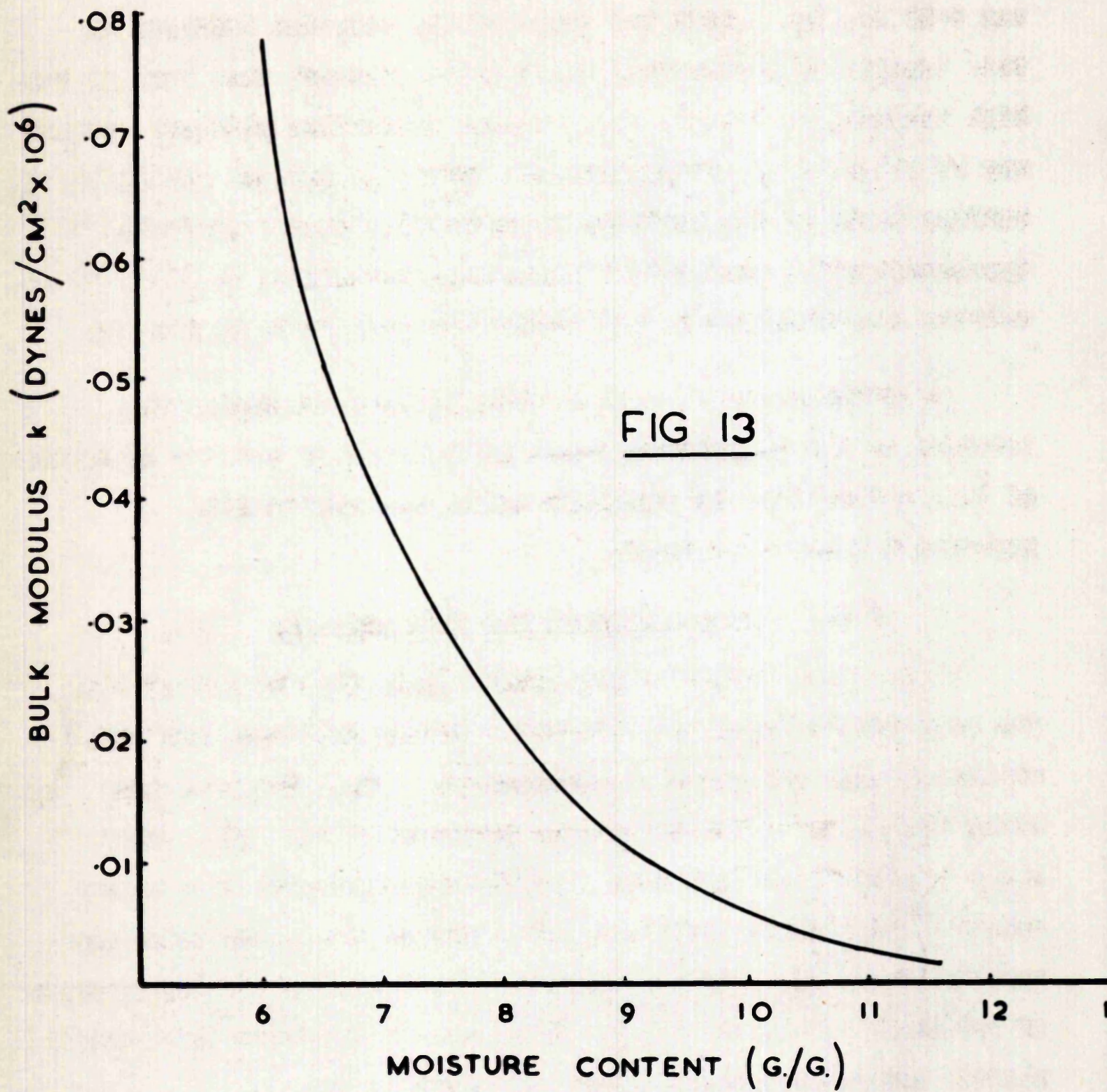
The fact that the lowest moisture content reached in the reproducible cycle (points 6 and 8) was higher than that at the same tension in the initial desorption, may be explained by the same effect, so that, if the fibre matrix became less compressible due to these entanglements, it would subsequently hold more water at this tension. This explanation is supported by the fact that, at very small tensions, the subsequent moisture contents were lower than during the first desorption, the entanglements here preventing expansion of the matrix to its former size.

1 (b) Hysteresis.

The second important result is that the final sorption cycle exhibits moisture content hysteresis, demonstrating conclusively that sorption hysteresis is not confined solely to sorption from the vapour phase. In view of the fact that the fibre matrix was at all times water-logged, mechanisms associated with the emptying of capillaries cannot explain this hysteresis. The hysteresis must therefore arise from the physical or mechanical properties of the fibre matrix rather than the liquid water. Thus the mechanism proposed by Barkas (§19b) to account for hysteresis in the vapour sorption isotherm of cellulosic materials may well be extended to the present matrices of fibres. If this is the case, the hysteresis must arise from the plasticity of the matrix and its component fibres. Of all the mechanisms suggested to account for sorption hysteresis, this one alone therefore is applicable over the whole range of the sorption isotherm now covered.

1 (c) The Sorption Isotherm at Saturation.

The results from this experiment also yield valuable information regarding the shape of the sorption isotherm at tensions corresponding to the highest equivalent relative humidities yet recorded. Apart from the change in scale, the shape of the isotherm is seen to be very similar to the upper portion of the vapour sorption isotherms shown in FIG. 5. As indicated previously, the highest equivalent relative humidity attainable with the porous plate technique, namely 0.9999999, corresponds to



a tension of 0.01 cm. Hg. In this experiment however, owing to the height of the sample, the minimum tension at its top surface was 0.03 cm. Hg. From the shape of the sorption isotherm as this tension is approached, there is no evidence that even at this high humidity, a readily determinable saturation moisture content may be obtained by extrapolation. Thus the initial difficulty of extrapolation of the isotherm as saturation vapour pressure is approached still persists at these high humidities in spite of the extreme magnification of the vapour pressure scale in FIG. 12.

It is therefore of considerable interest to replot the isotherm on the logarithmic basis as outlined in §18 but discussion of this matter will be postponed until the results from Experiment 2 are considered.

1 (d) Calculation of the Bulk Modulus.

It has been indicated previously (§20) that by re-plotting the sorption isotherm as a tension - volume isotherm, the bulk modulus of the matrix may be determined. This has been done using the reproducible desorption isotherm of FIG. 12. Since $k = -Vdp/dV$ it was necessary for the determination of k at any moisture content, to determine the slope of the isotherm at the corresponding value of V . This was done graphically for a series of arbitrary values of V and a graph of the resultant bulk modulus plotted against moisture content is shown in FIG. 13.

It will be seen that the order of magnitude of k is considerably lower than that of most materials whose elastic properties

are normally determined mechanically. Thus, while the bulk moduli of steel, cellulose and wood are of the order 10^{12} , 10^{11} and 10^{10} dynes/cm.² respectively, the lowest value found for this fibre matrix (above 9 g./g. moisture content) is of the order 10^3 dynes/cm². This represents the lowest value of k that may be studied conveniently by the porous plate technique which thus increases considerably the range of materials whose elastic properties may now be measured by application of controlled stresses.

It will be seen also that the bulk modulus is very sensitive to changes in moisture content, increasing by ten times as the moisture content falls from approximately 10 to 6 g./g. This is no doubt due to the greater stability to the fibre matrix which results from the increasing degree of contact of individual fibres as the water is withdrawn.

§28. EXPERIMENT 2. AIR ENTRY AND THE EFFECT OF BEATING.

Two samples of approximately 0.3 g. of unbleached kraft pulp were used in this experiment, the first (A) being unbeaten and the second (B) being lightly beaten for 6 hours in the Lampen ball mill. The fibres were formed into cylinders as described previously (§22) but without any particular precautions to maintain a steady rate of flow. In the case of the beaten fibres the rate of flow was very much slower and it was obvious that attempts to build up tall cylinders of wet-beaten pulps would be very difficult by this technique, and all subsequent experiments

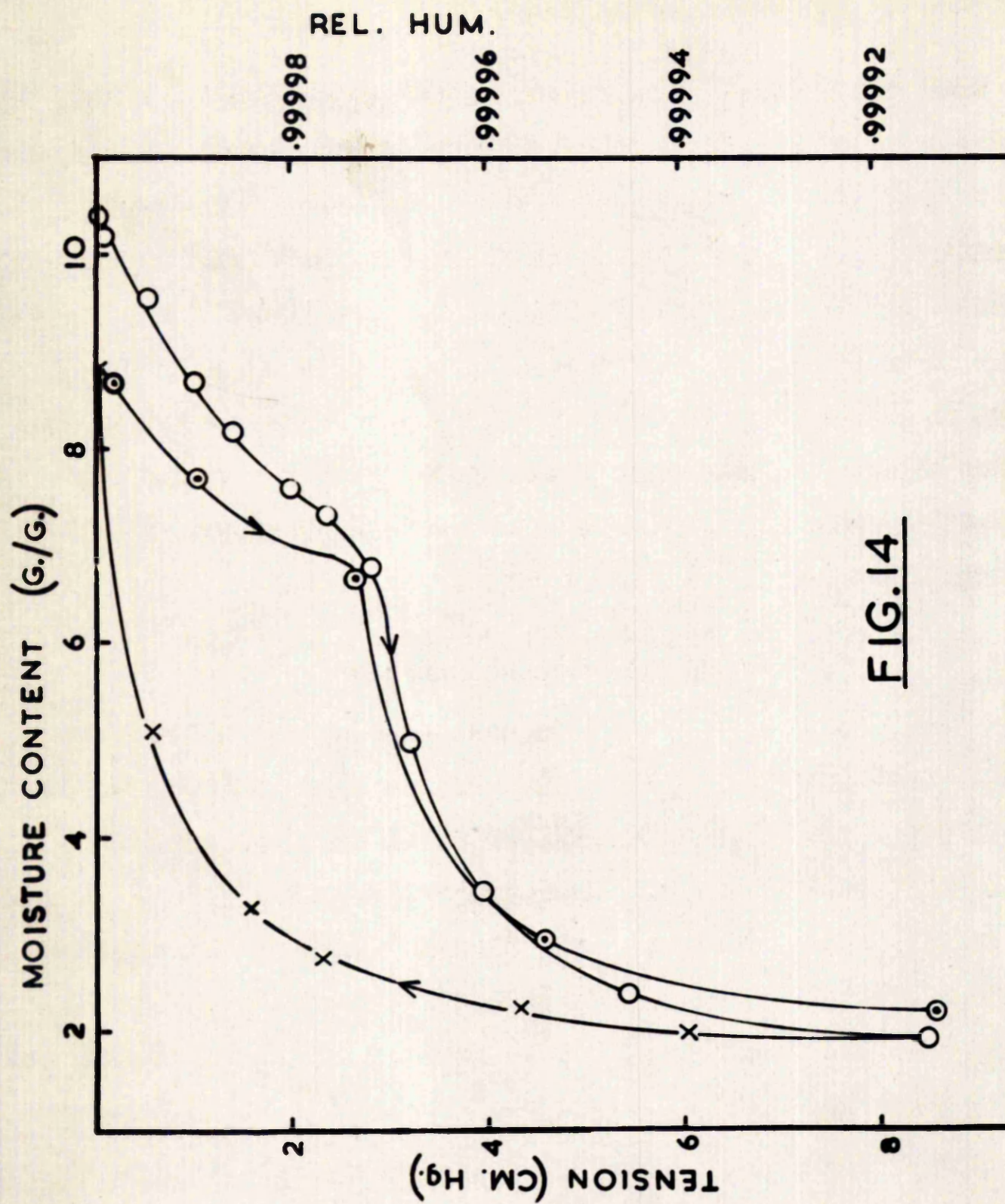


FIG. 14

were carried out on unbeaten pulps.

When the cylinder was placed on the porous plate, excess water was added and the initial desorption commenced from as high a moisture content as possible. A maximum tension of approximately 9 cm. Hg. was reached in each case after which one complete sorption - desorption cycle was performed. The change in the total height of both cylinders was measured with each change in tension but no attempt was made to measure the corresponding changes in diameter. No surrounding liquid was used. The results from cylinder A, which will be considered first, are shown in FIG. 14.

2 (a) The Desorption Isotherm.

It will be seen from FIG. 14 that the initial desorption followed a smooth curve until a tension of approximately 2.5 cm. Hg was reached and that the range of moisture contents covered, i.e. from 10 to 7 g./g., was comparable with those in Exp. 1 over this range of tension. The initial slope of the isotherm was steeper than in Exp. 1, but this is probably due to the fact that the initial tension (nominally zero at the porous plate) was greater throughout the cylinder owing to its height, initially 2.9 cm. The tension effective at the top of the cylinder was therefore approximately 2 mm. Hg greater than at the base throughout the experiment.

At 2.5 cm. Hg tension, an inflexion in the slope of the isotherm occurred, after which a rapid decrease in moisture content

accompanied further increase in tension. This is attributed to the simultaneous emptying of the largest capillaries as air entered the matrix, an explanation which will be confirmed when dimension changes are considered (para. 2c). After this rapid decrease in moisture content, the isotherm again became very steep, the remaining 2 g./g. of water being distributed in very small capillaries in which large increases in tension were necessary to remove even small quantities of water.

The fact that a large decrease in moisture content occurred over a narrow range of tension indicates that a considerable fraction of the water was held in capillaries having the equivalent radius of 40μ corresponding to this tension. This is of the same order as the thickness of the fibres themselves, which, as repeating units in the matrix, may be expected to produce many capillaries of similar size.

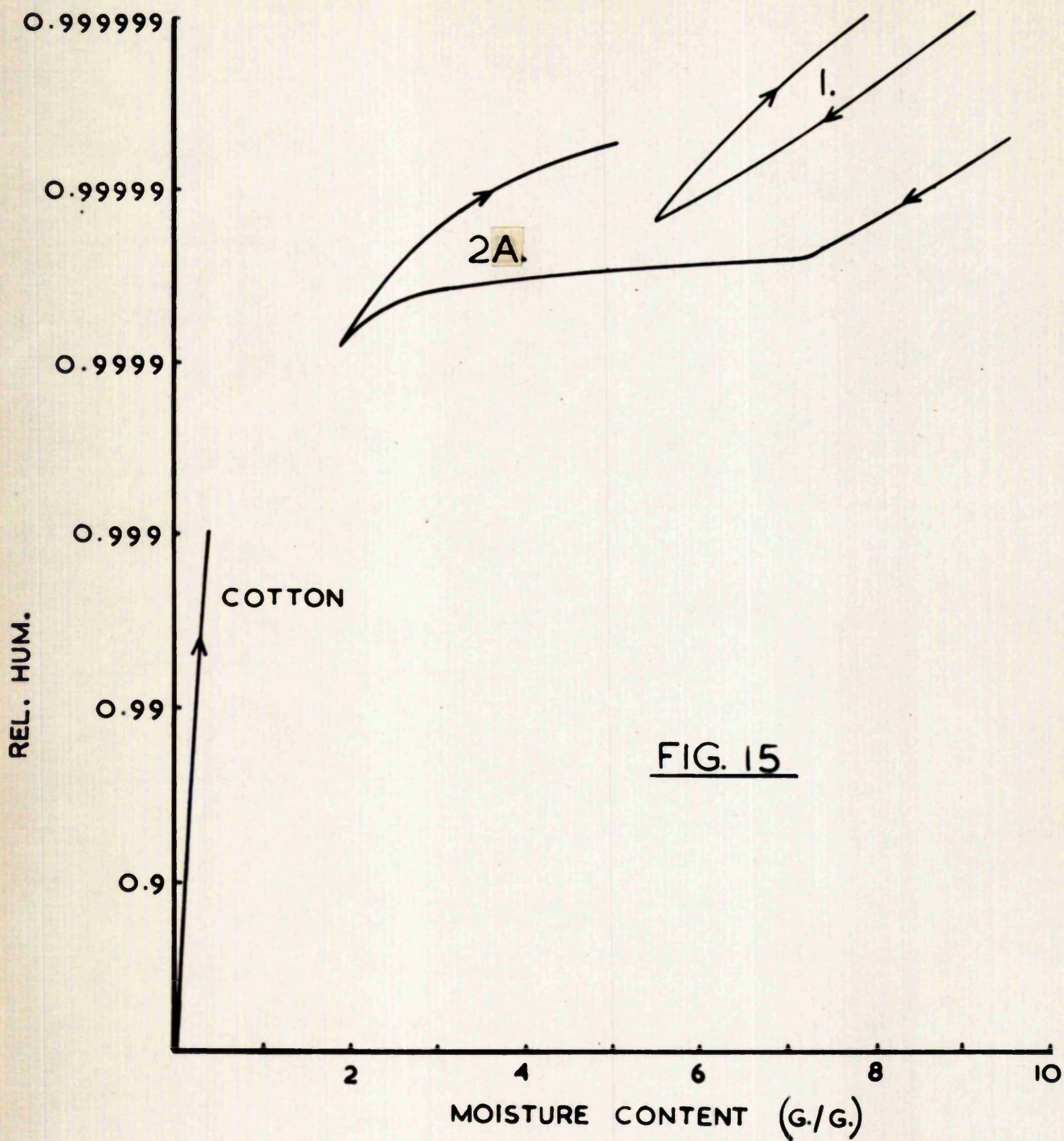
2 (b) Moisture Content Hysteresis.

