THE ABSORPTION OF WATER BY HAIR, AND ITS DEPENDENCE ON APPLIED STRESS

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It has been reported by White and Stam that the equilibrium water content of human hair is decreased by the application of a tensile stress. This result is shown to be inconsistent with general thermodynamics, which predicts an opposite effect in the case when liquid absorption is accompanied by longitudinal extension, as it is in hair. Experiments with horsehair, in which the water content in the stressed and unstressed states, at 75·5 % relative humidity, was determined by weighing, showed a small increase in water content on applying a tensile stress, the effect amounting to 0·28 % on the dry weight for a stress of 482 kg/cm^2. This increase was in quantitative agreement with the thermodynamic theory.

Subsidiary measurements of dimensional changes accompanying the application of tension indicated a small increase of volume of the amount to be expected from theoretical considerations. Data are also presented for the length changes which accompany water absorption, and for the water absorption as a function of relative humidity.

Curves are included for the theoretical increase of water content with longitudinal tensile stress over the whole range of humidity, and for the theoretical decrease in water content under lateral compressive stress. The latter effect may be as much as 200 times the former, on account of the anisotropy of swelling.

STATEMENT OF THE PROBLEM.—The mechanical properties of a textile fibre are, in general, extremely sensitive to changes in its water content. The study of all the factors which may affect the water content is therefore a matter of considerable importance. One such factor, to which relatively little attention has been given, is the applied stress. The data of White and Stam [1] for hair lead to the conclusion that, at a given relative humidity, the equilibrium water content is *reduced* by the application of a tensile stress, the reduction (which was partially reversible) amounting to about 50 % for a stress of 120 kg/cm^2.

On the other hand, for vulcanized rubber swollen with liquid hydrocarbons, it has been established both experimentally [2, 3] and theoretically,[4] that tensile stresses lead to an *increase* in the equilibrium liquid absorption. In view of this difference it seemed desirable to re-examine the question of the dependence of water content in fibres on tensile stress. It will be shown that White and Stam's conclusion is not supported by thermodynamic theory, which requires that for a material (such as hair) which increases in length on absorbing water, the effect of tension is to *increase* the amount of liquid absorbed. This theoretical prediction is confirmed experimentally for horsehair.

THEORETICAL RELATIONS.—*General equations.*—The fundamental theory of the relation between the amount of liquid imbibed by a gel and the stresses to which it is subjected has been worked out by Barkas [6] and applied to the determination of swelling stresses in wood. Essentially it is an extension of the ordinary thermodynamic theory of osmotic pressure or swelling pressure. Let us consider the most general case of a rectangular block of swollen anisotropic gel, of dimensions x, y and z and volume V, subjected to (compressive) forces X, Y and Z per unit area acting on the surfaces respectively normal to the x, y and z axes, and in equilibrium with the surrounding vapour at pressure p. We define the differential swellings s_X, s_Y, s_Z in the x, y and z directions by [6]

$$\begin{aligned} s_X &= yz\left(\frac{\partial x}{\partial m}\right)_{XYZ} = \frac{V}{x}\left(\frac{\partial x}{\partial m}\right)_{XYZ}, \\ s_Y &= \frac{V}{y}\left(\frac{\partial y}{\partial m}\right)_{XYZ}, \\ s_Z &= \frac{V}{z}\left(\frac{\partial z}{\partial m}\right)_{XYZ}, \end{aligned} \tag{1}$$

in which, e.g. $(\partial x/\partial m)$ is the increment of length in the x direction per unit mass of liquid absorbed, with all the forces held constant. (It is important to distinguish between *forces* (calculated on some initial area) and *stresses*, calculated on the actual area in each state).

If, now, the forces are increased by amounts dX, dY, dZ, the change dp in vapour pressure required to maintain equilibrium at the initial liquid content is given by the equation,

$$s_X\mathrm{d}X + s_Y\mathrm{d}Y + s_Z\mathrm{d}Z = v\,\mathrm{d}p, \tag{2}$$

v being the volume occupied by 1 g of vapour at the pressure p.

