WATER EFFECTS ON YOUNG'S MODULUS OF H-BONDED SOLIDS

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Synopsis   Paper is treated as a member of the class of hydrogen-bond dominated solids for which the author derived a set of equations connecting E to the effective number of H-bonds per cm^3, N, and to the parameters of this bond. In this paper it is shown that the effect of water on such solids is to reduce E in one of two modes or regimes. In regime (1), a unimolecular reaction leads to a simple breakdown of H-bonds on addition of water. In regime (2), which begins when the regain exceeds a critical value equal to the B.E.T. monomolecular layer, the reaction is still unimolecular in N, but is complicated by a co-operative breakdown phenomenon as envisaged by Frank and Wen's 'flickering clusters' concept. Equations derived using these concepts and a co-operative index, C.I., based on Starkweather's thermodynamic calculations, are checked against all data available to the author on paper, other cellulosics, Nylon 66 and wool with satisfactory results.

1—Introduction

IN a paper given to the American Chemical Society in September 1954, ideas were formulated connecting Young's modulus, E, of paper, regenerated cellulose and other solids, in which the hydrogen bond is predominant, and hence controls E, to the density of hydrogen bonds per unit volume of the solid, N, and the properties of this bond. These tentative ideas were further developed and published in 1957,[1] but with the added concept that the well-known phenomenon of a loss in E as these solids adsorbed water was quantitatively related to the loss in N as water disrupted hydrogen bonds connecting cellulosic chains together. A very simple formula was derived for cellulose $\ln (E_w/E_0) = -w$, where E_w is the modulus of the cellulosic sheet or fibre at regain w, gms. H$_2$O/g dry solid, and E is the modulus at $w = 0$. Although it was very gratifying when later in 1965 Craver and Taylor[2] showed that this equation applied to E_w for paper up to near saturation when E was measured dynamically by a sonic method, both the data available in 1957 and later results indicated that, generally, the equation only applied up to a value of w

equal to approximately $\frac{1}{6}$ of the saturation regain. Above $w \simeq \frac{1}{6}(w_{sat.})$, a new phenomenon appeared wherein more than one hydrogen bond seemed to break on the addition of one molecule of water to cellulosic sheets or fibres. The number of bonds breaking co-operatively was empirically determined from the data and found to vary with w, reaching high values up to 12 in some instances, before subsiding again. This co-operative phenomenon was called 'an autocatalytic reaction', or 'a wedge effect'. A function ϕ was extracted from the data so that a 'co-operative index' equal to $(1 + \phi)$ was published as an empirical parameter, depending on w, but no explanation of the mechanism beyond the designation was offered. The co-operative index so determined equalled the number of hydrogen bonds which seemed to break down co-operatively on the addition of a molecule of water to the cellulosic network of hydrogen bonds.

About the same time, Zimm[3] in 1953 and Frank and Wen[4] in 1957, were laying down the foundations of two apparently unrelated theories. Zimm proposed a thermodynamic derivation of a cluster integral which indicated the propensy of a solute molecule either to aggregate near other solute molecule(s) or to be repelled by them in a solution[3] or when sorbed by a polymer.[5] These studies culminated in a study by Starkweather[6] in 1975, in which the number of H_2O molecules per cluster is extracted from adsorption and desorption isotherms of water onto cellulose or other polymers. In parallel with these developments, Frank and Wen[4] developed their 'flickering cluster' concepts of hydrogen-bonded systems which led to a series of extensive studies by Némethy and Scheraga[7] on the building up of hydrogen-bonded molecules into clusters and their dissolution into monomeric species, in water, in solutions, and in protein systems. For example, at room temperature they found the average number of H_2O per cluster to be 57.

It has now become possible to combine the concepts of Frank and Wen, of Zimm, and of Zimm and Lundberg—the latter in the form of Starkweather's number of H_2O/cluster—with the hydrogen bond theory of the mechanical properties of hydrogen-bonded sheets in a direct manner, using no adjustable parameters, to yield a simple formulation of the dependence of E on w throughout the range of w from zero to saturation.