During the subsequent adsorption, the moisture content rose to a value only a little less than the initial desorbing value. Completion of the hysteresis loop was not to be expected at this stage since, as seen in Exp. 1, the first point in the initial desorption was not reached from a reproducible cycle. A striking feature of the adsorption isotherm was the fact that there was no comparable inflexion at the tension of 2.5 cm. Hg which would correspond to the simultaneous filling of the larger capillaries.

It is certain however, that these capillaries had been filled to a considerable extent, in view, firstly, of the high moisture content reached and, secondly, of the repetition of the phenomenon of air entry at the same tension on the second desorption. Presumably the filling occurred gradually below 2 cm. Hg tension where the slope of the adsorption isotherm decreases rapidly. Although the rate of approach to equilibrium was slower than during desorption, there was no suggestion that the lower moisture contents were due to non-attainment of equilibrium. This irreversibility led to a large moisture content hysteresis (5 g./g. at a tension of 2 cm. Hg) which, in this case, appears to be attributable largely to the non-reversible emptying and filling of the capillaries for which a possible explanation is offered below.

The second desorption isotherm was similar in shape to the first but, as in Exp. 1, crossed it to reach a slightly higher moisture content at the maximum tension. It is possible that as before, this difference was due to the change in the elastic properties of the cylinder during the first cycle but dimension measurements only partially confirm this explanation. It is more likely that at least some of the difference resulted from a slight but unknown evaporation of water from the sample to the walls of the surrounding vessel.

In order to examine the sorption isotherm more closely as the saturation moisture content is approached, the results for this experiment have been re-plotted on the logarithmic basis (see §18)



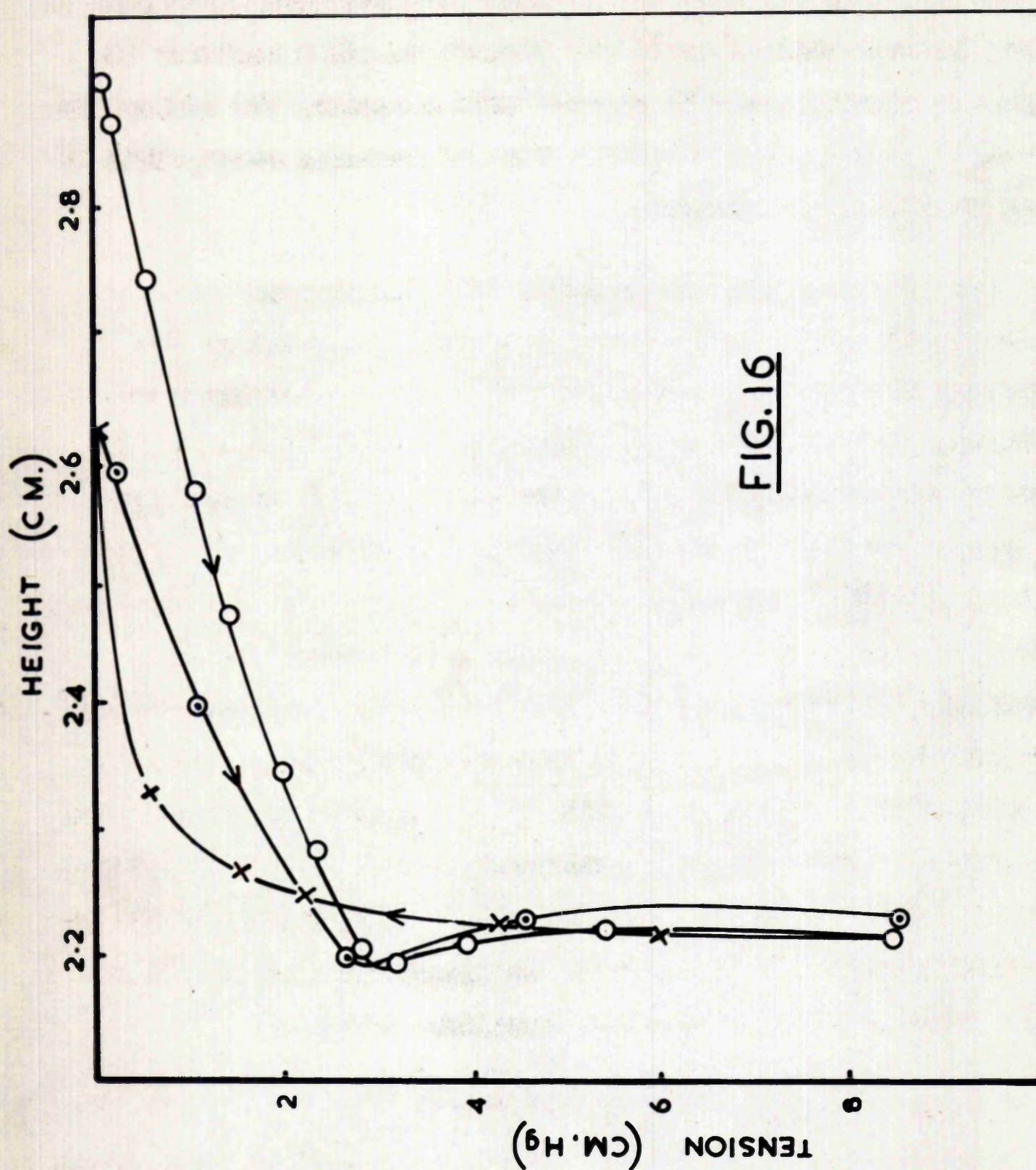


FIG. 16

in FIG. 15, together with those which were postponed from Exp. 1. It may be seen that, even to the highest relative humidity to which the results could be plotted with accuracy, the adsorption isotherms of the pulps showed no sign of becoming asymptotic to a limiting moisture content.

Also shown on the same graph is the vapour adsorption isotherm for cotton taken from FIG. 6 (§18). Although the isotherms for Exp. 1 do not appear to be even approximately continuous with that of the cotton, a possible explanation, in terms of air entry, is suggested by the results from Exp. 2A. The rapid reduction in moisture content accompanying air entry produced a portion of the desorption isotherm which was nearly horizontal when plotted on this scale, after which, as the equivalent humidity was lowered still further, the slope of the isotherm changed and approached that of the cotton. Although the curves when extrapolated still do not appear continuous with each other, the difference in moisture content remaining between them is probably less than 1 g./g. and could be accounted for by hysteresis, since one corresponds to desorption from the water-logged state and the other adsorption from dryness.

2 (c) Changes in Height.

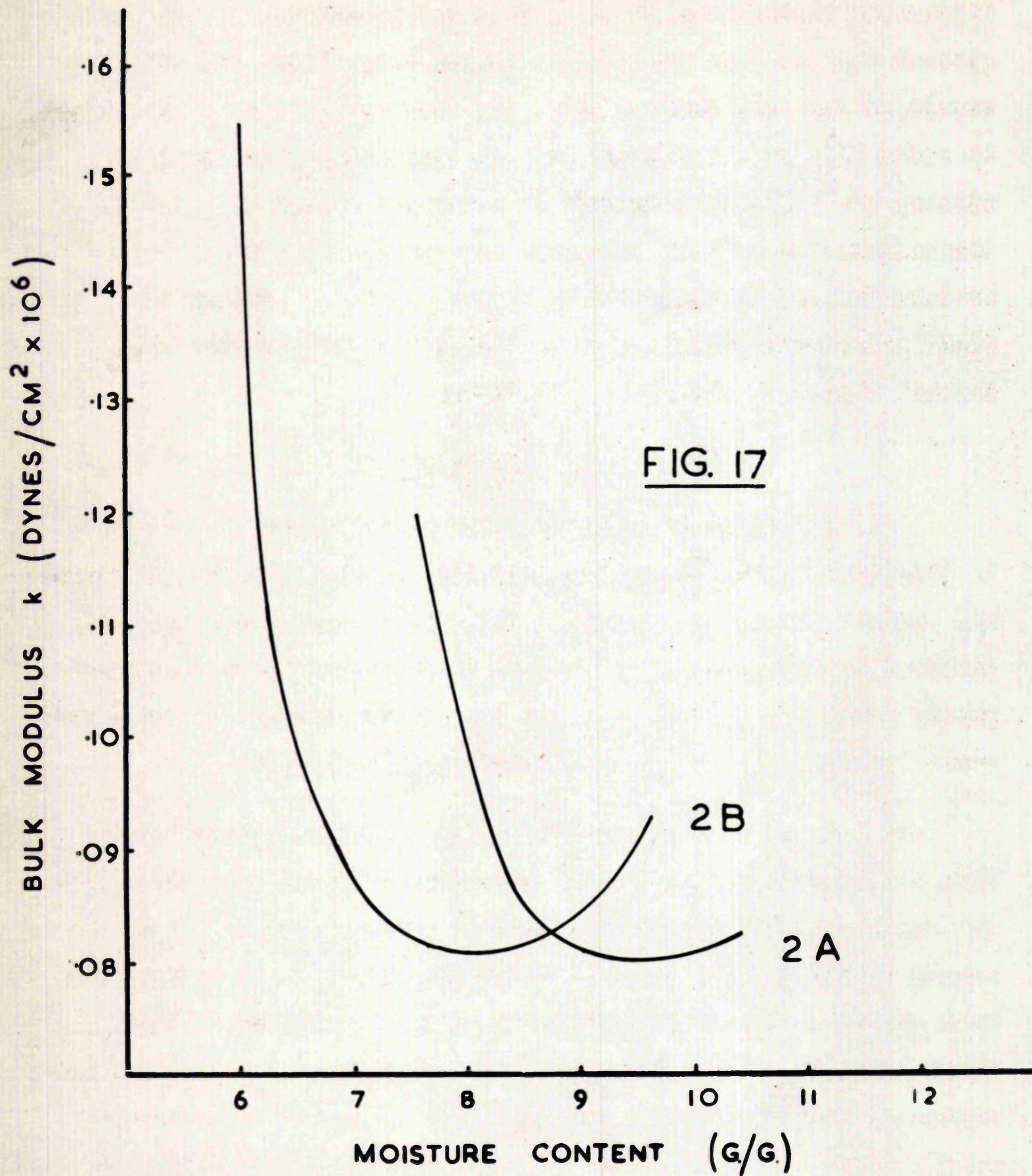
The total height of the cylinder was measured following each change in tension and a graph of these changes is shown for cylinder (A) in FIG. 16. The smooth curve of decrease in height,

down to a tension of 2.5 cm. Hg, corresponds to the desorption isotherm over this range but at the point where air entered the matrix an abrupt change in the strain curve also occurred. Beyond this point a slight increase accompanied the increasing tension. This increase is attributed to the fact, that, although the hydrostatic tension in the remaining water increased, the average compressive stress on the matrix as a whole was actually reduced due to the recession of the menisci into the interior of the matrix. It is at this point that the simplifying assumption regarding equivalence of the stress on the matrix to the hydrostatic tension in the liquid breaks down, and calculation of moduli on this basis becomes impossible. Although in this experiment no direct measurement of the change in diameter was made, it was observable that this changed very little compared with the change in total height owing to the anisotropy of the matrix. To a first approximation therefore, the change in volume of the cylinder matrix may be determined from its change in height. Up to the point where air entry occurred, this volume would be expected to equal the volume of water removed. Beyond this point however, where the height, and consequently the volume, of the matrix remained nearly constant, the water removed through the plate must be replaced by an equal volume of air which could thus be calculated approximately. For its exact determination however, the external volume of the cylinder must be measured.

2 (d) Hysteresis in Longitudinal Strain.

It will be seen from FIG. 16 that the increase in height during adsorption followed a smooth curve throughout. The irreversible filling of the capillaries is thus confirmed by the irreversible strain curve which showed further that no appreciable expansion of the matrix occurred until the tension fell below 1 cm. Hg.

From all this data a mechanism may be suggested to explain hysteresis. When a meniscus recedes, and air is drawn part way into the fibre matrix, the fibres which form the boundaries of this pocket of air are subjected to comparatively large directional stresses instead of a uniform hydrostatic tension acting over their entire surface. Since they are not rigidly held, they will move under this stress away from the air pocket which therefore becomes larger in equivalent radius. If, due to plastic or frictional effects, this movement of the fibres is not purely elastic, the capillary will tend to remain larger and, during the following adsorption, it will not fill until a lower tension than that at which it emptied is reached. In terms of the present results, the enlargement that would be required to account for the change in tension from 2.5 to 1.5 cm. Hg would be from an equivalent radius of 40μ to one of 70μ , which is less than the thickness of one fibre. This does not seem unreasonable. As higher moisture contents are reached, the inter-fibre contacts are reduced and with them the frictional restraints, as a result of which the



fibres may then return to their original positions. This would account for the fact that on the second desorption, air entry occurs at the same tension as in the first desorption. It should be noted that this mechanism for the irreversible emptying and filling of capillaries depends on an actual change in the size of the capillaries and not merely an irreversible behaviour of the menisci in them as suggested by McBain, Cohan and Foster for rigid adsorbents (§19a). It is thus a further extension of Barkas' theory of plasticity and hysteresis.

2 (e) The Bulk Modulus.

Although change of height as well as of volume was measured in this experiment, it was not possible to calculate the longitudinal Young's modulus E_1 from this data alone, since the vertical compression occurred in response to a hydrostatic stress and not a purely longitudinal one. If the transverse strains are relatively small however, E_1 will be approximately the same as k .

The bulk modulus was determined up to the air entry point from the sorption isotherm for comparison with the results of Exp. 1. Its variation with moisture content is plotted in FIG. 17 on the same scale as in FIG. 13. Although the change in bulk modulus with moisture content follows the same type of curve as for the first pulp, it will be seen that, particularly at the high moisture contents, the values are about ten times higher. Since it is a stiffer fibred pulp as a result of its method of production, a