Uniaxial stress.—When the only force acting is a uniaxial tension eqn. (2) reduces to

$$s_X\mathrm{d}X = -v\,\mathrm{d}p = \frac{V}{x}\left(\frac{\partial x}{\partial m}\right)_X \mathrm{d}X,$$

or

$$\left(\frac{\partial p}{\partial X}\right)_m = -\frac{V}{v}\cdot\frac{1}{x}\left(\frac{\partial x}{\partial m}\right)_X. \tag{3}$$

This equation gives the change in vapour pressure, at constant liquid content, corresponding to an increase in the force (per unit initial area) by dX. To convert this to change in liquid content at constant vapour pressure, $(\partial m/\partial X)_p$, we make use of the identity

$$\left(\frac{\partial m}{\partial X}\right)_p = -\left(\frac{\partial m}{\partial p}\right)_X\left(\frac{\partial p}{\partial X}\right)_m, \tag{4}$$

so that (3) becomes

$$\left(\frac{\partial m}{\partial X}\right)_p = \frac{V}{v}\cdot\frac{1}{x}\left(\frac{\partial x}{\partial m}\right)_X\left(\frac{\partial m}{\partial p}\right)_X,$$

or

$$\left(\frac{\partial m}{\partial X}\right)_p = \frac{V}{v}\cdot\frac{1}{x}\left(\frac{\partial x}{\partial p}\right)_X. \tag{5}$$

It is usual to express the water content of a fibre in terms of q, the weight of water per g of dry material. It is therefore desirable to write eqn. (5) in these terms. If ρ_m is the density in the swollen state, the volume V has the weight $V\rho_m$ and contains $V\rho_m/(1 + q)$ g of dry material, hence the change in water content per g of dry material is, from (5),

$$\left(\frac{\partial q}{\partial X}\right)_p = \frac{1+q}{V\rho_m} \cdot \left(\frac{\partial m}{\partial X}\right)_p = \frac{1+q}{v\rho_m} \cdot \frac{1}{x}\left(\frac{\partial x}{\partial p}\right)_X.$$

Substituting l for x, the longitudinal dimension, this may be written

$$\left(\frac{\partial q}{\partial X}\right)_p = \frac{1+q}{\rho_m v p_0} \cdot \frac{1}{l}\left[\frac{\partial l}{\partial (p/p_0)}\right]_X, \tag{6}$$

where p_0 is the saturation vapour pressure of the pure liquid. Thus eqn. (6) expresses the dependence of water content on tension in terms of the variation of length with relative vapour pressure or relative humidity.

EXPERIMENTAL

The experiments which it was necessary to carry out in order to test the applicability of eqn. (6) were the following:

(i) determination of change in equilibrium water content due to the application of tensile stress;

(ii) determination of change in relative length as a function of relative humidity (r.h.).

In addition, for the sake of completeness, and in order to provide a check on the technique employed, measurements were made on

(iii) the relation between water content and r.h.

THE EFFECT OF TENSION ON WATER CONTENT.—*Apparatus and methods employed.*—The material employed in these experiments was white horsehair (obtained from W. E. Hill & Sons, Bond Street, London), which was degreased by successive Soxhlet extractions in ether and alcohol. Horsehair was chosen in preference to human hair in order to increase the total weight of material which could be accommodated. The water content was determined directly by weighing, and was not, as in White and Stam's experiments, derived from measurements of fibre dimensions.

The method employed was to attach eight loops of hair H, having a total length of 360 cm, to a brass frame, the tension being applied by means of calibrated stainless steel springs S (fig. 1). The whole assembly was suspended from the arm of a balance (reading to 0·0001 g) in a temperature- and humidity-controlled vessel consisting of a large bottle closed by a metal cap C carrying the tube L through which the suspending wire passed. The final equilibrium weight of the hair was determined with the tension alternately applied and removed. The relative humidity was maintained at 75·5 % by means of salt solution (P). The temperature was maintained by immersion in a water thermostat at 25·00° C.