It will be useful for the derivation of this relationship between E and w to give a brief summary—highlighting only those concepts to be used later in the derivation—of the following empirical and theoretical background knowledge:

(*1*) Adsorption of water as illustrated by cellulose.
(2) Frank and Wen's 'flickering clusters' concepts.

(3) Zimm–Lundberg–Starkweather clusters of H_2O on cellulose and other similar solids—e.g., Nylon 66.

(4) Dependence of E on N, the number of effective hydrogen bonds per unit volume of cellulosic sheets or fibres.

These will be combined to yield

(5) The co-operative breakdown of hydrogen bonds on adsorption of water resulting in lowering of E.

2—Background summaries

2.1—Adsorption of water on cellulose

THIS is a complicated subject. An excellent summary exists in Stamm's 'Wood and Cellulose Science'.[8] For the present purposes, the following are the principal findings to be noted:

(1) When never-dried cellulose is first desiccated to zero regain, it follows an irreversible curve of w vs p/p_0, the ratio of the partial to saturation pressure of water in its atmosphere.

(2) Subsequent sorption and desorption curves are reproducible but there is hysteresis between the two curves. The ratio of w for the adsorption curve to w for the desorption curve at a given p/p_0 is very nearly constant for the whole range of w. For example, this ratio is 0.86 ± 0.02 for 23 different wood pulps. Thus, one curve is easily calculable from the other with reasonable accuracy. (Nylon, on the other hand, has no hysteresis.)

(3) The sorption of N_2 on cellulose even below $-195.7°$ C (the liquefaction temperature of N_2) is about 1 per cent of the sorption of water at equal relative vapour pressure. It is concluded that water opens up new surfaces by breaking hydrogen bonds on being adsorbed on cellulose. These surfaces disappear on desorption. Thus, for the purposes of studying hydrogen bond breaking by adsorption of water, the adsorption curve is of primary import; not the desorption curve.

(4) BET analysis shows that the adsorption of water on cellulose is of type II—i.e. *as if* a monomolecular layer is formed at some value of w, equal to w_m, then this is followed by polymolecular layer adsorption. The number of layers is between 6 and 8 at the fibre saturation value. w_m for cotton cellulose is approximately 0.03, for holocellulose pulp 0.06, sulphite pulp approximately 0.04, for lignin 0.05, for rayon and other regenerated cellulose approximately 0.06 and for wood 0.04–0.05, all in grams H_2O/g cellulose. Thus, for paper, $w_m = 0.04$ to 0.06 probably covers the range although 0.07 has been reported on occasion. The fibre saturation value of w is variously reported between 0.25 and 0.33 gms H_2O/g cellulose. It is very difficult to obtain this parameter

experimentally as sorption by capillary condensation follows adsorption without a break.

(5) Even though w_m, the regain when a monolayer appears to be complete, is a mathematical construct, yet cellulose behaves as if this value for the regain is physically significant in adsorption phenomena. However, in cellulose it appears that condensation in the second layer probably begins long before the first layer is complete, since the sorption curves are smooth and not stepped.

2.2—*Frank and Wen's 'Flickering Clusters'*[4]

These ideas were based on the nature of the hydrogen bond itself. Frank and Wen's ideas are probably best understood by a direct quotation of their clear statement: '. . . hydrogen bond formation is an acid-base interaction, and that when the bond is formed molecule *a* becomes more acidic and *b* more basic than an unbonded water molecule. This, in turn, has the consequence that the *a–b* bond will be strengthened if *a* can also bond (acidically) with another molecule *c* and/or *b* (basically) with *d*, and that the existence of the *a–b* bond will promote the tendency of *c–a* and *b–d* bonds to form.' It will be found that the following statement by Frank and Wen will be directly used in the derivation of the relationship between *E* and *w*. Hence a portion of it is emphasised:

> 'We, therefore, postulate that the formation of hydrogen bonds in water is predominantly *a co-operative phenomenon, so that, in most cases, when one bond forms several (perhaps "many") will form, and when one bond breaks, then, typically, a whole cluster will "dissolve"*. This gives a picture of flickering clusters, of various sizes and shapes, jumping to attention, so to speak, and then relaxing "at ease".' (Italics mine.)