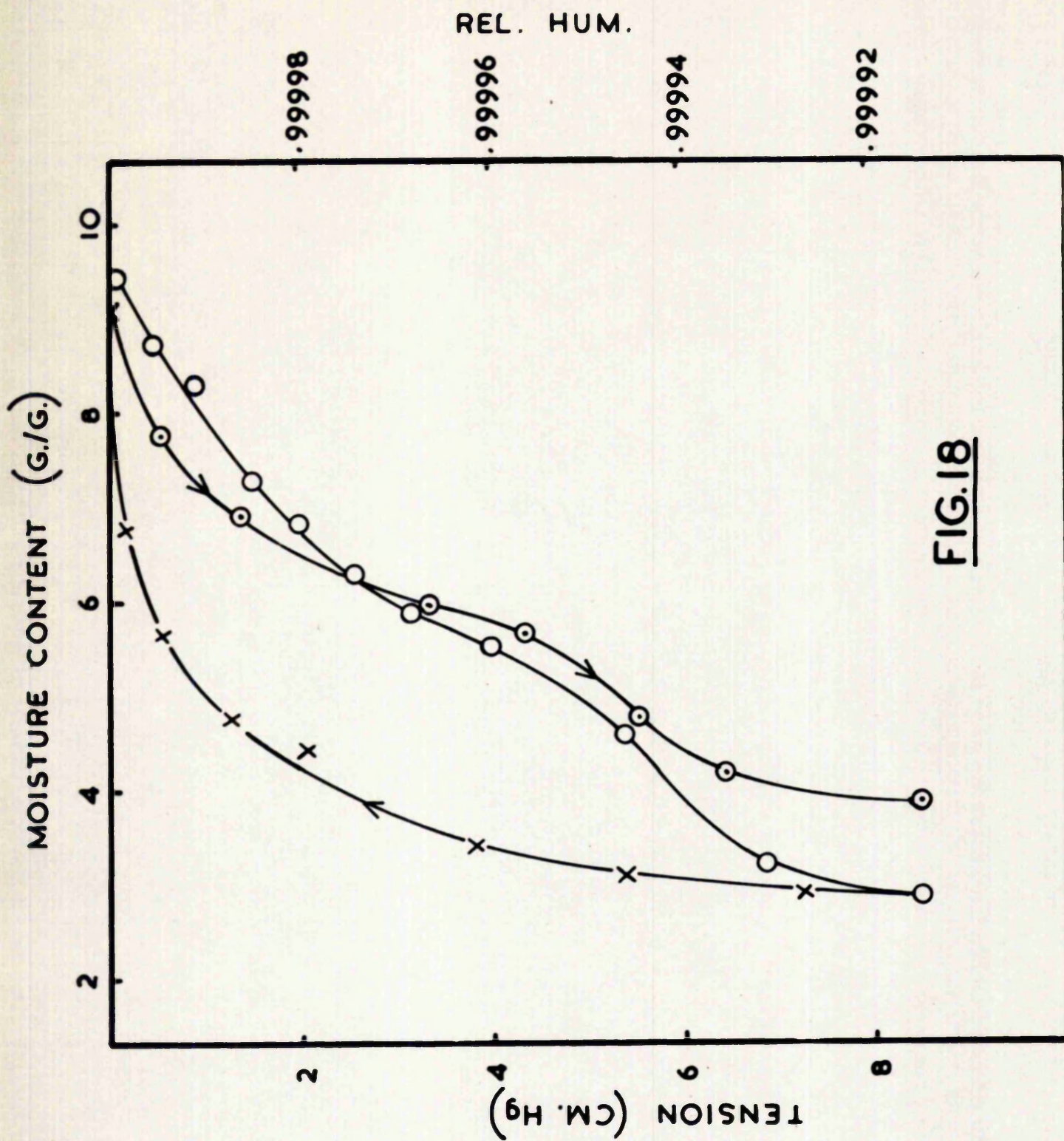


FIG. 18

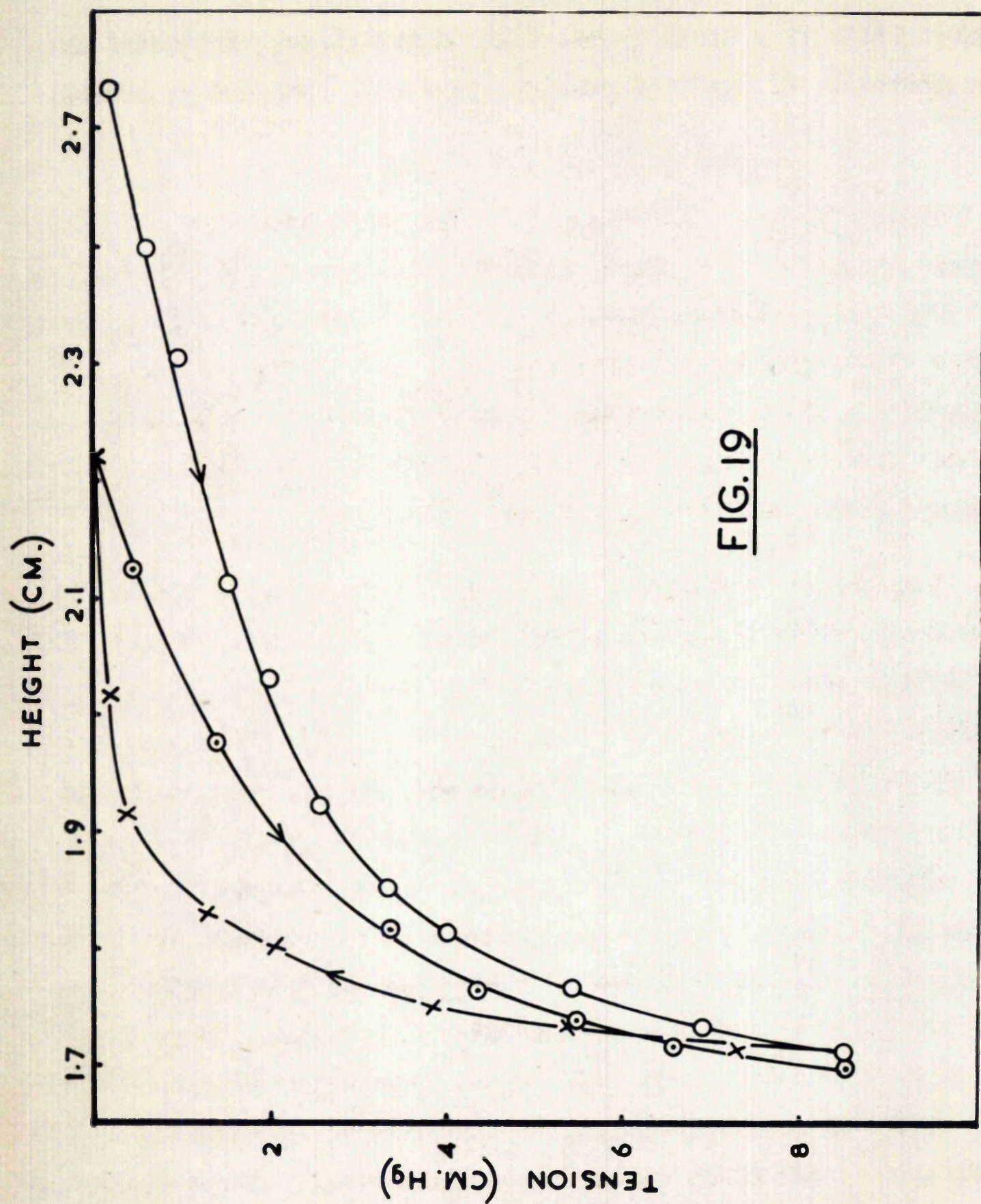


FIG. 19

higher value of k is to be expected, although the variations in the formation of the test samples could also have had an effect.

2 (f) Effect of Beating.

Comparable data for the sample that was beaten for six hours in the Lampen mill are shown in FIGS. 18, 19, and 17. Not all the differences between the results need be attributable to beating in view, once again, of the possible variations in the preparation of the cylinders, but several important differences may be interpreted readily in terms of the known effects of beating on the pulp.

From FIGS. 14 and 18, it will be seen that, although desorption commenced from approximately the same moisture content, (10 g./g.), the moisture content of the beaten pulp at the largest tension reached was greater by at least 1 g./g. This is no doubt due to the larger proportion of small capillaries resulting from fibrillation during beating. For the same reason also, the inflexion of the isotherm during air entry is less marked and occurs at a higher tension, indicating that the largest capillary spaces in the cylinder of beaten fibres are smaller than in the unbeaten sample and spread over a wider size range. In other respects the sorption isotherms of the beaten and unbeaten fibres were generally similar, showing considerable hysteresis and repetition of air entry on the second desorption. The decrease in the magnitude of the hysteresis (maximum 2 g./g.) may be significant however, and could be explained by the fact that the

increased inter-fibre contacts reduce the tendency of the capillaries to change in size following air entry.

On comparing the changes in height of the two samples (FIGS. 16 and 19), a marked difference is seen, since, in the beaten sample, the decrease in height continued smoothly to the largest tension reached. From this it follows that the entry of air was not sufficiently rapid to cause a reduction in the effective stress on the matrix so that no relaxation occurred. From this data alone therefore, the evidence of air entry cannot be confirmed. As indicated previously, confirmation is possible only by comparison of the volume of water removed with the volume change of the matrix measured directly. The absence of a kink in the sorption isotherm need not necessarily indicate that air has not entered the matrix, since a matrix having a smooth distribution of capillary sizes (or for instance, V-shaped capillaries) might not show an inflexion on air entry.

The change in bulk modulus with change in moisture content up to the air entry point for the sample of beaten pulp is shown also in FIG. 17. In both samples there was an initial decrease in k with decreasing moisture content. This decrease cannot be explained readily in terms of the properties of the pulp, but an explanation may be found in the neglect of the height of the cylinder when calculating the applied tension. The effect is absent from the results of Exp. 1 using a very thin sample even at

higher moisture contents. In a cylinder 3 cm. high, the nominal tension occurs only at its base, the tension increasing upwards until, at the top of the cylinder, it is greater by ρgh ($= 0.2$ cm. Hg) until, at the top of the cylinder, it is greater by ρgh ($= 0.2$ cm. Hg) as

of this order of magnitude, the moisture content of the cylinder will be considerably lower than it would be if the nominal stress occurred throughout. The sorption isotherm will therefore be steeper than it should be at these low tensions and the values of k correspondingly too large. This explanation will be confirmed following the elimination of the stress gradient in Exp. 5.

The curves showing variation of k with moisture content are similar in shape for both samples, but the corresponding moduli are obtained at moisture contents about 1 g./g. lower in the beaten than in the unbeaten fibres. For moduli above approximately 0.1×10^6 dynes/cm²., the rate of increase with moisture content appears much greater in the case of the beaten fibres. These effects could be explained if, at high moisture contents, where fibre contacts are fewer, the compressibility of the matrix is determined largely by the stiffness of the fibres. At much lower moisture contents where inter-fibre contacts may become the predominant factor, beaten pulps may ultimately attain higher moduli than unbeaten ones.

§29. EXPERIMENT 3. MEASUREMENT OF VOLUME CHANGE.

For this experiment, a sample of 0.1929 g. unbeaten bleached sulphite (spruce) pulp was formed into a cylinder as before and transferred to the sorption apparatus in the absence of any surrounding liquid. Desorption was followed to a tension of 23 cm. Hg, during which changes in total height and diameter were determined as described in §24, using thirteen equal segments for the diametral measurements. The experiment was abandoned at this tension owing to misting of the inside of the glass cell and consequent difficulty in measuring the diameter of the sample. In removing the sample for determination of moisture content at the end of the experiment, a further volume of water was accidentally lost so that the volume of the cylinder (V_w) calculated from this final moisture content was too low by an unknown amount. Comparison of V_m with V_w calculated on this basis, for the initial reading on the cylinder (when no air was present), showed a discrepancy of 0.065 cc. in a total volume of 1.620 cc. This difference was therefore added to all values of V_w and 0.34 g./g. to the moisture contents. This was probably justified in view of the subsequent close agreement in changes in both V_m and V_w down to the air entry point.

The volume of the cylinder was calculated from the dimension measurements using the formula

$$V_m = \frac{\pi}{4} \cdot \frac{1}{n} \cdot \frac{\sum d^2}{m^2}$$

where 1 is the height of the cylinder, $\sum d^2$ the sum of the squares

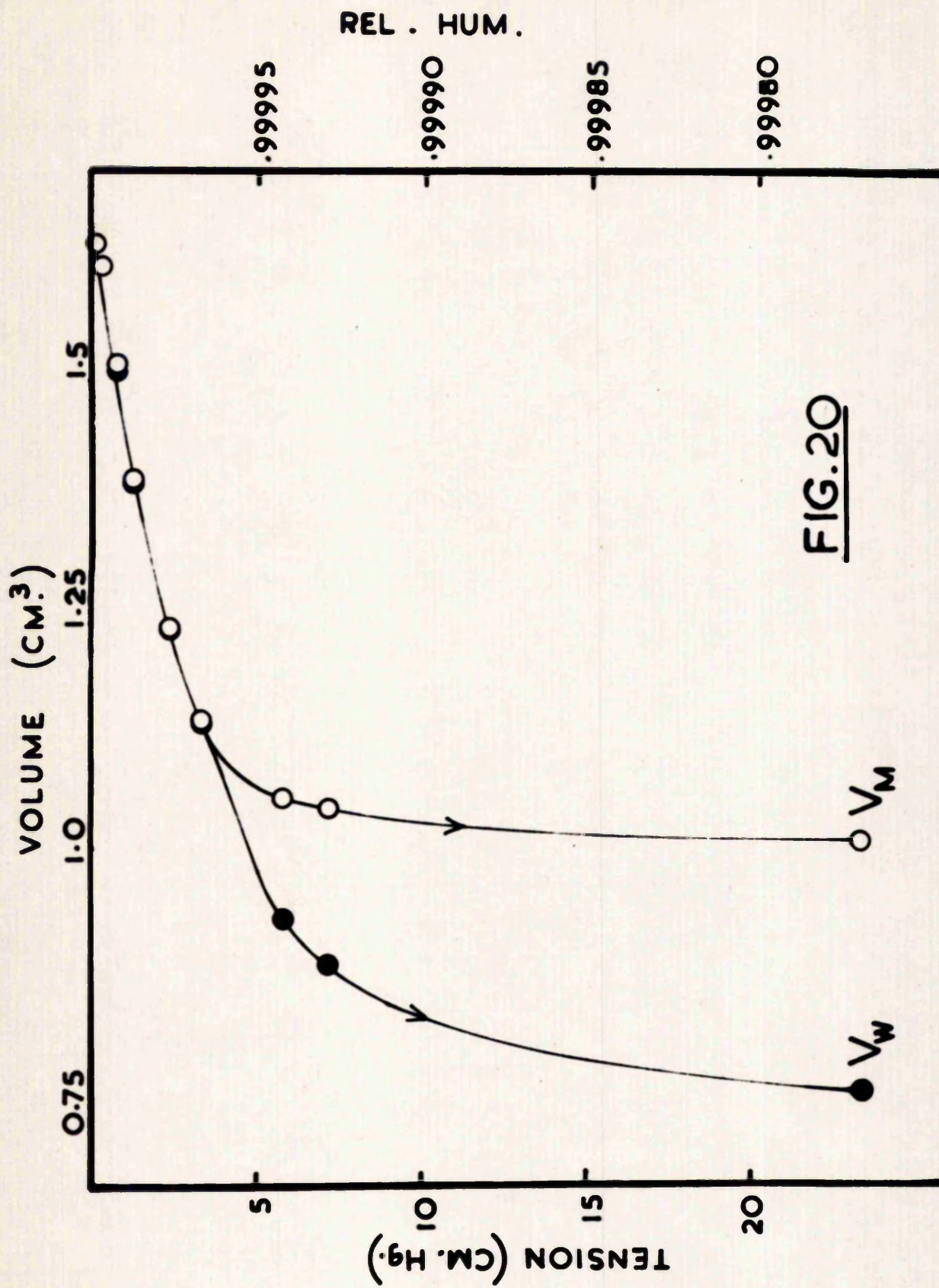
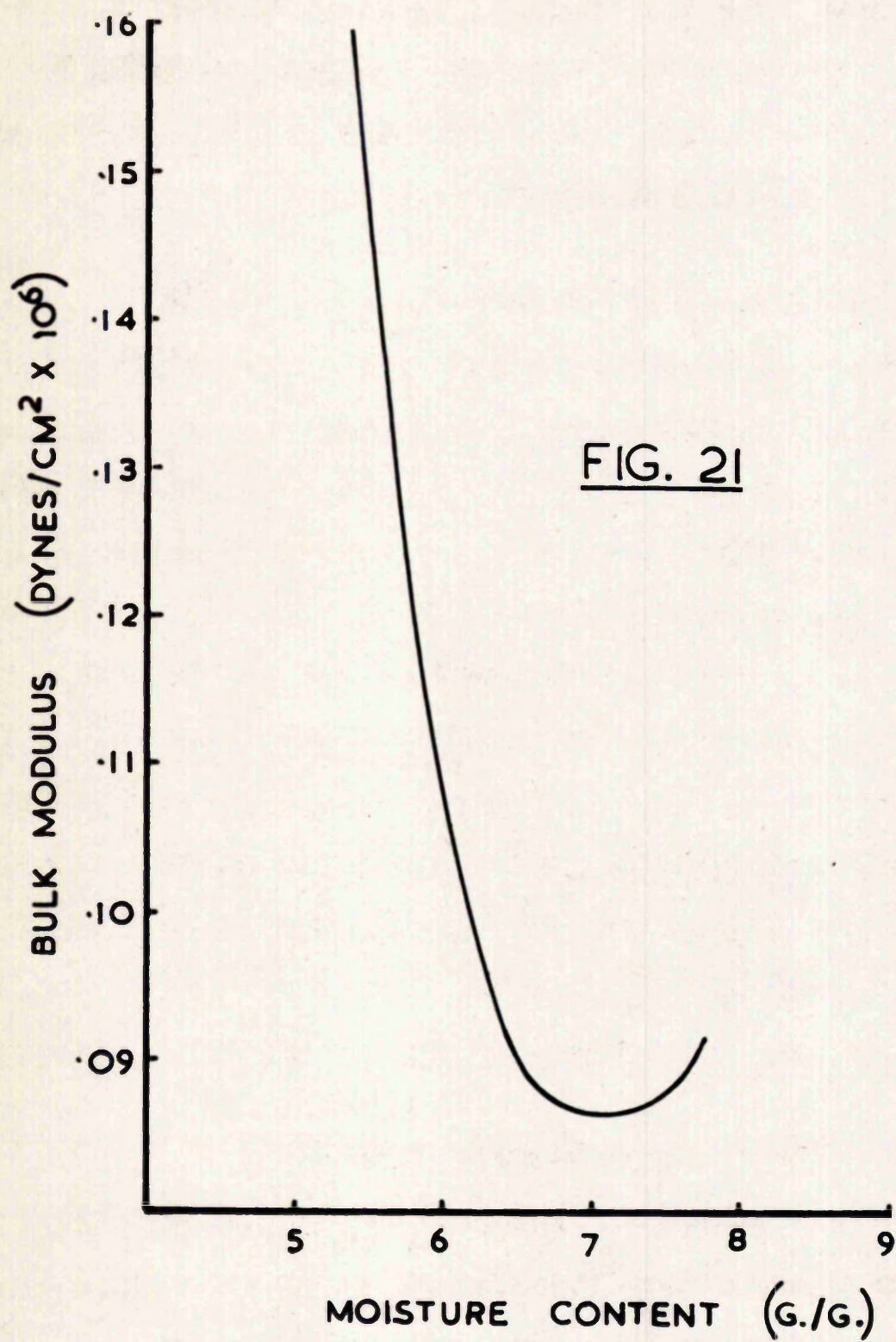


FIG. 20



of the diameters of the image, n the number of segments and m the magnification of the image. Values of V_m have been tabulated together with the tension, moisture content and V_w calculated from the corrected moisture content, in TABLE 3. The same data is also presented graphically in FIG. 20 showing changes in V_m and V_w with change in tension.

3 (a) The Sorption Isotherm and the Bulk Modulus.

Down to the tension at which air enters the matrix, the sorption isotherm, corresponding to the graph of V_w in FIG. 20, will be seen to be generally similar in shape to those of the previous samples of pulp although the moisture contents (TABLE 3, col. 3) were lower by approximately 2 g./g. than in the preceding unbeaten pulp, 2A. This may be explained by the fact that it is a softer and finer pulp. This explanation is supported by the fact that the graph of the bulk modulus (calculated from the sorption isotherm) below this tension, plotted against moisture content in FIG. 21, resembles more closely that of the beaten kraft pulp 2B (see FIG. 17), although slightly lower at corresponding moisture contents.

3 (b) Confirmation of air entry.

As indicated previously, quantitative confirmation of air entry was to be expected from comparison of V_m and V_w and this is shown clearly in the results from the present test.

TABLE 3

Showing sorption and strain measurements on fibre sample 3.