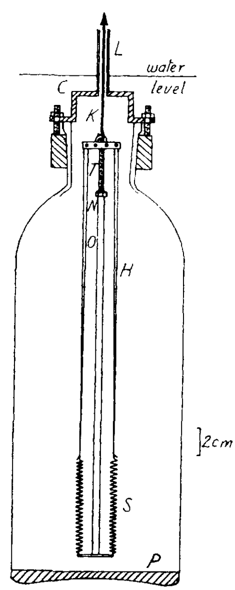

FIG. 1.—Stretching frame and humidity chamber. (2 hairs only shown.)

To apply the stress, the frame was removed and the threaded rod T withdrawn from the outer tube O and held in place by means of the nut N. This necessitated exposure of the hair for not more than 10 min to a lower relative humidity (between 39 and 65 %). In order to secure a standard starting point, and to ensure that the final equilibrium was approached always from the same direction, the hair was given a conditioning at 40·4 % r.h. and 25° C for 1 h after each such exposure to the laboratory atmosphere before being returned to the standard 75·5 % r.h. The approach to equilibrium could be followed by intermittent weighing; the minimum time allowed for the final equilibrium reading was 20 h. Except when weighing was in progress the frame was disconnected from its suspension and the tube L closed with a rubber stopper (not air-tight). Examples of the changes in water content during the preliminary conditioning and subsequent approach to equilibrium are shown in fig. 2.

For the determination of the dry weight of the fibre the salt was replaced by magnesium perchlorate. Seven days at 25° C appeared to be sufficient for constancy of weight to be achieved.

Stress relaxation.—The hairs were chosen so that variations in mean cross-sectional area for individual fibres were within ± 5 % of the average. Owing to the imperfect elasticity of hair, there was a noticeable lengthening of the fibres, with consequent relaxation of the spring tension, after the initial application of the stress. It is well known

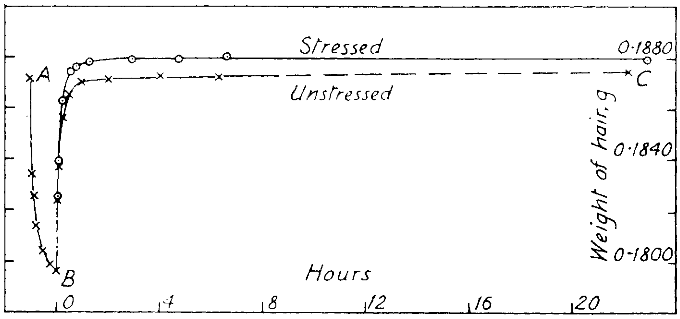

FIG. 2.—Rate of approach to equilibrium for stressed (195 g load) and unstressed hair. AB, 40·4 % r.h., BC, 75·5 % r.h.

that such stress relaxation progressively diminishes with the lapse of time, and rough observations indicated that 90 % or more of the total lengthening had occurred within the first hour of immersion at 75·5 % r.h. Consequently we may without serious error assume that the final equilibrium water content is determined by the final stress as measured on removal from the humidity-controlled vessel.

For the higher of the two stresses employed the mean load relaxed from 253 to 195 g per hair—a reduction of 23 %—while the mean length of hair increased from 3·8 % to 7·5 % above its unstressed length. Under the lower stress condition the load fell from 119 to 110 g, while the length increased from 3·1 % to 3·7 % above the unstressed length.