Tension cm. Hg	Relative humidity P/Po	Moist. content g./g.	Total height (l) k cm.	R.M.S. diam. (\bar{t}) cm.	V_v cm ³ .	V_m cm ³ .	Long. strain $\frac{l_0 - l}{l_0}$	Trans. strain $\frac{t_0 - \bar{t}}{t_0}$	$\frac{l_0 - l}{l_0 - \bar{t}}$ $\frac{\bar{t}}{t_0}$
0.020	0.9999998	7.73	1.370	1.226	1.620	1.620	---	---	---
0.105	0.99999990	7.63	1.355	1.224	1.595	1.595	0.011	0.0017	6.5
0.570	0.99999944	7.03	1.290	1.213	1.485	1.495	0.059	0.0098	6.0
1.110	0.9999989	6.43	1.205	1.206	1.370	1.375	0.121	0.0162	7.5
2.175	0.9999979	5.65	1.095	1.195	1.220	1.225	0.210	0.0256	8.2
3.145	0.9999969	5.18	1.025	1.190	1.130	1.135	0.252	0.0293	8.6
5.715	0.9999944	4.12	0.955	1.182	0.925	1.050	0.303	0.0357	8.5
7.050	0.9999931	3.89	0.945	1.182	0.880	1.035	0.310	0.0357	8.7
11.345	0.999989	3.71	0.935	---	0.845	---	0.318	---	---
23.265	0.99977	3.22	0.925	1.178	0.750	1.005	0.325	0.0391	8.3

(1) (2) (3) (4) (5) (6) (7) (8) (9) (10)

Above a tension of 3 cm. Hg, the changes in V_m and V_w were in very close agreement and, if the initial correction of 0.065 cm.³ due to loss of water is accepted, provided a valuable check on the accuracy of the technique. (This accuracy will be confirmed in the next experiment.) At tensions greater than 3 cm. Hg however, the volume of the matrix changed little as further water was withdrawn, the differences between V_m and V_w confirming that air had commenced entering the matrix. At 23 cm. Hg tension it occupied approximately 25 per cent. of the total volume of the cylinder.

The absence of a marked inflexion at the air entry point is probably due to the wider range of capillary sizes in this softer pulp; the slightly higher tension at which air entry occurred (greater than 3 cm. Hg) indicates also that these capillaries resemble more closely those of the beaten sample, 2B (FIG. 18).

3 (c) Transverse and Axial Strains.

From measurements of the dimensions of the cylinder, it was possible to compare the magnitudes of the transverse and axial strains and to observe the variation of the former over the length of the cylinder. The total height l and root mean square diameter, $\bar{t} = \sqrt{\sum d^2/nm}$, are shown in cols. (4) and (5) in TABLE 3 together with changes in these dimensions expressed as integral strains in cols. (8) and (9) and the ratio between them in col. (10).

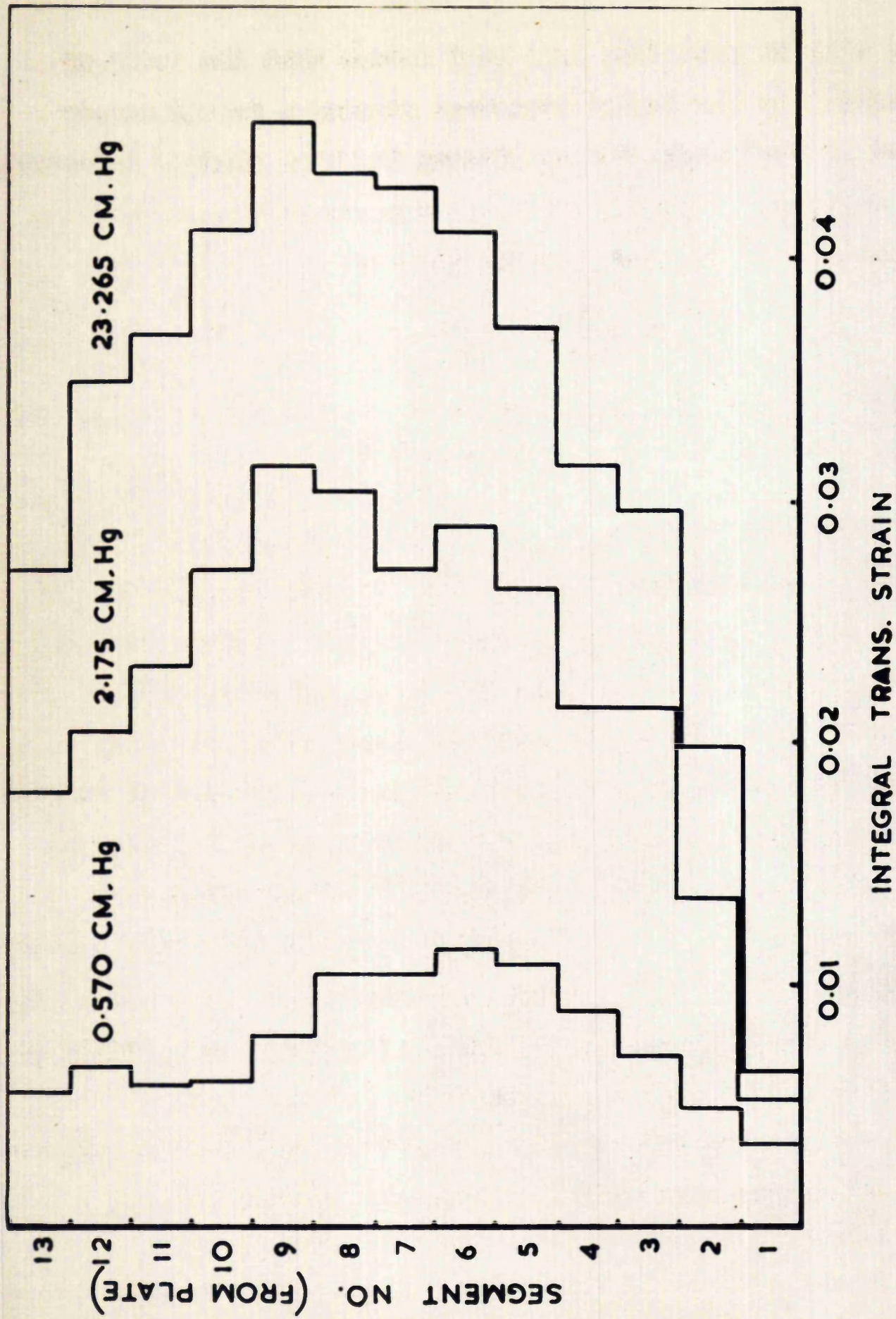


FIG. 22

It will be seen from this last column that the ratio of longitudinal to transverse shrinkage reached a fairly steady value of approximately 8.5 confirming the high elastic anisotropy of the cylinder. Since, for small changes in dimensions, the volume strain for the cylinder is given by

$$\frac{\Delta V}{V} = \frac{\Delta l}{l} + \frac{2\Delta \bar{t}}{\bar{t}},$$

the volume strain, if assumed to be due to changes in height only, would be approximately 20 per cent. too low.

To demonstrate the variation in transverse strain at different heights in the cylinder, $(\bar{t}_0 - \bar{t})/\bar{t}_0$ for each of the thirteen segments are shown at three selected tensions (0.570, 2.175 and 23.265 cm. Hg) in FIG. 22. It will be seen that considerable variation in transverse strain occurred, since shrinkage at the centre of the sample was greater than at either end. The smallest strain occurred at the end of the cylinder in contact with the porous plate which obviously acted as a restraint. Since the cylinder was inverted before being placed on the porous plate this end corresponded to its top end when in the tube during formation. No similar restraint was present at the other end (no wire screen disc being present in this experiment), and the fact that the strain at this end was smaller than in the centre must be due to internal restraints within the matrix itself.

In this sample the effects of both these restraints appeared to extend almost to the middle segments since no appreciable length of the cylinder appeared to behave uniformly. It is therefore clear that any moduli determined for the cylinder as a whole will not represent the behaviour of the matrix in an unrestrained condition. This appears to be an insurmountable disadvantage of the technique since firm contact with the porous plate is invariably necessary. Some improvement may be effected by not inverting the cylinder on the porous plate so that the internal and external restraints are present at the same end, in the expectation that the top half would be sufficiently far from these restraints to behave in a uniform manner. This was done in the following experiment.

However, the behaviour of cylinders in the subsequent experiments did not appear to be entirely consistent with these observations, and a completely satisfactory explanation of all these effects cannot at present be advanced. It is suspected that, in preparing the cylinders, variations other than those actually examined may be of considerable importance and call for further study.

§30. EXPERIMENT 4. VARIATIONS WITHIN THE CYLINDER.

In this experiment, unbeaten bleached sulphite pulp, similar to that in Exp. 3 was used. On this occasion however, it was oven-dried for four hours and weighed (0.2181 g.) before re-dispersing in water to form the test cylinder. A small hydrostatic head only was employed during its preparation and it was not strongly compressed before transfer to the sorption apparatus. At the time of transfer its moisture content was merely reduced to approximately 6 g./g. for ease of handling. One mark was placed on its side approximately half way along its length so that longitudinal strains in the top and bottom halves could be studied separately. Its weight and hence its moisture content were determined immediately before placing it on the porous plate at a small tension. The cylinder was not inverted and no restraint was applied to its upper end. Benzene saturated with water (specific gravity 0.88) was used to surround the cylinder and, as it was desired to complete a sorption cycle without the entry of benzene into the matrix, a maximum tension of 1.5 cm. Hg only was applied. Unfortunately, the experiment again had to be abandoned before completion as the seals in the rectangular glass cover were eventually softened by the benzene, but the results up to this point were nevertheless of considerable value.

Since changes in moisture content could be measured only for the cylinder as a whole, the volume of the entire matrix V_m was

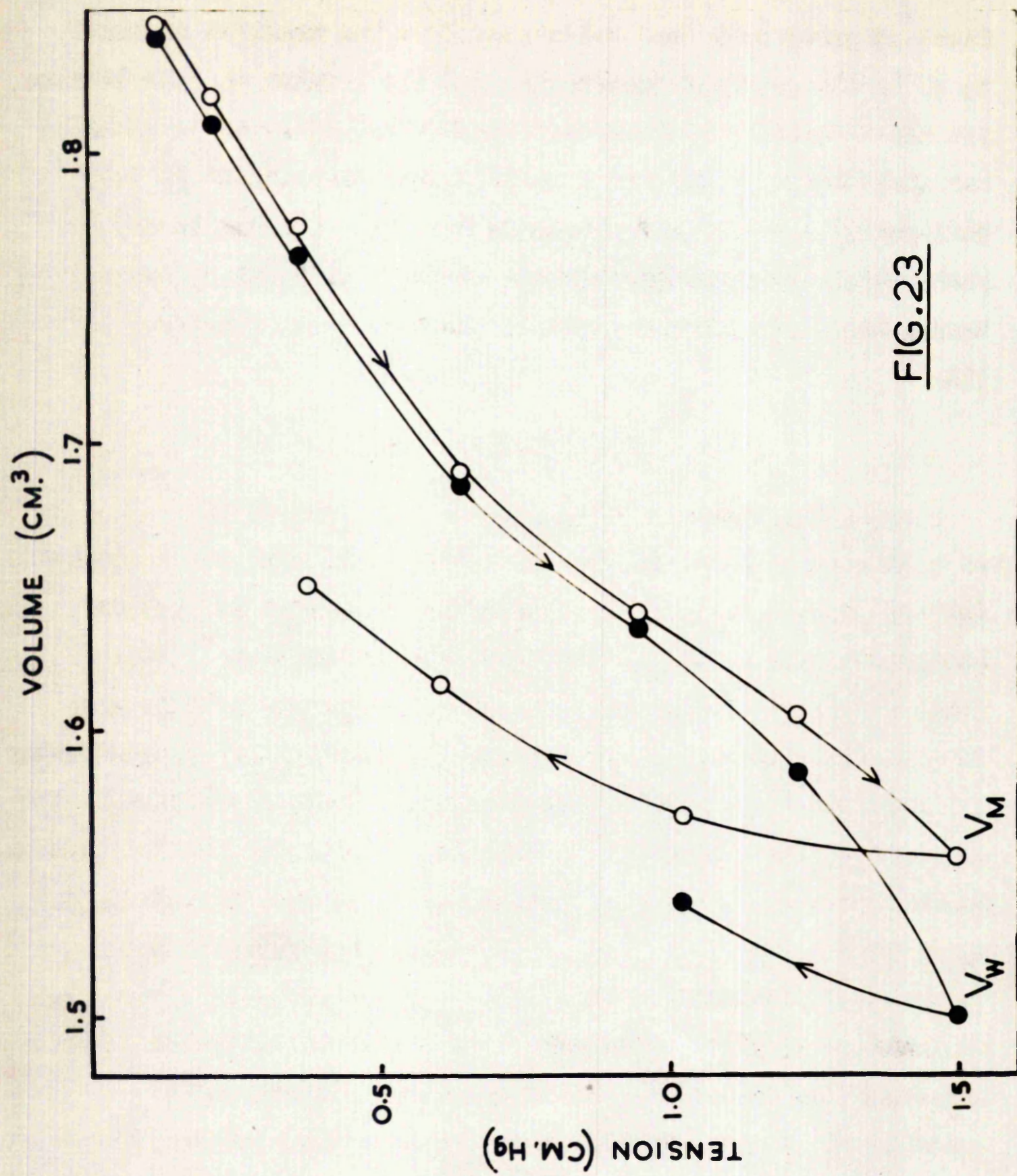


FIG. 23

first compared with that calculated from the moisture content V_w as in the previous experiment, and the results at each tension are shown together with the actual moisture contents in TABLE 4, and graphically in FIG. 3. Each tension corresponds to the difference in hydrostatic pressure between the water in the plate and the surrounding benzene at the same level, allowance having been made for the depth of the benzene as described in §12.

4 (a) The Sorption Isotherm.

From comparison of TABLES 3 and 4, it will be seen that, up to a tension of 1 cm. Hg, the moisture contents of the two pulps differed by 0.2 g./g. only, although, for reasons to be shown later, this good agreement may have been fortuitous. From TABLE 4 and FIG. 23, it will be seen also that up to this same tension there was excellent agreement between V_m and V_w confirming the precision of the measuring techniques since no empirical corrections were necessary in this case. For the last two points on the desorption isotherm, increasing divergence between V_m and V_w occurred indicating that at these tensions entry of the benzene had commenced. This tension is less than half that at which air entered the same pulp in the previous experiment and is explained, in accordance with equation (1), by the lower interfacial tension (approximately 30 dynes/cm.) between water and benzene.

TABLE 4.

Showing moisture content and volume changes on fibre sample 4.

Tension cm. Hg	Relative humidity	Moisture content g./g.	V_w cm ³ .	V_m cm ³ .
0.119	0.9999988	7.82	1.850	1.845
0.213	0.9999979	7.68	1.820	1.820
0.362	0.9999965	7.48	1.775	1.775
0.639	0.9999937	7.11	1.695	1.690
0.944	0.9999907	6.87	1.645	1.640
1.216	0.999988	6.65	1.595	1.605
1.493	0.999985	6.27	1.510	1.555
1.019	0.999990	6.42	1.550	1.570
0.600	0.9999941	—	—	1.615
0.371	0.9999964	—	—	1.650

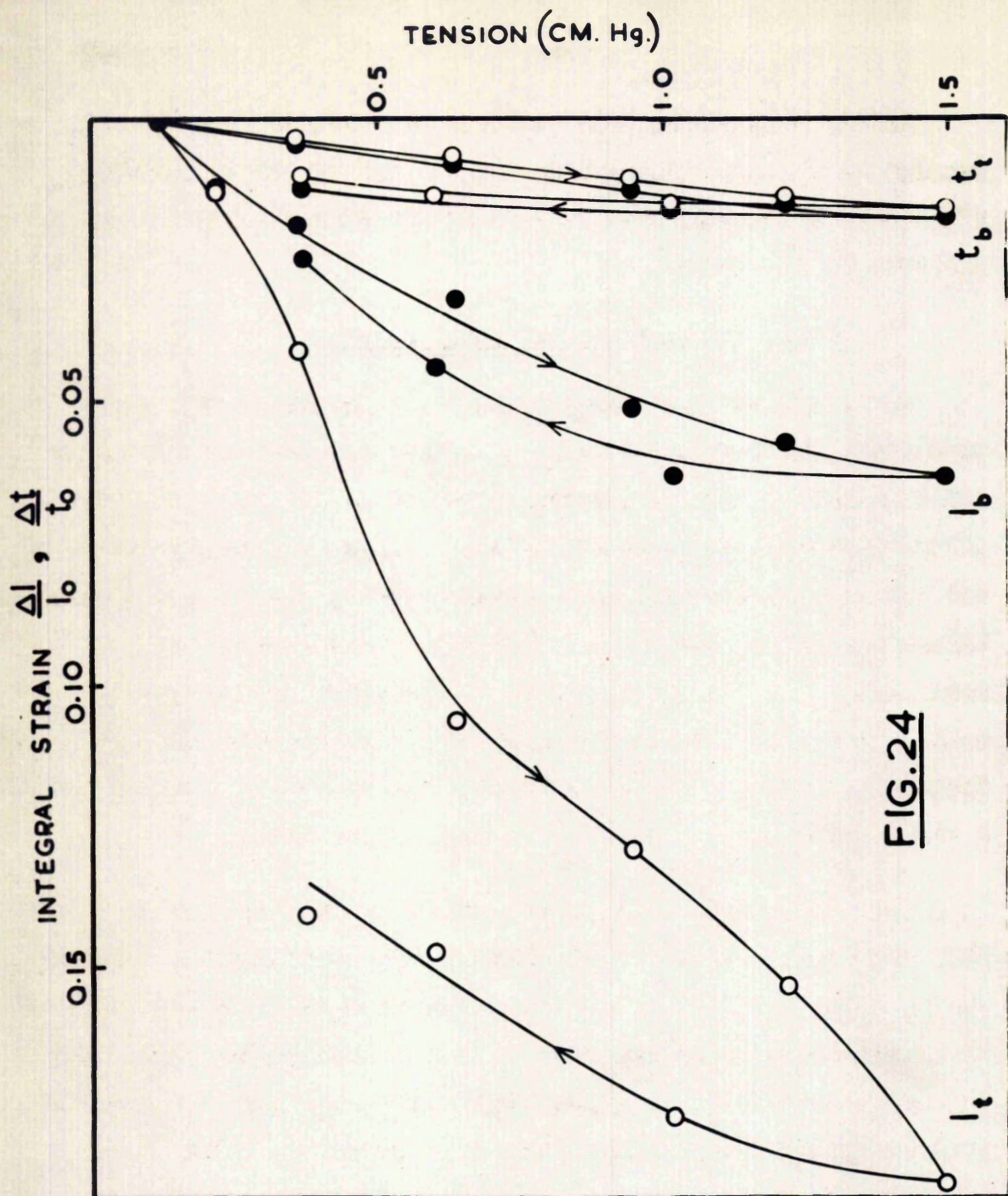


FIG. 24

During adsorption, hysteresis again appeared, but for reasons to be considered below, was not due to the irreversible filling of the capillaries so much as irreversible strains in portions of the matrix.

4 (b) Transverse and Axial Strains.

As in the previous experiment, the diameter of each of the thirteen equal horizontal segments of the cylinder was measured, and in addition, the longitudinal strains in the top and bottom halves were also followed separately. Since the cylinder was not inverted when placed on the porous plate, the top and bottom halves correspond also to the position of the cylinder during formation. In FIG. 24 are shown the longitudinal strains in each half of the cylinder together with the diametral strains determined as a mean for each half of the cylinder. The suffixes t and b refer to top and bottom halves respectively.

Considering the longitudinal strains first, it will be seen that the top and bottom halves behaved very differently, the strain in the top half being approximately three times as great as in the bottom. Before considering the reason for this, there is another important difference to be noted. So far as could be judged from the incomplete experiment, the strain in the lower half, if not irreversible, appeared to be returning to zero as the original tension was again approached. The top half however appeared to contain a large permanent strain.

It is suggested that these effects arise during the formation of the cylinder in which, in this case, only small stresses were applied. As explained previously (§22), the top half, which was last to be formed, was less compressed than the lower half, and on application of a tension during the sorption measurements showed the phenomena of non-reversibility that were observed during the first cycle in Exp. 1. The lower half, having been compressed already during formation, was in a condition more nearly corresponding to the reproducible cycle in Exp. 1.

Of the total change in height, $3/4$ was thus contributed by the top half. The shape of the sorption isotherm for the whole cylinder was therefore determined largely by the top half, as can be seen by comparing FIGS. 23 and 24.

As in the previous experiment, the transverse strains were much smaller, (in this case $1/4$ of the smaller longitudinal strain) and further, agreed to less than 10 per cent. between the top and bottom halves. Although the actual Young's moduli cannot be determined from this data alone, the results suggest that pre-stressing the sample affects predominantly the longitudinal compressibility.

The most important properties of the matrix may be explained readily from the known structure of the cylinder in which the fibres lie predominantly in the transverse plane. The large

longitudinal strains in the cylinders may be produced by bending of the fibres without appreciable slippage of the fibres over one another, and, since their resistance to bending is small, E_1 for the matrix as a whole may also be expected to be low. For this reason also weak inter-fibre bonding, as the fibres are first brought into closer contact, may be sufficient to prevent recovery on release of the stress, and may thus lead to the irrecoverable strains observed during the first cycle. On the other hand, transverse strains in the matrix will involve either longitudinal strains in the fibres themselves or sliding of one fibre over the other, to which resistance may be expected to be greater. This argument may account also for the permanent transverse strain that was apparent in both halves of the cylinder in the present experiment although, as explained in connection with the large hysteresis of sample 2A, these frictional effects may be reduced at very high moisture contents.

The importance of this experiment in relation to the development of the present technique lies in showing the large variation which may occur within any one sample. The conditions of preparation were such as to show this effect at its maximum and in the following experiment an attempt was made to reduce it. The variations within each cylinder also reduce the validity of comparisons between them when made on the basis of mean values for each cylinder as a whole.

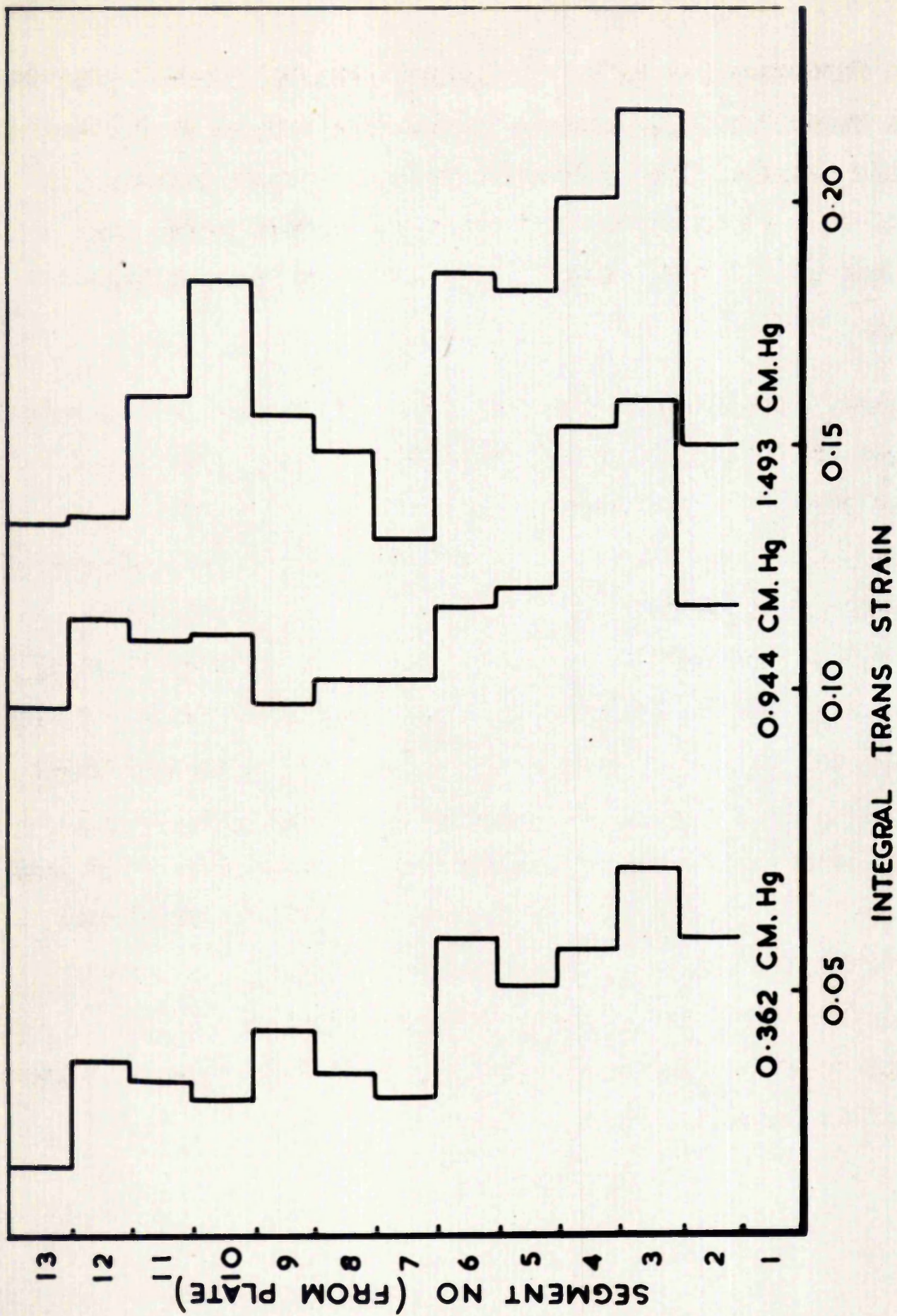


FIG.25

A further point to be considered from the present experiment is the variation of transverse strain with height in the cylinder. For this purpose, the transverse strains in each segment are plotted separately for several tensions (0.362, 0.944 and 1.493 cm. Hg) in FIG. 25 for comparison with the previous cylinder (FIG. 22).

These results show that the behaviour of the two cylinders was very different in several respects. Firstly, the strains did not appear to vary systematically with the height of the cylinder, although the effect is exaggerated by the doubling of the scale of the strain axis. There was some evidence of restraint at the base of the sample but, for optical reasons, it was not possible to measure the diameter of the bottom segment. However, the effect of the restraint did not appear to extend beyond the third segment from the base and was probably not significant at the top. It seems hardly reasonable to suppose that mere inversion of the cylinder would produce these changes and other evidence, e.g. comparison of strains in the two cylinders at the same tensions, suggests that other factors such as the preliminary oven-drying of this sample of fibre may have been partly responsible.

§31. EXPERIMENT 5. APPLICATION OF A LONGITUDINAL STRESS.

In this final experiment to be described, an attempt was made to combine many of the observations so far recorded within one experiment on a single sample. All experimental refinements, suggested by the previous tests, were incorporated in this final technique, details of which have already been described. In addition, a closer study of the variations in the longitudinal strain was desirable, and the effect of directional stresses, leading to the possible calculation of other elastic moduli, was attempted.

An unbeaten kraft pulp (not identical with that in Exp. 2A) was used for these measurements as it had practical advantages over the softer pulp, in ease of handling, and (it was expected) in showing less tendency towards plastic deformation. Its oven-dry weight, determined this time from matched air-conditioned samples, was 0.2026 g. and its initial moisture content when placed on the porous plate was 7.68 g./g. The cylinder was formed under a large hydrostatic head and strongly compressed and released while still surrounded by water in the tube. The cylinder was not inverted but a wire mesh disc was placed on its top end, to carry the weight subsequently added. The weight of this disc when immersed in the surrounding isobutyl benzoate was 0.1146 g.. Its equivalent compressive stress was of the same order as the accuracy of the tension measurements and could therefore be neglected. The depth of the surrounding isobutyl

benzoate varied slightly during the course of the test but, again, the pressure changes due to these variations could be neglected.

Since Exp. 1 had indicated that, below the air entry point, a reproducible cycle could be established for a small sample, an attempt was made to establish such a cycle for this larger cylinder. For this purpose tensions alternating between 0.020 and 0.810 cm. Hg were applied until, after six such alternations, occupying one week, reproducible moisture contents were obtained. Detailed results were not recorded during this phase of the experiment, but it was observed that with each successive cycle, the range of moisture content covered between the two tensions decreased from 2.40 g./g. to 1.97 g./g. This was analogous to the change in shape of the isotherm between the first and subsequent cycles in Exp. 1 in which the corresponding adjustments took place entirely during the first cycle.

Starting from the maximum tension, a sorption cycle of nine points was then carefully plotted over a period of five days during which dimension changes were also recorded. For the measurements of transverse and longitudinal strains, the cylinder was divided into 17 and 5 equal segments respectively, all of which were measured with each change of tension. A small weight was then placed on top of the cylinder. Its weight, when immersed in the isobutyl benzoate, was 1.4107 g. and the corresponding longitudinal stress, assuming a mean diameter of

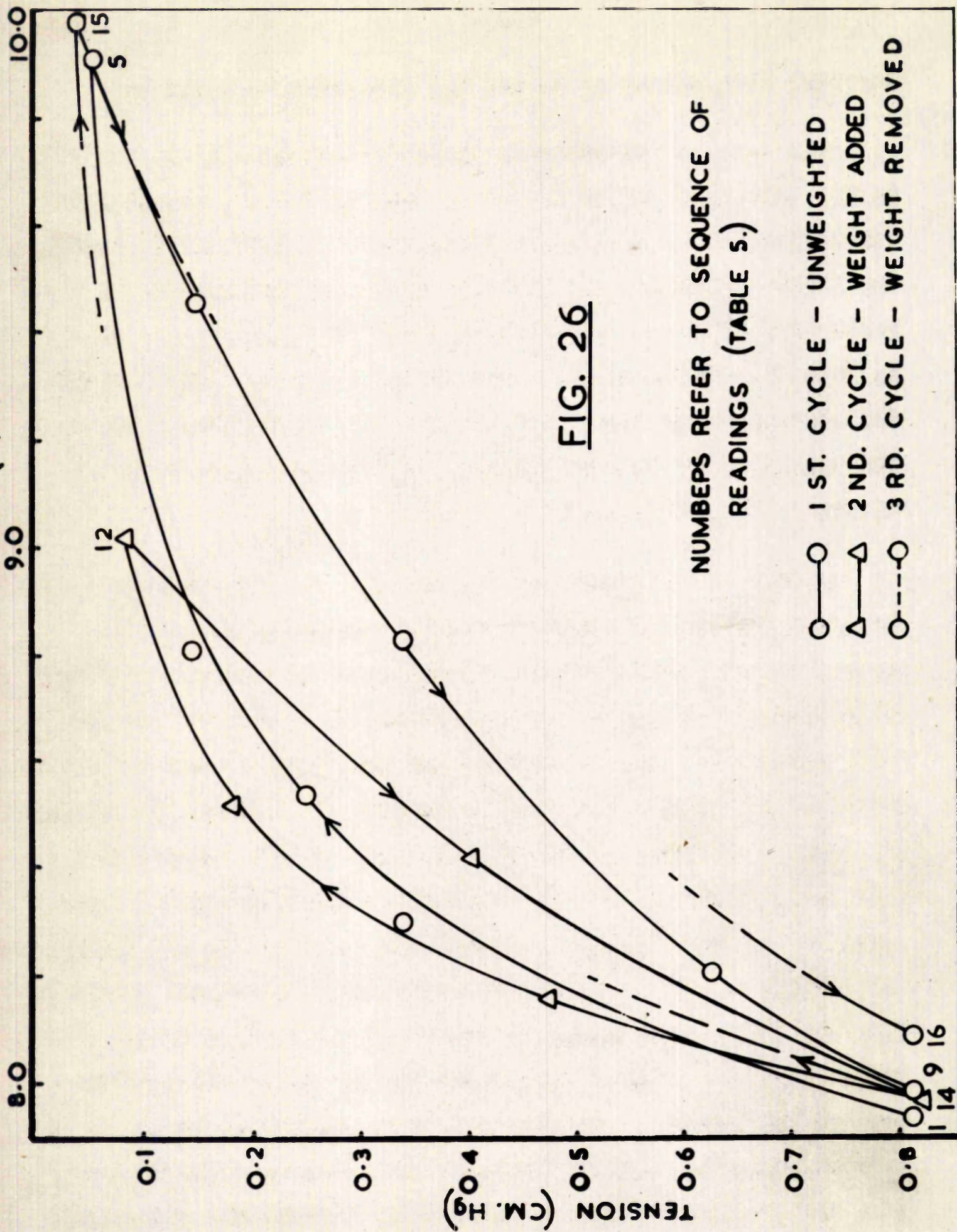
1.2 cm. for the cylinder, was 306 dynes/cm.² or 0.0230 cm. Hg tension. A second cycle was performed in the presence of this weight, during which dimension changes were measured as before. It was observed that, at the conclusion of this cycle, the sample had not returned to its original dimensions. The weight was then removed and a further cycle was performed on the unweighted sample. At the conclusion of this cycle the cylinder had returned approximately to its original dimensions and moisture content.

Unfortunately, considerable difficulty in measuring diameters was experienced due to surface irregularities; graphs of the transverse strains could not be drawn with certainty and some of the quantitative value of the experiment was thereby lost. Further cycles with and without the weight on the cylinder were repeated in an attempt to confirm the observations, but, as these were not completely satisfactory, the experiment was abandoned after a total period of four weeks. The experiment was thus not without the difficulties to be expected in the first application of a new technique and results from the first three cycles only can be considered quantitatively. Lack of time prevented repetition for inclusion in this Thesis.

5 (a) The Sorption Isotherms.

In discussing the results of this experiment, consideration will be given first to the sorption isotherms, which are shown for the first three cycles in FIG. 26. The corresponding data,

MOISTURE CONTENT (G./G.)



together with values of V_m and V_w , are shown in TABLE 5.

The initial reproducible cycle (points 1 to 9) is similar in its general characteristics to that of Exp. 1, but covered deliberately a smaller range of tension and moisture content, the latter never falling below 8 g./g. The phenomenon of hysteresis in the absence of air entry (see Exp. 1) was confirmed, in this case reaching a maximum of 0.6 g./g. moisture content. The difference in moisture content, (0.01 cm.³ actual volume) at the beginning and the end of the cycle lasting five days is within the experimental error.

On adding the weight at the maximum tension, there was no detectable change in shape or moisture content, even after several hours. This was due to the relative incompressibility (i.e. higher value of k) of the cylinder at the total tension of 0.81 cm. Hg then being applied. As the tension was reduced, the effect of the weight became more important until, at the minimum tension of 0.085 cm. Hg (point 12), the moisture content was 0.30 g./g. lower than in the unweighted condition at the same tension. Further increase in moisture content was not considered advisable since the weight might cause large permanent strains. When the tension was again increased to its maximum value (point 14), the moisture content was found to be approximately the same as before. For reasons to be considered below, it is probable that the moisture content was actually slightly lower than this, because a slow loss of water through the surrounding

TABLE 5.