Four cycles of loading and unloading were carried out at the higher stress, followed

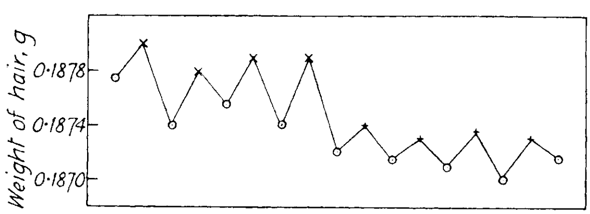

FIG. 3.—Weight changes on repeated stressing.
○ unstressed, × load 195 g, + load 110 g.

by four cycles at the lower stress. After the first cycle at any stress the length changes were repeatable, i.e. there was no evidence of continuous lengthening of the fibre under the action of the stress.

The calculation of the stress was based on the assumption (not strictly correct but sufficient for the purpose) that in the absorption of water the volumes of water and fibre were additive, the dry fibre density being taken as 1·32.[1] In deriving the percentage difference on stressing allowance was made for the unstressed length of hair under the clamping screws (*ca.* 2 % of the whole).

The observed weight changes in successive cycles of loading and unloading are reproduced in fig. 3, from which it is seen that the effect of tension is considerably greater than the irregular fluctuations. From these data the following mean weights for the stressed and unstressed fibre are obtained. The weight of the dry fibre was 0·1586 g. The effect

TABLE 1

	load 195 g	load 110 g
mean weight, stressed	$0{\cdot}1879_0$	$0{\cdot}1873_4$
,, ,, unstressed	$0{\cdot}1874_4$	$0{\cdot}1871_2$
difference, % of dry weight	0·28	0·14

is small, but in the direction required by the theory. A quantitative comparison with the theory is given later.

LENGTH CHANGES ON SWELLING.—*Small load.*—For the determination of length changes a 30-cm length of hair (degreased) was supported in the humidity-controlled vessel by means of an attachment to the cap C (fig. 1). The load was applied by means of a wire attached to the upper end of the hair and passing through the tube L. Length changes were obtained by observation of the movement of the wire against a fiduciary mark on L through a travelling microscope. The whole assembly could be quickly transferred from one bottle to another when it was desired to change the humidity. The relative humidities corresponding to the salt solutions used were determined, to an accuracy of about 1 %, by direct vapour pressure measurements.

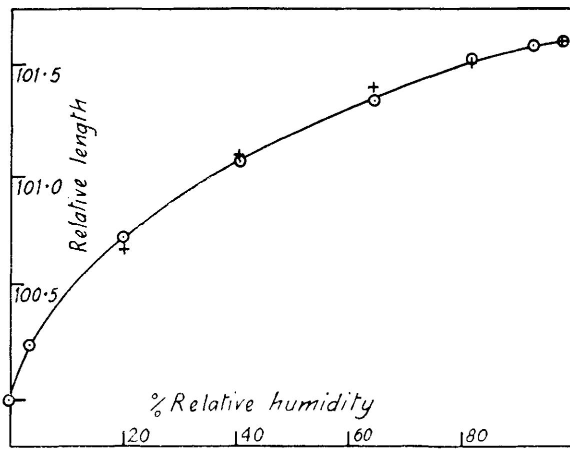

FIG. 4.—Relative length as function of relative humidity.
load 5 g, ⊙ r.h. decreasing, + r.h. increasing.

Fig. 4 shows the changes in length (referred to the dry length) over the whole range of humidity, allowing 20 h for the attainment of equilibrium or such additional time as the experiments on water content (see below) showed to be necessary at any particular value of r.h. In this experiment the load was 5 g (*ca.* 12 kg/cm^2) which was about the minimum necessary to ensure straightness of the fibre.

It is noteworthy that no hysteresis is apparent in this experiment, though on the basis of the observed hysteresis in water content (see below) such an effect would be expected (and would have been readily detectable) if the length were a function of water content only. A possible reason for this is discussed below.