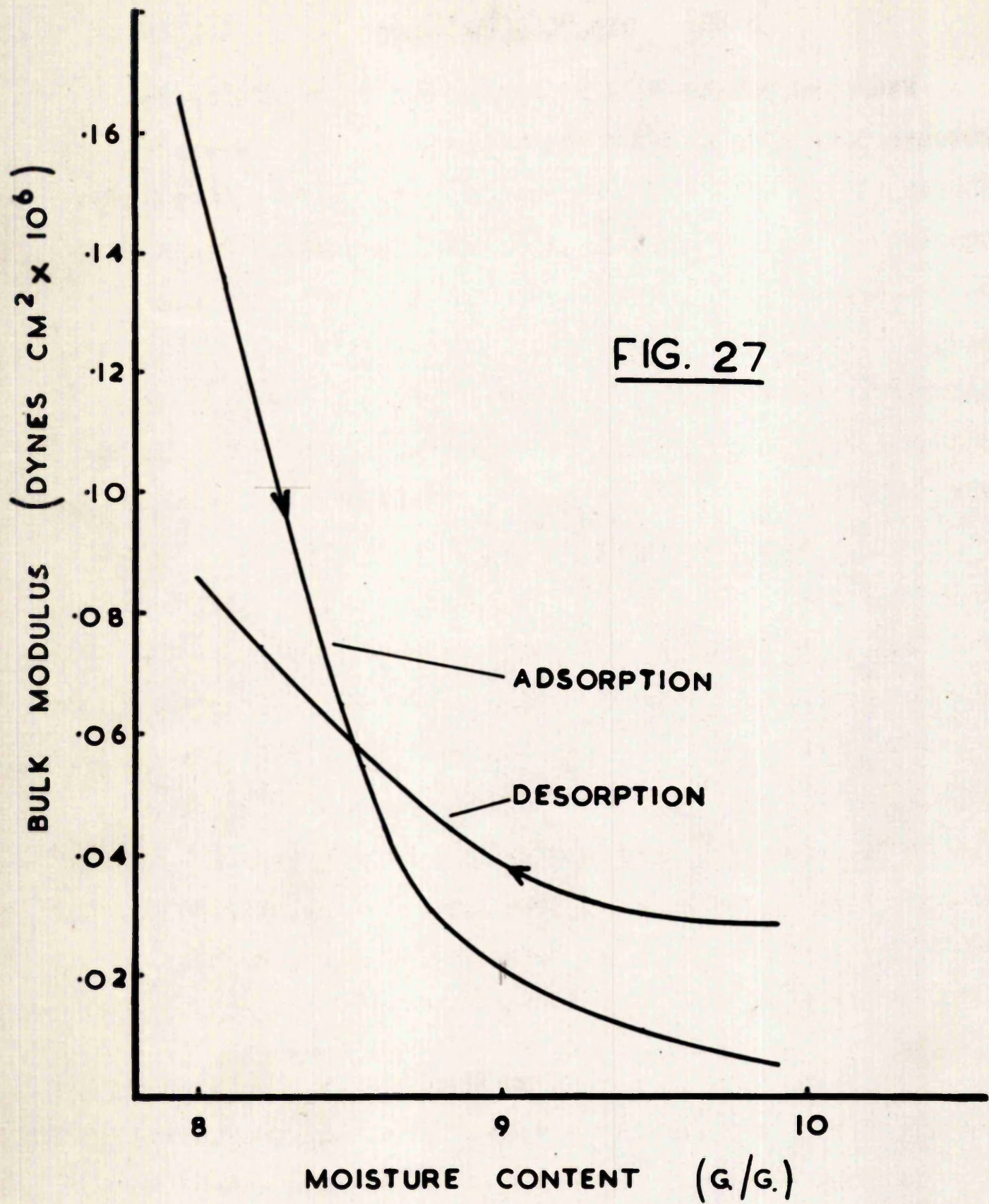
Showing moisture contents and volume measurements for the first three cycles on sample 5.

	Condition of cylinder	Tension cm. Hg	Relative humidity p/p ₀	Moist. content g./g.	V _w cm. ³	V _m cm. ³	V _w - V _m
1	First cycle cylinder unweighted.	0.810	0.9999920	7.94	1.745	1.735	0.010
2		0.340	0.9999967	8.30	1.819	1.790	0.029
3		0.250	0.9999975	8.54	1.867	1.840	0.027
4		0.145	0.9999986	8.81	1.921	1.890	0.031
5		0.055	0.9999995	9.91	2.145	2.110	0.035
6		0.150	0.9999985	9.46	2.052	2.015	0.037
7		0.340	0.9999967	8.83	1.926	1.905	0.021
8		0.625	0.9999938	8.21	1.799	1.775	0.024
9		0.810	0.9999920	7.99	1.755	1.740	0.015
9	Second cycle weight added	0.810	0.9999920	7.99	1.755	1.740	0.015
10		0.475	0.9999953	8.16	1.790	1.780	0.010
11		0.180	0.9999982	8.52	1.862	1.835	0.027
12		0.085	0.9999992	9.02	1.965	1.925	0.040
13		0.405	0.9999960	8.42	1.843	1.780	0.063
14		0.820	0.9999919	7.97	1.750	1.710	0.040
14	Third cycle weight removed	0.820	0.9999919	7.97	1.750	1.710	0.040
15		0.040	0.9999996	9.98	2.160	2.070	0.090
16		0.810	0.9999920	8.09	1.775	1.735	0.40

liquid (e.g., 0.01 cc. per week) would produce an apparent upward drift in the moisture content measurement. On removing the weight no dimension changes in the cylinder were detected and a further cycle between the original tension limits was then completed (points 15 and 16). The final moisture content was apparently a little higher than its initial value although this also could be accounted for by the loss of water.

In TABLE 5 are shown the values for V_m and V_w for the first three cycles. Details of the dimensions from which V_m was calculated will be shown separately when discussing individual strains. It will be noticed that, during the first and last cycle, the difference between V_m and V_w appeared to increase at increasing tensions. That this is not due to air entry is evident from the fact that V_m and not V_w is the smaller quantity. The difference is probably due to the method of measuring the total height of the cylinder, namely from the topmost black dot on its side instead of, as before, the centre of the top end. A slight difference in behaviour of opposite sides of the cylinder could thus produce errors in the calculated volume. At the end of the first and third cycles, i.e. at the same tensions, the V_m values were almost identical with the initial value and it is this fact that suggests that the slight increase in V_w is due to loss of water by evaporation.

FIG. 27



5 (b) The Bulk Modulus.

From the volume changes during the first cycle, the average bulk modulus of the entire matrix was calculated, and the variation of k with moisture content, during both adsorption and desorption, is shown in FIG. 27. Comparing the bulk moduli on desorption with those of previous samples shows that its value at a moisture content of 8 g./g. agrees fairly well with the similar unbeaten kraft pulp (sample 2A) although, at higher moisture contents, greater differences occur. This may be attributed to the presence of the surrounding liquid in which, in contrast with conditions in Exp. 2, the nominal tensions down to 0.05 cm. Hg represent the actual uniform strain over the whole matrix. This explanation is supported by the form of the variation of k at very high moisture contents. In both the present sample and in the very thin sample of Exp. 1, the gravitational effect was negligible, so that the initial fictitious drop in k with decreasing moisture content observed in Exps. 2 and 3 has been eliminated. The real values of the bulk modulus at moisture contents of 10 g./g. are thus considerably lower than the minima recorded for pulps 2A and 2B.

From FIG. 27 it will be seen that the bulk modulus during desorption was very different from that during adsorption at the same moisture content. Hysteresis in the bulk modulus must inevitably be associated with sorption hysteresis since the volume strains measured from the sorption isotherm are used for

its calculation. It also follows that the adsorption and desorption curves of k against moisture content will cross for any closed sorption hysteresis loop. Nevertheless, the possibility of so plotting the variation of k with moisture content during both adsorption and desorption enables hysteresis to be expressed quantitatively in terms of the elastic properties of the matrix.

In this connection however, it should be realised that if hysteresis arises from plastic deformations of the matrix, the strains measured during sorption will include plastic as well as elastic components. The values of the moduli shown in FIG. 27 therefore cannot represent the true elastic moduli which would have to be determined by some method other than stress - strain measurement, e.g. vibrational methods ('instantaneous elasticity' Barkas (51)). A graph of these true elastic moduli with changing moisture content would still not show reversibility between adsorption and desorption however. This is due to the fact that, owing to plastic deformation, the structure, and hence the elastic properties, of the matrix change irreversibly during the hysteresis cycle. Its elastic properties at any moisture content will therefore depend on the sequence and magnitude of the previous stresses.

5 (c) Variations within the cylinder.

As in the case of the two previous cylinders, (Exps. 3 and 4), the integral transverse strain in each segment was plotted

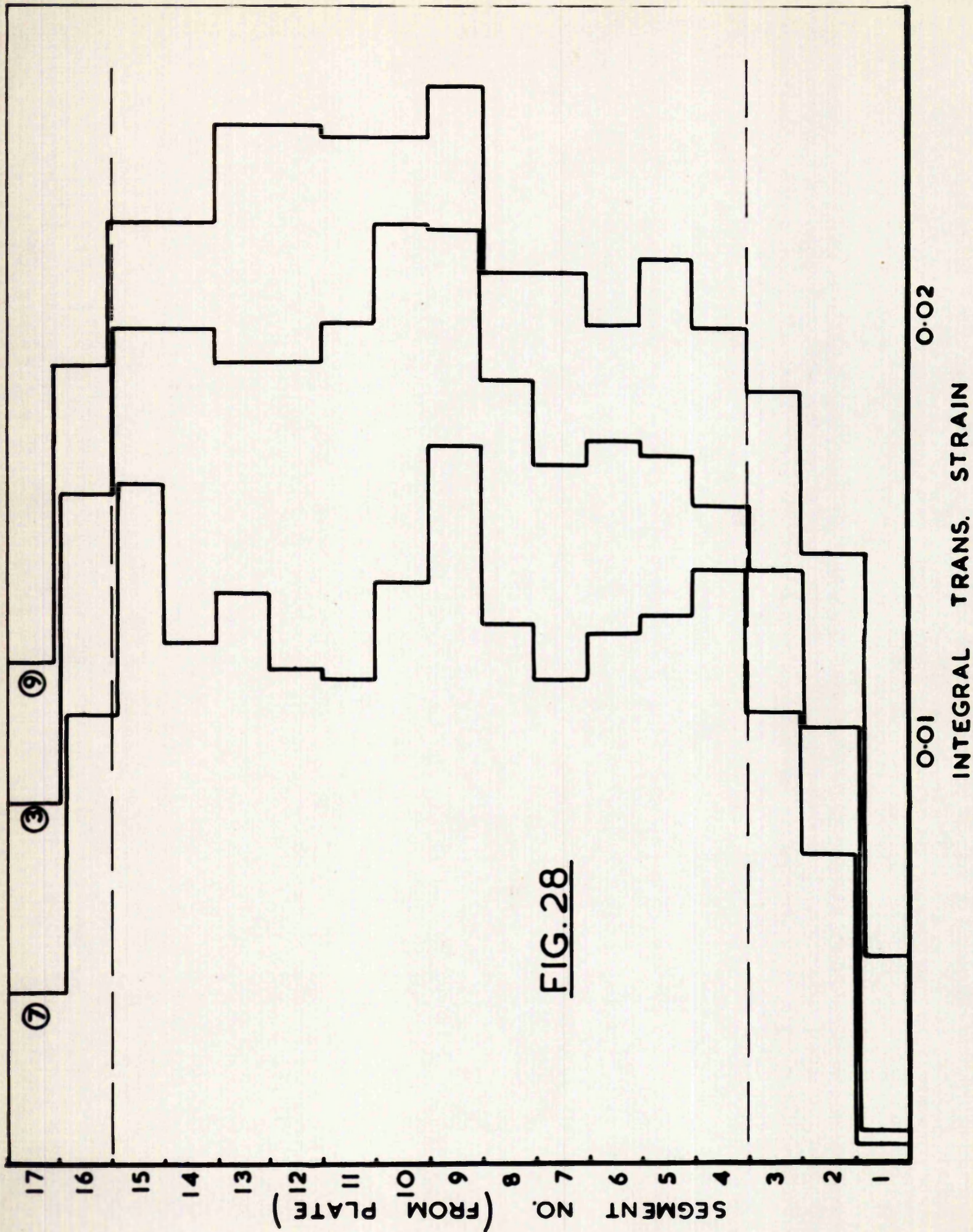
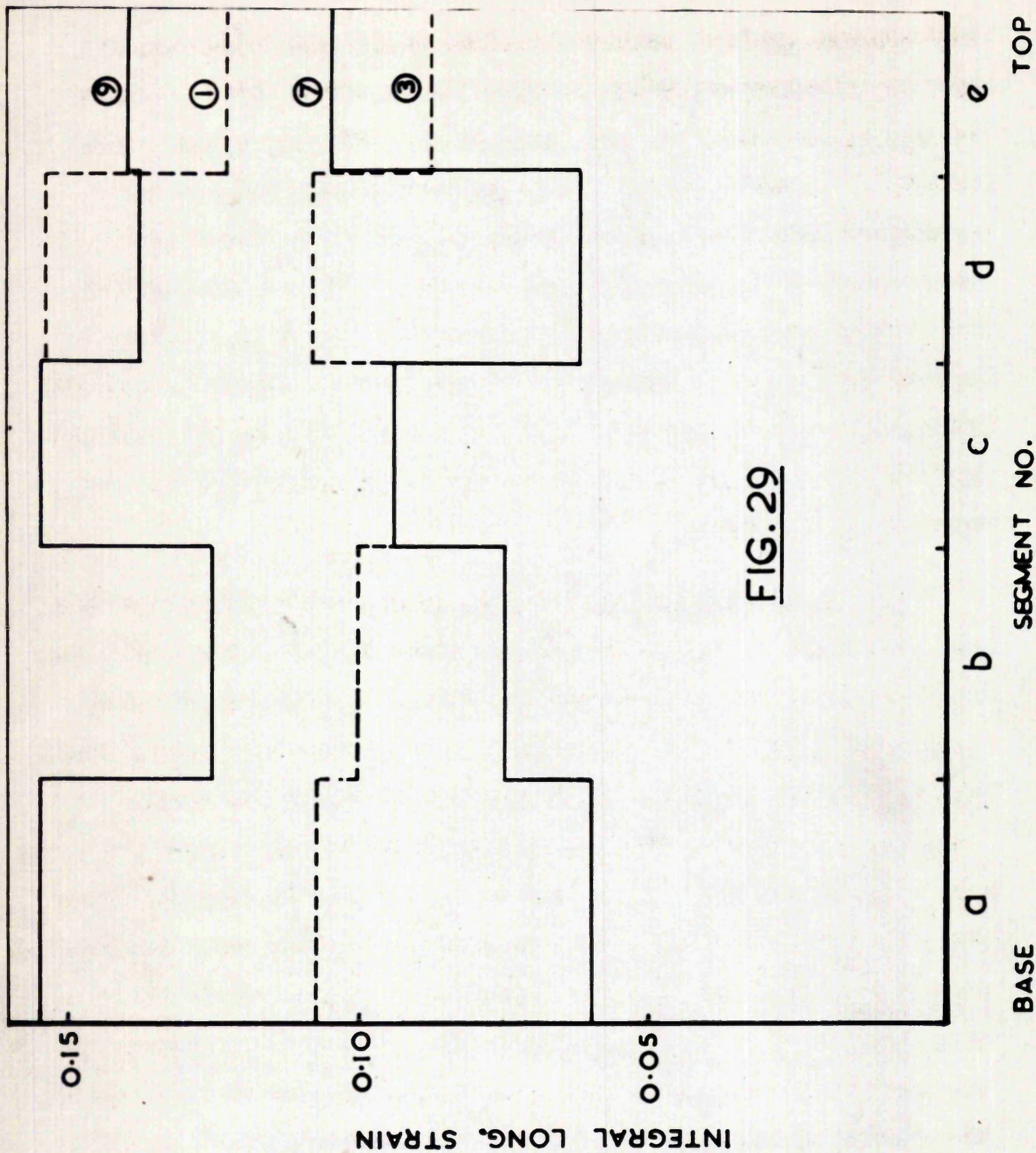


FIG. 28



for several applied tensions (0.250, 0.340 and 0.810 cm. Hg) and the results are shown in FIG. 28, in which the dimensions at the minimum tension are taken as an arbitrary zero. The effect of the end restraints is quite apparent but did not appear to extend beyond the third segment from either end. The centre of the cylinder behaved uniformly, as the residual variations could be attributed to random errors in measurement. In the subsequent calculations of the elastic properties of the matrix therefore, segments 1, 2, 3, 16 and 17 were disregarded and the mean values of the remainder taken as typical of the unrestrained matrix.