In order to obtain a more representative figure for the rate of change of length at the working point (75·5 % r.h.) five further fibres were studied over a limited range of r.h., i.e. from 97·4 % to 64·1 %, with r.h. decreasing. Taking the six fibres together, the variation in $\frac{1}{l} \cdot \frac{\partial l}{\partial(p/p_0)}$ was from 0·0088 to 0·0102, with a mean of 0·0097.

HIGHER STRESSES.—In principle, eqn. (6) implies that $\mathrm{d}X$ shall be small. In practice, $\mathrm{d}X$ has to be large in order to obtain a measurable effect of stress on water content ($\mathrm{d}q/\mathrm{d}X$). It is therefore relevant to enquire whether the dependence of length on r.h. varies significantly with applied stress.

Experiments at higher stress suffer from the difficulties introduced by creep and other manifestations of imperfect elasticity, which interfere with the reversibility of the process. This is illustrated in fig. 5 which represents further data on the particular hair which had been carried through the humidity cycle shown in fig. 4. After loading with 100 g (*ca.* 270 kg/cm^2) for 3 days at the highest humidity the length corresponding to the point B_1 was reached. Drying for 7 days over magnesium perchlorate produced a contraction to the point C_1. On increasing the humidity, allowing sufficient time to reach the equilibrium water content at each point, the curve C_1DB_2 was traced, while subsequent reduction yielded B_2EC_2. Two effects are prominent: first, a continuous extension, by which B_2 and C_2 are greater than B_1 and C_1, and secondly, an *increased* length in the half-cycle corresponding to increasing humidity, giving rise to a closed loop in the opposite sense to hysteresis. This type of behaviour may perhaps account for the absence of hysteresis in the length changes under the 5-g load, the normal effect of hysteresis in water absorption being probably masked by this opposite effect, present in much smaller degree.

The effects shown in fig. 5 indicate a departure from reversible behaviour which was so great that over a certain region dl/dp was actually negative. Such departures would be expected to become smaller as the range of variation of humidity is reduced. That this is so in the present example is shown by a further experiment, in which the stressed hair was taken through several cycles over a more restricted range of relative humidity. Data thus obtained are shown in fig. 6. The filament was first taken through two cycles from 64·1 % to 81·5 % r.h. and back under a load of 5 g (A and B). The load was then increased to 90 g (*ca.* 240 kg/cm^2) for 2 days, causing extension to C_1. Successive cycles of

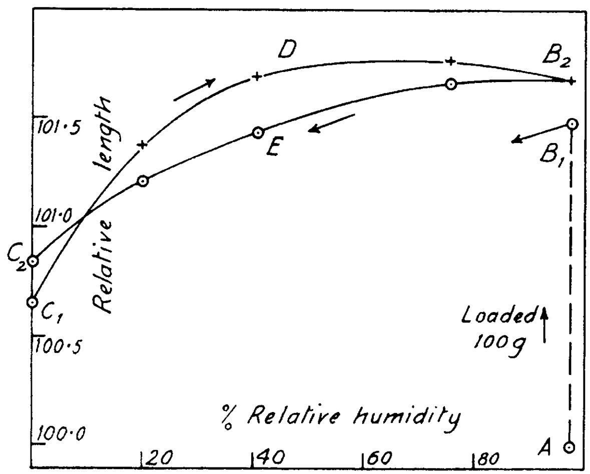

FIG. 5.—Relative length as function of relative humidity ; load 100 g.

humidity produced changes indicated by the points D_1C_2, D_2C_3, etc., suggesting an approach to an ultimately reversible condition. The mean length change over the fourth cycle was 0·56, which compares with 0·68 under the original light load. Although the evidence is not conclusive, this experiment suggests that any effect of stresses of the order of magnitude of those employed in the present work on the variation of length with relative humidity, under reversible conditions, may be left out of account.

THE VAPOUR PRESSURE ISOTHERM.—The dependence of water content on r.h. was studied on 16 lengths of hair, of total length 360 cm, suspended in the humidity vessel. To change the relative humidity the sample was transferred from one bottle to another containing the appropriate salt solution. This transference required only a few seconds' exposure, which was not enough to produce an important change in water content. At each value of r.h. the rate of approach to equilibrium was followed, and time was allowed for constancy of weight to be achieved. The time allowed was not less than 20 h at any value of r.h.; it was increased to several days at the lower humidities.

The cycle was started from 97·4 % r.h., using a sample which had been previously dried. Fig. 7 shows the curves obtained with the humidity first decreasing, then increasing, and finally decreasing again. The approximate coincidence of the first and third curves shows the hysteresis loop to be definite and reproducible. No attempt was made to obtain 100 % r.h. owing to the special difficulties involved under that condition.

In fig. 7 the data of Chamberlain and Speakman for human hair are shown for comparison. While in the lower humidity range their curve is practically identical with the author's, there is a significant difference above 90 % r.h. Whether this is due to a real difference in the material, or to some experimental defect, is not certain.

CALCULATED AND OBSERVED EFFECT OF STRESS.—In this section the experimental values of the change in water content dq, for two different values of the stress dX, given in table 1, are compared with figures derived from the theoretical equation (6), using the experimental value of 0·0097 for $\frac{1}{l}\cdot\frac{\partial l}{\partial(p/p_0)}$. The calculation refers to an r.h. of 75·5 %, at which the water content in the unstressed state was 17·8 %. The dry fibre density was taken to be 1·32, and the specific volume in the swollen (stressed) state, assuming additivity of volume, was 0·795. Other data required are v, the specific volume of water

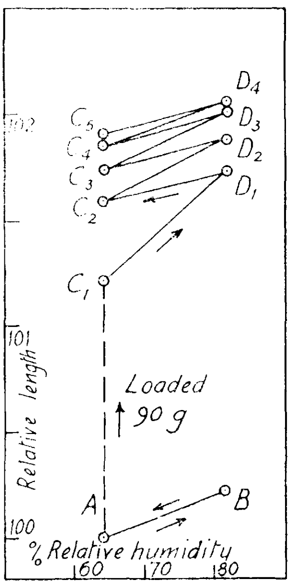

FIG. 6.—Length changes over limited cycle of humidity.

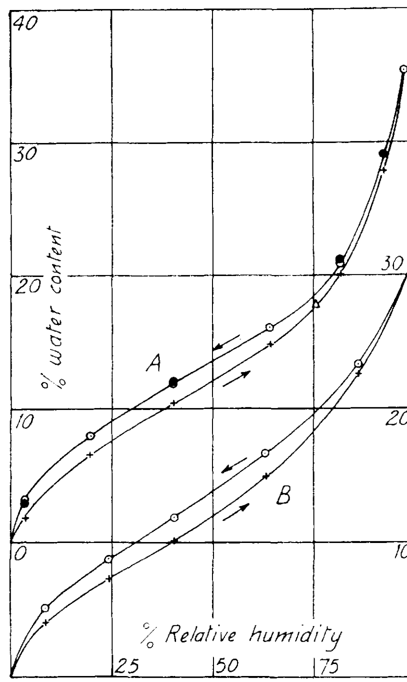

FIG. 7.—Water content against relative humidity. A, author; ⊙ r.h. decreasing, 1st run, + r.h. increasing; ● r.h. decreasing, 2nd run; Δ point from stressing experiment. B, Chamberlain and Speakman.

vapour at 75·5 % r.h., 25·0° C, which is 5·80 × 10⁴ cm³/g, and p_0, the saturation vapour pressure of water, namely 0·0323 kg/cm². The figures obtained are given in table 2.

TABLE 2

load per hair (g)	stress (kg/cm²)	dq (% on dry weight) calc.	obs.
195	482	0·24	0·28
110	263	0·13	0·14

The agreement is satisfactory, and in fact rather better than would be expected, in view of the experimental error, estimated at ± 25 %.