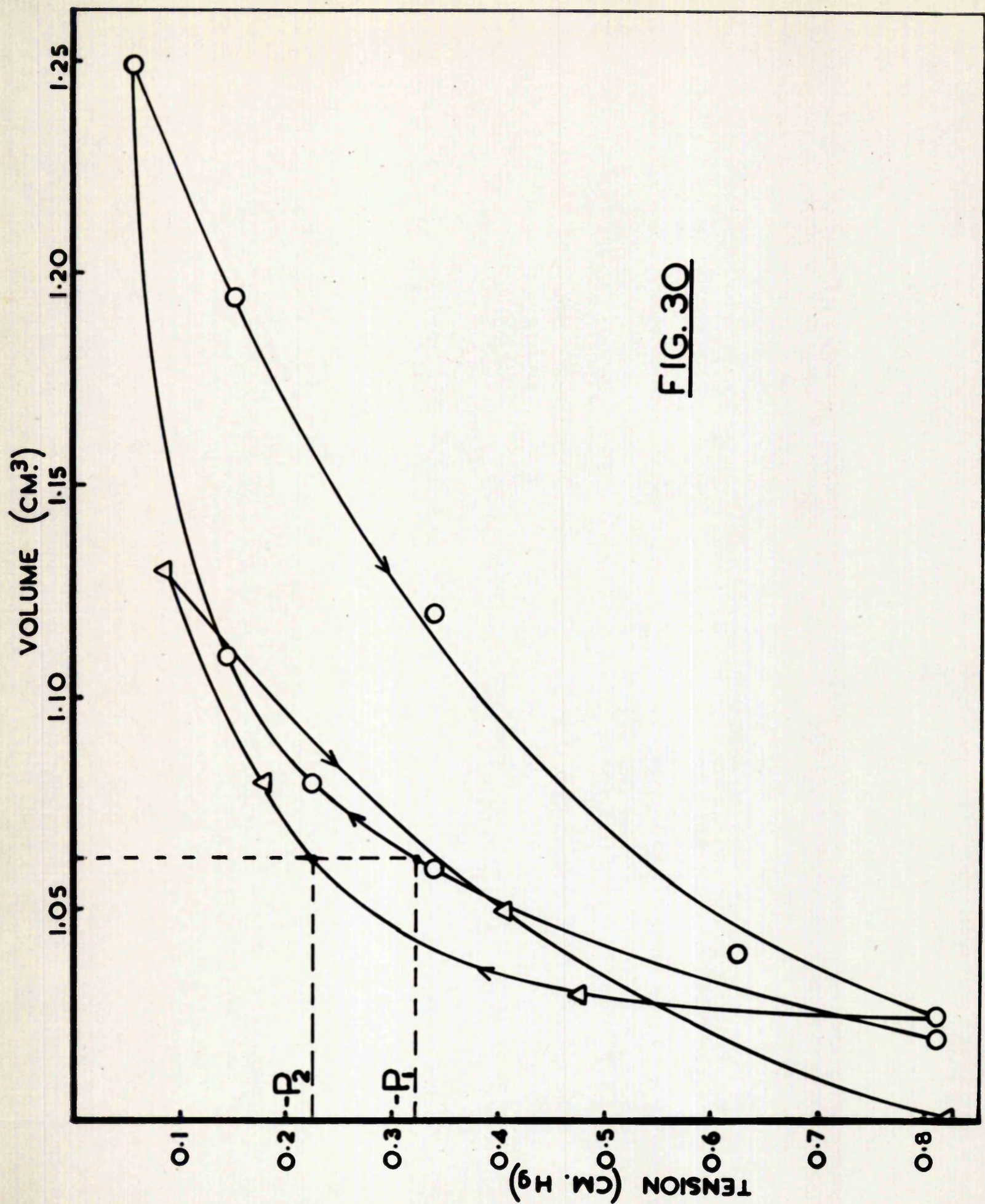
The variations in longitudinal strain with height for the five segments in the cylinder, are shown in FIG. 29, again using the dimensions at the minimum tension as a condition of zero strain. Although the variations in strain appear large, these are due partly to the limited sensitivity of measurement (± 0.005 cm. corresponding to a strain of 0.02). Throughout the cylinder, there does not appear to be any systematic variation exceeding this magnitude, and in determining the mean longitudinal strain for the cylinder as a whole, all five segments were therefore used. Since the error in measurement of strain for the whole cylinder was still ± 0.005 cm., the relative error in the strain measurement was thereby reduced by five. Strictly, the longitudinal strains should be determined only on that portion of the cylinder used in determining the transverse

strain, but the loss in sensitivity in so doing would more than offset the error introduced by neglecting the end effects in using the whole cylinder.

5 (d) Calculation of Other Elastic Moduli.

In order to determine the six elastic constants as described in §21, it is necessary to measure four quantities, namely, the transverse and longitudinal strains under appropriate hydrostatic tensions, with and without the additional longitudinal stress present. In attempting to derive these quantities from data of the present experiment, it is necessary to decide under what conditions of the cylinder the two sets of strains are to be determined. This decision is critical in view of the rapid change in the bulk modulus (and, almost certainly, other moduli also) with changing conditions, e.g. moisture content. In the present instance, a condition of constant moisture content (constant volume strain) is chosen although it does not follow that the longitudinal and transverse strains will also be identical, nor that the distribution of capillary sizes in the matrix will be the same. (Conditions of constant stress are not considered since the applied stress is not a property of the matrix.)

The strain equations set out in §21 apply, strictly, to materials whose elastic properties do not vary with strain. Where the moduli are not constant, the above equations must be expressed in differential form. Thus the integral strains



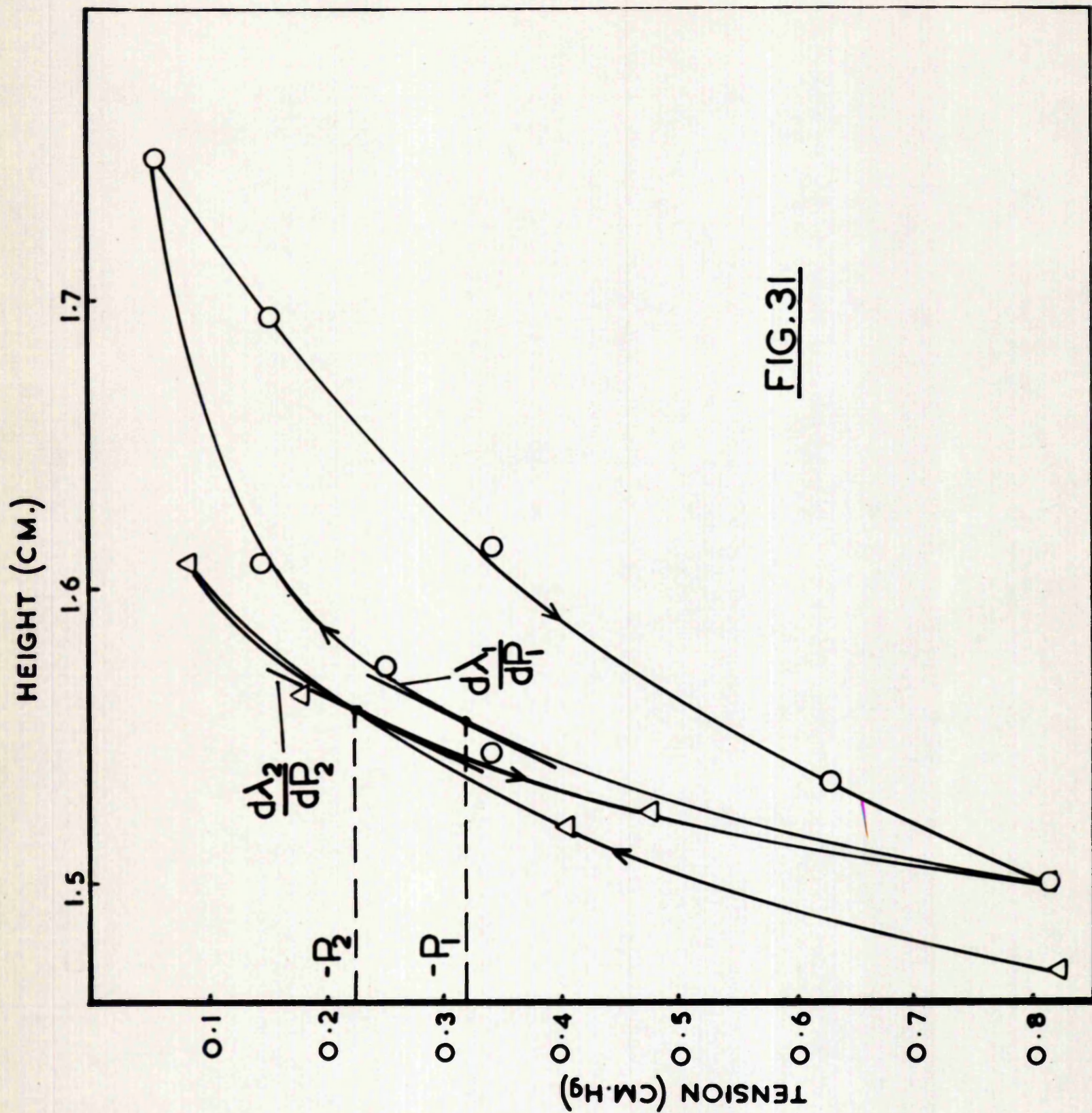
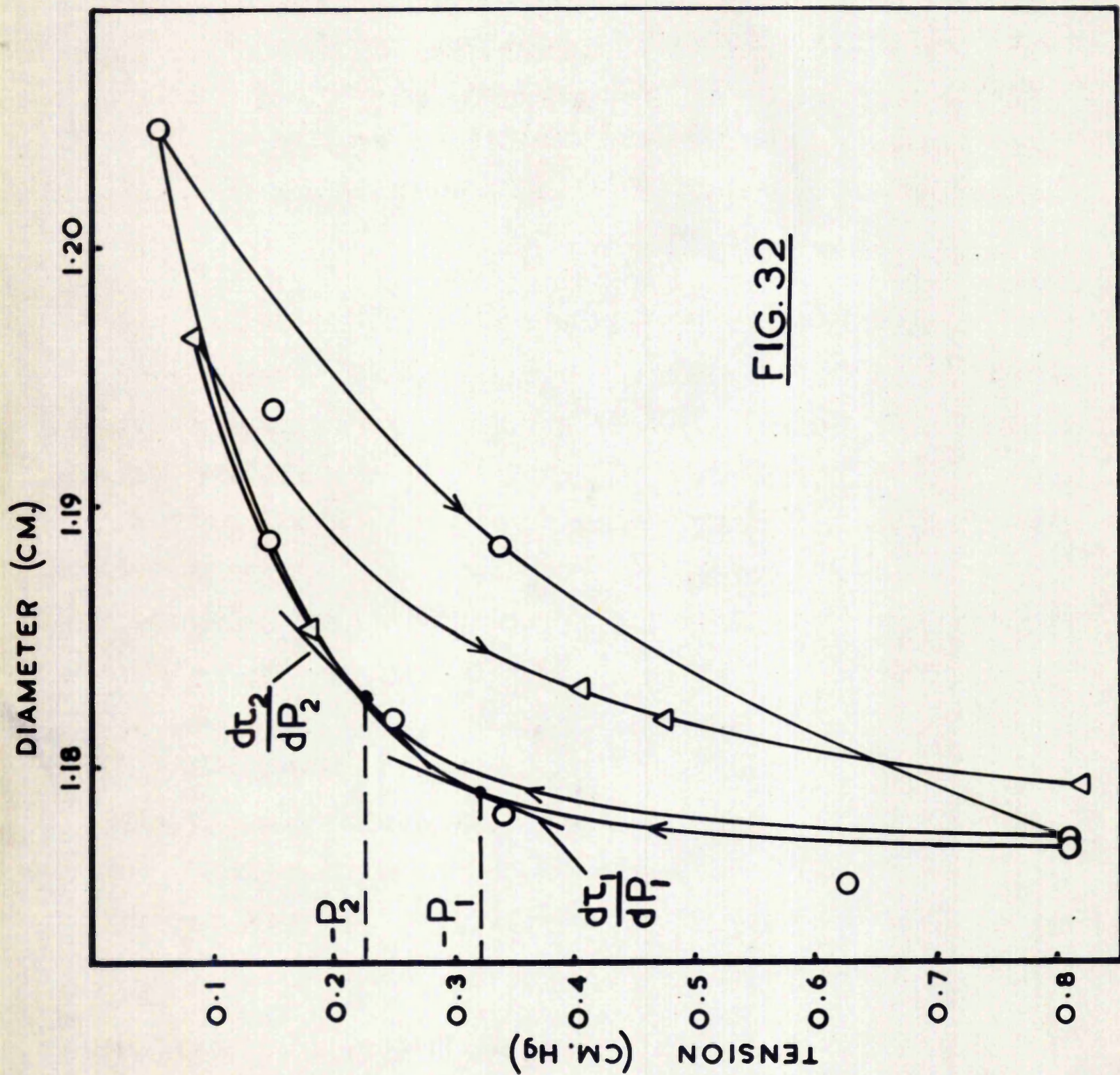


FIG. 31



$d\lambda/\lambda = \lambda$ and $d\tau/\tau = \tau$, resulting from a stress P , must be replaced by $d\lambda$ and $d\tau$ resulting from an increment in stress dP . In order to solve the simultaneous equations (19), (21), (23) and (24), for the unknown moduli, knowledge of $d\lambda/dP$ and $d\tau/dP$ is sufficient and these may be obtained from the slopes of the corresponding stress - strain curves at points of equal moisture content.

In order to provide the necessary data, curves are required which show change in moisture content (total volume), height, and diameter, with tension. Attempts to prepare these for the central uniform portion of the cylinder are shown in FIGS. 30, 31 and 32 respectively for the first and second cycles. Unfortunately, it became clear that the data were insufficient to plot the curves with sufficient accuracy for the subsequent calculations. This was all the more critical because of the necessity to determine gradients, in which large variations could be obtained from different methods of fitting the curves to the existing data. Attempts at calculation of the moduli from this experiment were therefore abandoned regretfully, although the procedure to be followed in making such calculations may be indicated.

As in the case of determination of bulk moduli, distinction must firstly be drawn between the adsorption and desorption isotherms. In the following illustration, the adsorption isotherms will be used. From FIG. 30, an arbitrary moisture

content is selected (it must lie within the range covered during both the weighted and unweighted cycle) and the tensions, $-P_1$ and $-P_2$, are noted at which this moisture content is reached without and with the added weight.

From the graph of length against tension (FIG. 31), the slopes $d\lambda_1/dP_1$ and $d\lambda_2/dP_2$ of the two curves are determined at the tensions $-P_1$ and $-P_2$ respectively. Similarly, from the graph of diameter against tension (FIG. 32), the slopes $d\tau_1/dP_1$ and $d\tau_2/dP_2$ are determined at the same two tensions. The constants of the four equations in their differential form are thus evaluated, and the elastic moduli determined. These moduli all correspond to the arbitrary moisture content during adsorption. By repeating this process for a series of moisture contents, firstly from adsorption and then from desorption data, graphs of the six elastic moduli against moisture content may be plotted in a manner similar to the graph of k against moisture content in FIG. 27.

A check of the accuracy of the determination could be obtained from direct determination of k from a graph of V_w against tension, and comparison with the value of k which may now be calculated from equation (22). Determination of k from a graph of V_m on the other hand would not provide such a check, since the values of V_m themselves involve the transverse and longitudinal strains used in determining the directional moduli.

The remarks in paragraph 5(b) regarding the effect of plasticity on the calculated bulk moduli apply here also, so that these values can not be regarded as the true elastic moduli of the matrix. They will thus be dependent on the pre-history of the sample, and further experiments, between different moisture content limits, may be expected to yield different elastic moduli.

BRITISH BOARD

CONCLUSION



In this final portion of the Thesis, it is proposed to summarise some of the more important theoretical and practical observations that have been described so far. For convenience, these have been placed under three headings relating to capillary sorption, rheological behaviour and paper-making technology, respectively.

§32. PROPERTIES OF LIQUIDS IN CAPILLARIES.

A detailed analysis of the behaviour of liquids in equilibrium in capillaries has been presented in §8 to §17. It has been shown that, as a result of the reduction in vapour pressure of water on application of a hydrostatic tension, equilibrium retention of water in porous materials becomes possible at reduced vapour pressures. By suitably controlling the applied hydrostatic tension in the liquid, its vapour pressure may be controlled with a sensitivity far exceeding that possible by vapour control methods at corresponding humidities. In certain porous materials (see below), the hydrostatic tension may be used also to effect changes in moisture content by liquid, instead of vapour, transfer. These principles have been embodied in the porous plate technique for determination of the sorption isotherms of these porous materials near the saturation vapour pressure.

A number of experimental refinements has been introduced to increase the sensitivity of control of the applied tension and, as a result, it has been possible to determine the sorption

isotherm to equivalent humidities as high as 0.9999999. One of the more important of these refinements has been the replacement of the surrounding air phase by an immiscible liquid of unit density, thereby eliminating some of the stress gradients due to gravity which, with thick samples, would limit the adsorption of water at very low tensions.

It has been shown that, in the range of relative vapour pressure covered, the porous plate technique is complementary to vapour control methods of determining the sorption isotherm. Although it has not been practicable, in these experiments, to determine the sorption isotherm by both techniques on the same material, graphical methods have indicated that, if determined on samples initially in the same condition, a single smooth isotherm will probably be obtained. Experimental confirmation of this point would be difficult however, since the intervening relative humidities around 0.999 are outside the lower and upper limits respectively of the two techniques.

In addition to the limitation in the range of relative vapour pressure over which the porous plate technique may be used, other practical limitations must also be considered. Provided that information regarding the elastic properties of the sorbent is not required, its compressibility may be any value. In the absence of dimensional strains, changes in sorption at these humidities will be due almost entirely to emptying and filling of capillaries, so that any material having an appreciable fraction of capillaries with equivalent radii in excess of $1/\mu$ will theoret-

cally show measurable changes of moisture content during tension cycles on the porous plate. In practice however, two further requirements are necessary for rapid equilibrium, firstly the capillaries must all be interconnected to permit liquid flow, and, secondly, the shape of the sample must be such as to present a continuous close contact with the porous plate.