In addition to the result reported here several other experiments were performed, and in all cases the water content increased on the application of the stress. One such preliminary experiment has already been published.[5] It is considered that the present result is the more accurate, on account of minor improvements in details of technique developed during the course of the work.

MEASUREMENT OF DIMENSIONAL CHANGES.—While the primary object of the present work was the determination of changes in water content on stressing, for which purpose the direct weighing method is completely unambiguous, the question of the accompanying volume change is of some importance. A subsidiary experiment was therefore carried out in which the effect of tension on the longitudinal and lateral dimensions of horsehair was determined.

The fibre was mounted in a small chamber maintained at 25·0° C and 75·5 % relative humidity. The stress could be applied by means of a spring without removing the hair from the chamber. The length between fixed marks was measured by means of a cathetometer, and the diameter was obtained by projecting an image of the fibre on to a ground-glass screen, under a magnification of 550. The fibre could be rotated to permit of measurements of two mutually perpendicular diameters; this was necessary on account of the

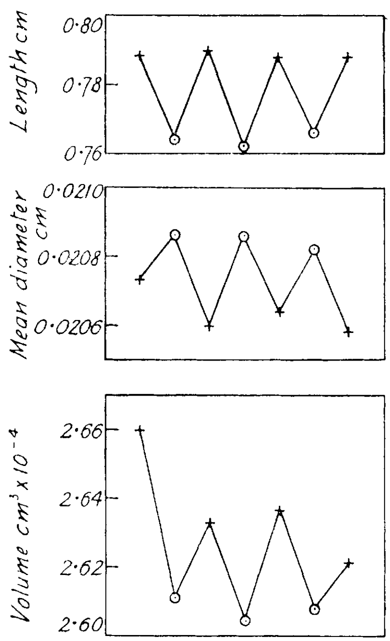

FIG. 8.—Dimensional changes on repeated stressing:
○ unstressed, + stressed, 517 kg/cm².

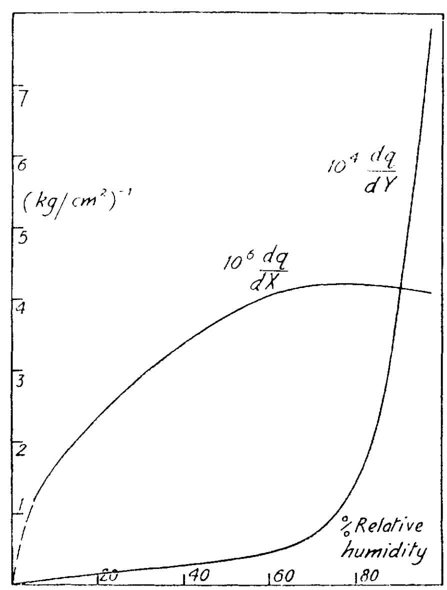

FIG. 9.—Calculated dependence of water content q on longitudinal stress X and transverse stress Y.

slight ellipticity of the cross-section. The diameter was always measured at a particular point on the fibre. The image could be measured to 0·5 mm, correspondinng to an accuracy of about 0·5 % in a single measurement of diameter.

A typical result is reproduced in fig. 8, which represents the changes in length, mean diameter and volume on successive loading and unloading, time being allowed after each such change for the attainment of equilibrium. With a stress of 517 kg/cm² the mean increase in length, over three cycles, was 3·2 %, and the corresponding decrease in diameter 1·0 %, giving an increase of volume on stressing of 1·2 %.