The relative importance of capillary and molecular sorption over the full range of the sorption isotherm has been considered. The conclusion has been reached that, with increasing relative humidity, the proportion of capillary sorption occurring will increase steadily, although some increase in molecular sorption will occur right up to the saturation vapour pressure. Provided the surface properties of the porous sorbent are such that capillary condensation is capable of occurring at all, it is seen that, as the higher humidities are approached, the quantity of water held by capillary sorption increases very rapidly. This rapid increase accounts for the difficulties commonly met in attempting to estimate the 'saturation' moisture content by extrapolation of the vapour adsorption isotherm from lower values. The present experiments have shown conclusively that these difficulties persist even at humidities as high as 0.999999.

No attempt was made here to derive the moisture content at saturation vapour pressure from the present data, in view of the uncertainty of the extrapolation. However, an alternative method of plotting the sorption isotherm using $-\log(1 - p/p_0)$

instead of p/p_0 raised the possibility of revealing any tendency for adsorption to reach a limiting value at the saturated vapour pressure. At one extreme, a rigid porous adsorbent should have a limiting value corresponding to the condition when all menisci have zero curvature. Addition of further water in this case would cause the water surfaces to become convex, thereby attaining a vapour pressure in excess of the saturated value. At the opposite extreme, the saturated vapour pressure of a solution, even a colloidal solution, will theoretically never be reached by the addition of pure water.

In the case of a fibre matrix, the form taken by the isotherm will depend on whether, at the saturated vapour pressure, the fibres exist as a coherent matrix or whether they will be dispersed by thermal diffusion of the water. Circumstantial evidence, supporting the first possibility, is seen in the tendency of the matrix to retain its structure when completely immersed in a large volume of still water. Although the forces of cohesion are probably immeasurably small, the matrix may be regarded theoretically as a coherent porous material at the saturation vapour pressure, in which case a limiting moisture content will be reached. It has been shown in §20 that, even when all menisci have zero curvature, i.e., there is no difference in hydrostatic pressure between the water and the surrounding medium, the surface tension in the menisci will maintain a compressive stress on the fibre matrix. This residual

compressive stress also will contribute to the cohesion of the matrix at the saturated vapour pressure.

The results of these experiments have been of value in explaining the mechanisms of sorption hysteresis in cellulosic materials, since it has been shown that quite large hysteresis may occur in completely water-logged systems. This fact, together with Barkas' observations of hysteresis in molecular sorption, have proved that irreversible emptying and filling of capillaries is not necessary to explain all sorption hysteresis. On the other hand, Barkas' theory of sorption stresses and plastic deformation may be applied over the entire sorption isotherm since, at no point on it, are moisture content changes unaccompanied by irreversible dimensional strains.

At intervening moisture contents, when partially filled capillaries are present, surprisingly large moisture content hysteresis is observed, involving more than half the total water held on desorption. It is suggested that reproducible, cyclic, but irreversible, changes in size of the capillaries are involved, as a result of frictional deformations within the matrix, although these may not necessarily be reflected in its external dimensions. The very large moisture content difference in the case quoted would arise if most of the water were held in capillaries covering a narrow range of sizes. If, during each cycle, they all change in size, even by only a small amount, there will be a moisture content hysteresis between the tensions at which they

fill and empty, corresponding to their total volume. The magnitude of the moisture content hysteresis at any tension is thus a (complex) function of the proportion of capillaries emptying and filling at that tension and the enlargement they undergo during each cycle. It is recognised that a mechanism depending, for instance, on changes of contact angle, could possibly account also for this large hysteresis, although, for circular capillaries, it may be shown that the change in equivalent radius of meniscus curvature from 40 to 80μ would involve hysteresis of 60° in the contact angle if the receding contact angle were zero. Since portion of the capillary surface will still consist of liquid water menisci, hysteresis of the contact angle on the exposed fibre surfaces comprising the remainder of the capillary would probably need to be greater than 60° in this case. The exposed fibre surfaces would retain adsorbed water in equilibrium with the equivalent vapour pressure.

§33. PRINCIPLES OF ELASTICITY APPLIED TO 'SOFT' MATERIALS.

The porous plate technique for the measurement of the sorption isotherm may be used also for the examination of the elastic properties of porous materials. For this purpose, different structural properties of the porous material may be desirable. Since determination of the bulk modulus requires that a hydrostatic stress should act on all external surfaces of the sample, air entry must be avoided. An ideal material would thus be one possessing capillaries smaller than those corresponding to the maximum

tension it was desired to apply, i.e., in the extreme case, smaller than $1/\mu$. In addition, the materials should show measurable elastic strains at the tensions applied. For instance, a volumetric strain of 1 per cent. at a tension of 1 atmosphere would yield a bulk modulus of 10^8 dynes/cm.² which probably represents the upper limit of bulk modulus that may be measured by this technique. The range of bulk moduli which may be measured conveniently by conventional methods, is from approximately 10^9 to 10^{12} dynes/cm.².

The results from the present experiments have demonstrated that the theories of elasticity, which are applied normally to relatively rigid materials such as metals ($k = 10^{12}$ dynes/cm.²), may be used also to characterise materials falling within the scope of the porous plate technique. The lowest bulk modulus which may be studied in this way appears to be of the order 10^3 dynes/cm.², corresponding to the value of paper pulp at the highest moisture content here reached, i.e. 11 g./g. In this condition it was too deformable to be lifted by hand and further uptake of water was limited by its own weight (in air). The obvious difference in compressibility of extreme materials such as steel and pulp are thus accounted for by a ratio in bulk modulus of 10^9 . It is possible that the porous plate technique could be used to study the elastic properties of soft materials such as porous rubbers or plastics, gels, fine particle aggregates such as clays and soils, as well as fibrous materials.

It is probable however, that strains in many soft materials will include a large measure of plastic deformation so that moduli determined from stress - strain curves may not be the true moduli. If, in addition, the moduli of the material change rapidly with increasing strain, practical as well as theoretical difficulties in measuring the moduli are increased. The present tests have shown clearly that both plastic deformation (strain hysteresis) and change in bulk modulus occur in wet paper pulp, but a possible method of determining other moduli of such materials has also been indicated briefly.

That wet paper pulp possesses measurable elastic, as well as plastic, properties is proved in the present experiments by its ability to undergo reproducible cycles of strain during corresponding cycles of increasing and decreasing stress, i.e. by its reversion to an original condition of strain merely by removal of the stress. This need not be unexpected, since its individual fibres are highly elastic in the direction of their length, so that strains in the pulp matrix, involving flexural strains in the fibres, should therefore contain some elastic component.

§34. PROPERTIES OF PAPER PULPS - APPLICATION TO
PAPER-MAKING TECHNOLOGY.

It remains finally to summarise the sorption and elastic properties of paper pulp and their possible importance in practical paper-making. In this respect many important observations have been made although, with the single exception

of the lightly beaten kraft pulp 2B, unbeaten pulps only have been studied. It should be noted particularly that all tests, and conclusions drawn from them, refer to equilibrium conditions only. The dynamic properties of the wet pulp, also extremely important in paper-making technology, have not been considered in these experiments.

The first of the observations has been referred to above, namely that wet paper pulp may be regarded as an elastic, as well as plastic, material and is thus capable of recovering at least partly from the stresses imposed on it in the course of its formation into a paper sheet. The existence of a reproducible sorption cycle shows that relaxation of the hydrostatic tension in the presence of excess water will lead to re-absorption of this water by the de-watered pulp. This phenomenon has long been recognised in the making of paper. However, these experiments have shown for the first time that, following such re-absorption of water, the second desorption to the same tension will leave the pulp in a wetter state, because the irreversible changes occurring in the first cycle lead to a higher retentivity. The magnitude of this effect will probably depend on a number of factors and, particularly it is suspected, on the maximum moisture content reached during the course of the absorption. The extent to which wet-beaten pulps would show this effect has not been studied.

It seems likely that when a previously de-watered pulp returns to very high moisture contents, changes in the matrix

may occur, and it is presumed that these are made possible by the reduction in inter-fibre contacts and increased freedom of movement of individual fibres. This could account for the fact that, in the first experiment, the reproducible loop commenced from the end of the first adsorption i.e. the irreversible changes occurring before this, took place during both the initial desorption and following adsorption. A similar effect appears in the last experiment where a residual strain was present at the end of the second cycle in which the weight was added. This strain was removed during the following adsorption to a high moisture content. In a similar manner, the relaxation at high moisture content of built in stresses has been used to account for the capillary hysteresis in Exp. 2.

The rapid increase in bulk modulus with decreasing moisture content noted generally in these experiments; accounts partly for the increasing difficulty in removing successive quantities of water by both hydrostatic tension and mechanical compression. Although, in the present experiments, measurements of k extend only down to moisture contents of 6 g./g., it is probable that further compaction of the wet pulp will increase the moduli until, ultimately, those of dry paper (10^{10} dynes/cm.²) are reached. Following air entry however, the resistance of the pulp to de-watering will depend also on the size distribution of the capillaries holding the remaining water. Unless this distribution changes appreciably with subsequent loss of water, the elastic properties of the pulp will become of secondary importance.

Mechanical compression of the pulp, such as may occur at the press rolls, may markedly affect the capillary sizes which, if made smaller, could result in an increase in the retentivity of the pulp at larger tensions. The effect of compression of very wet pulp is indicated from the results of Exp. 4, in which the difference between the upper and lower halves of the cylinder are attributed to relative compression. In this case however, the moisture content of the uncompressed pulp was higher since small tensions only were used and no air had entered the matrix. The differences in both sorptive and elastic properties that have been observed between the top and bottom of the cylinders in these experiments may contribute in part to the differences in the properties of opposite sides of a paper sheet, particularly if it is thick, and a further application of the porous plate technique to research in paper-making technology is thus suggested.

Measurement of the relative strains in the longitudinal and transverse directions confirmed the high degree of anisotropy in the paper cylinders, and, in view of the similarity of their formation with that of the pulp sheet, that of the pulp sheet also. Since the transverse dimensions of the pulp sheet do not change during de-watering on the wire, the changes in moisture content will be determined largely by its Young's modulus normal to the plane of the sheet. (On the other hand the important mechanical properties of the final paper depend on its moduli in the plane of the sheet.) It may be possible to modify the porous

plate technique to enable measurements to be made on portion of a continuous sheet which may be related more closely to the paper being formed on the paper machine wire. However, by neglecting the transverse strains in the cylinders used, an approximate idea of the elastic properties of the pulp in the direction of the cylinder axis may be obtained which will be related directly to the vertical strains in the pulp sheet.

The quantitative measurements of air entry, namely, the tension at which it occurs and the fraction of the total volume occupied at any larger tension, may be related to the conditions under which air is drawn through the pulp at the suction boxes of the paper machine. Of greater importance however, may be its effect on the elastic properties of the fibre matrix and the ultimate strength, permeability, and absorbency, of the final paper. Although the calculation of the bulk modulus from the sorption isotherm becomes invalid at tensions beyond the air entry point, the possibility of using the porous plate at these higher tensions for determination of moduli are not exhausted. For instance, the application of directional stresses to pads of fibres maintained at constant liquid tension beyond air entry has not been considered, but could well form an extension of the technique described in Exp. 5. In this way some elastic moduli of the pulp at much lower moisture contents may be determined.

In one experiment only was any attempt made to examine the effect of beating (§28), and this only to determine possible limitations of the porous plate technique. It was obvious however, that both sorption and elasticity studies using this technique are capable of yielding valuable information regarding the effect of beating on pulp properties. For instance, large differences between the beaten and unbeaten samples were observed in the range of moisture content corresponding to a given range of tension, (and consequently different retentivity at different tensions), the tension at which air entered the matrix, capillary size distribution, and bulk moduli at given moisture contents. Any of these quantities may be used, firstly, to characterise empirically the papermaking properties of the pulp, e.g. by comparison with standard pulp evaluation methods as reported recently by Hallan and Barkas*, and secondly, to determine fundamental physical and mechanical properties of the pulp which may lead to better understanding of the ultimate processes occurring in the formation of the paper sheet.

* Hallan, R. and Barkas, W.W., Proc. Tech. Sect. P.M.A., 34 (1953).

REFERENCES

- (1) Haines, W. B., J. Agric. Sci., 20, 97, (1930).
- (2) Schofield, R. K., Trans. Third Inter. Cong. Soil Sci., 2, 38,
(1935).
- (3) Preston, J. M. and Nimkar, M. V., J. Textile Inst., 43, T402,
(1952).
- (4) Brown, R. C., Proc. Phys. Soc. (Lond.), A59, 429, (1947).
- (5) Gurney, C., Nature, 160, 166, (1947), Proc. Phys. Soc. (Lond.),
A62, 639, (1948).
- (6) Bangham, D. H. and Razouk, R. I., Trans. Farad. Soc.,
33, 1459, (1937).
- (7) Yarnold, G. D. and Mason, B. J., Proc. Phys. Soc. (Lond.),
B62, 121, 125, (1949).
- (8) Porter, A. W., Proc. Roy. Soc., A79, 519, (1907).
- (9) Glasstone, S., 'Textbook of Physical Chemistry' p.238,
Macmillan (1951).
- (10) Tolman, R. C., J. Chem. Phys., 17, 333, (1949).
- (11) Koenig, F. O., J. Chem. Phys., 18, 449, (1950).
- (12) Porter, A. W., Phil. Mag., 14, 694, (1932).
- (13) La Mer, V.K. and Gruen, R., Trans. Farad. Soc., 48, 410, (1952).
- (14) Shereshefsky, J. L., J. Am. Chem. Soc., 50, 2966, (1928).
- (15) Chumtsov, K. V., Kolloid Zhur., 10, 47, (1948); 11, 4, (1949).
- (16) Henniker, J. C., Rev. Mod. Phys., 21, 322, (1949).
- (17) Cohan, L. H. and Meyer, G. E., J. Am. Chem. Soc., 62, 2715,
(1940).
- (18) Bulkley, R., J. Res. Nat. Bur. Stand., 6, 89, (1931).
- (19) Bastow, S. H. and Bowden, F. P., Proc. Roy. Soc., 151A, 220,
(1935).
- (20) Bowden, F. P. and Throssel, W. R., Proc. Roy. Soc., 209A,
297, (1951).
- (21) Haines, W. B., J. Agric. Sci., 15, 529, (1925).
- (22) Fisher, R. A., J. Agric. Sci., 16, 492, (1926).

- (23) Smith, W. O., Foote, P. D. and Busang, P. F., *Phys. Rev.*, 36, 524, (1930).
- (24) Harkins, W. D. and Jura, G., *J. Chem. Phys.*, 11, 560, (1943),
J. Am. Chem. Soc., 66, 919, (1944).
- (25) Bangham, D. H. and Razouk, R. I., *Trans. Farad. Soc.*,
13, 1463, (1937).
- (26) Barkas, W. W., *Proc. Phys. Soc.*, 48, 1, (1936).
- (27) Zsigmondy, R., *Z. Anorg. Chem.*, 71, 356, (1911).
- (28) Cohan, L. H., *J. Am. Chem. Soc.*, 60, 433, (1938); 66, 98,
(1944).
- (29) Foster, A. G., *J. Phys. and Coll. Chem.*, 55, 638, (1951),
J. Chem. Soc. 5, 1806, (1952).
- (30) Harkins, W. D. and Jura, G., *J. Am. Chem. Soc.*, 66, 1362, (1944),
J. Chem. Phys., 11, 430, (1943).
- (31) Carman, P. G. and Raal, P. A., *Nature*, 167, 112, (1951).
- (32) Ashpole, D. K., *Proc. Roy. Soc.*, 212A, 112, (1952).
- (33) Rees, W. H., *J. Text. Inst.*, 39, T351, (1948).
- (34) Neale, S. M. and Stringfellow, W. A., *Trans. Farad. Soc.*,
37, 525, (1941).
- (35) Pierce, F. T., *J. Text. Inst.*, 20, T133, (1929).
- (36) Hailwood, A. J. and Horrobin, S., *Trans. Farad. Soc.*, 42B,
84, (1942).
- (37) Cassie, A. B. D., *Trans. Farad. Soc.*, 41, 450, 458, (1945).
- (38) Stamm, A. J., 'Wood Chemistry', p. 465, Reinhold Pub. Corp.
(1944).
- (39) Barkas, W. W., *Proc. Phys. Soc.*, 48, 576, (1936).
- (40) Rao, K. S., *J. Phys. Chem.*, 45, 500, (1941).
- (41) Higuti, I., *Bull. Inst. Phys. Chem. Res. Tokyo*, 20, 180, (1941).
- (42) Everett, D. H. and Whetton, W. I., *Trans. Farad. Soc.*,
48, 749, (1952).

- (43) McBain, J. W., J. Am. Chem. Soc., 57, 699, (1935).
- (44) Foster, A. G., Proc. Roy. Soc., 146A, 129, (1934);
147A, 128, (1934).
- (45) Cohan, L. H., J. Am. Chem. Soc., 60, 433, (1938);
66, 98, (1944).
- (47) Gregg, S. J., J. Chem. Soc., 1942, 696.
- (48) Bangham, D. H. and Fakhoury, N., J. Chem. Soc., 1931, 1324.
- (49) Urquhart, A. R., Private communication.
- (50) Urquhart, A. R., J. Text. Inst., 20, T215, (1929).
- (51) Barkas, W. W., "The Swelling of Wood under Stress", H.M.S.O.
(1949).

A C K N O W L E D G E M E N T.

The author wishes to express his sincere appreciation of the encouragement and guidance given throughout by Dr. W.W. Barkas, F.Inst.P., who, as supervisor, made these investigations a pleasant as well as valuable experience.

Grateful acknowledgement is made also to Mr. S.A. Clarke, Chief, Division of Forest Products, and the C.S.I.R.O., Australia, for the Studentship which provided the opportunity for this research.