From the foregoing theory and assuming additivity of volumes, the calculated volume increase due to the additional water uptake under the action of the stress would be 0·32 %. In addition to this effect there is a direct effect of the stress on the volume, which is independent of any change in water content. Its magnitude, derived from the classical theory of elasticity (for an isotropic material) is

$$\frac{\Delta V}{V} = \tfrac{1}{3}K\Delta X, \tag{7}$$

where K is the compressibility coefficient. The appropriate value of K is not known, but in order to obtain an upper limit to the numerical magnitude involved we may not be far wrong in adopting a value of $5{\cdot}0 \times 10^{-11}$ cm^3/dyne, which compares with that for water ($4{\cdot}9 \times 10^{-11}$) or rubber ($5{\cdot}3 \times 10^{-11}$). From eqn. (7) this gives $\Delta V/V = 0{\cdot}85$ %, compared with the observed figure of $1{\cdot}2 - 0{\cdot}32$ %, or $0{\cdot}9$ % approximately. These figures are necessarily rather uncertain, and though not sufficient in themselves to establish an increase of water content on stressing, they are consistent with such an interpretation.

DISCUSSION

COMPARISON WITH EARLIER WORK.—The conclusion to be drawn from the experiments described above is that the changes in the water content of horsehair with stress are satisfactorily described by the general thermodynamic theory. It may be emphasized that this theory is applicable only when the condition of reversibility is satisfied. Thus, from the reversible increase of water content on applying tension established in the case of hair, it should not be presumed that in another fibre, under other conditions, irreversible effects leading to either an increase or a decrease in water content with applied stress may not take place. Such considerations may be relevant in assessing the significance of the apparently conflicting work of White and Stam already referred to. These authors worked round a cycle of humidity at each value of stress—a condition which may be less suitable for the purpose of establishing a reversible dependence of water content on stress than repeatedly traversing a cycle of stress at constant humidity, as was done in the present experiments.

$\mathrm{d}q/\mathrm{d}X$ *at other values of r.h.*—In fig. 9 the theoretical dependence of water content on tension, $\mathrm{d}q/\mathrm{d}X$, is shown as a function of relative humidity, up to 97·4 % r.h. This figure is based on the longitudinal swelling data of fig. 4 (which differs somewhat at 75·5 % r.h. from the mean for 6 hairs used in deriving the values given in table 2).

EFFECT OF LATERAL STRESS.—In the particular case of hair subjected to tensile stress the changes in water content are always small. This is because of the anisotropic swelling of the fibre, whereby the relative changes in the longitudinal dimension are only a tenth to a hundredth of the changes in lateral dimensions. It may be of interest to compare the effect of lateral compressive stresses on the water absorption. Let us consider a fibre having a rectangular cross-section of dimensions y and z. Let the length of the fibre be parallel to the x-axis, and the lateral surfaces normal to the y- and z-axes respectively. If the compressive stress Y acts on the pair of faces normal to the y-axis, while no stress acts on the remaining faces, the quantity $\mathrm{d}q/\mathrm{d}Y$ may be calculated from an equation of the form (6), in which y is substituted for l. Approximate values of $\dfrac{\partial y}{\partial(p/p_0)}$ may be computed from the known length changes, assuming additivity of volumes on absorption of water. Values thus obtained are shown in fig. 9, from which it is seen that $\mathrm{d}q/\mathrm{d}Y$ varies from about 6 times to about 200 times the corresponding $\mathrm{d}q/\mathrm{d}X$. The different shape of this curve from the $\mathrm{d}q/\mathrm{d}X$ curve reflects the increasing anisotropy of swelling with increase in r.h.

If, instead of the single stress Y, equal stresses were applied on both pairs of lateral surfaces (corresponding to a pressure all round a circular fibre), the change in water content would be doubled (eqn. (2)). Under these conditions a lateral stress (all round) of, for example, 100 kg/cm^2 would give a change in water content, at 93 % r.h., of 10 %, out of a total water content of 28 %.

Effects of this kind might well be of practical importance. For example, in yarn or cord, the effect of tension, together with twist, is to produce a lateral compression on the fibres. Under such conditions an overall tension may produce a *reduction* of water content, owing to the much higher sensitivity of the water content to lateral than to longitudinal stresses. The present analysis suggests that it might be possible to obtain information about the lateral compressive stress between fibres from a study of their water absorption.

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