In the present paper, it will be postulated that hydrogen bonds in cellulose and other hydrogen bond dominated solids (e.g., Nylons)—as in water—break co-operatively when water is added.

2.3—*Zimm–Lundberg–Starkweather's clusters of H_2O on polymers*

Zimm[3] postulated a cluster integral G_{11} for a molecule 1 in a mixture of molecules of types 1 and 2. In an incompressible system in which the fugacity is proportional to the volume fraction, G_{11} turns out to be equal to $-v_1$, the partial molecular volume of type 1. This means that the molecule excludes its own volume to other molecules of its own type, but otherwise the distribution of type 1 molecules is not affected. Ideal solutions give, therefore, $G_{11}/v_1 = -1$. Later, Zimm and Lundberg[5] showed that for certain polymer systems $G_{11}/v_1 > -1$ and may even become positive. This means that the concentration of molecule 1 in the neighbourhood of a given type 1 molecule

is greater than the average for the whole system. In other words, when $G_{11}/v_1 > -1$ molecules of type 1 tend to cluster around each other in groups rather than be distributed randomly throughout the type 1/type 2 system. Physically, the picture is of the first molecule opening up the structure of the polymer so that it is easier, and hence, more probable, for a second molecule of its type to land in the neighbourhood of the first molecule than elsewhere where the structure is still closed tight. 'A string of molecules might occupy one wedge-shaped cavity, for example.'[5]

Starkweather, first in 1963[9] and later in 1975,[6] applied these ideas to water/polymer interactions. He uses $c_1 G_{11}$ for the cluster function where c_1 is the molar concentration of molecules of type 1. Then $(c_1 G_{11} + 1)$ is a measure of the mean number of H_2O molecules/cluster.

Starkweather used the data of Morrison and Dzieciuch[10] on adsorption and desorption of water on cotton cellulose to calculate the number of H_2O/cluster for the two curves.

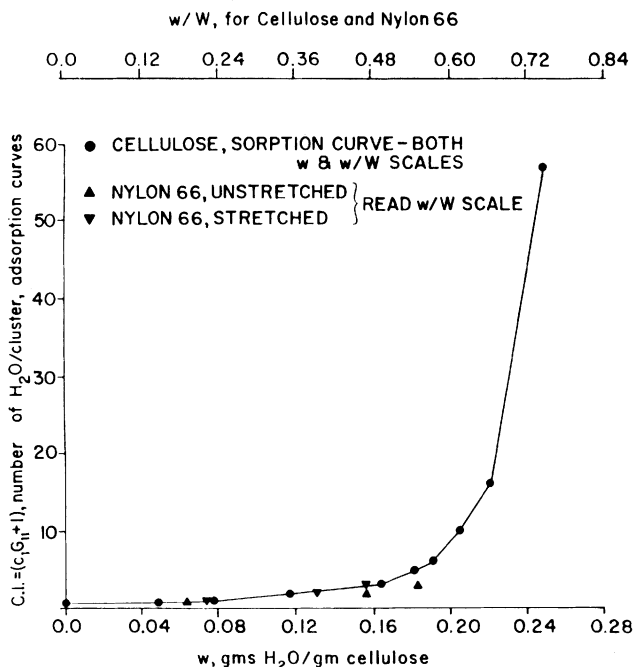

Fig. 1—C.I., the Co-operative Index as calculated by Starkweather[6] for cellulose and Némethy and Scheraga[7] for liquid water (saturation), for the sorption curve of water on cotton cellulose *vs. w* and *w/W* for both cellulose and Nylon 66

On the hypothesis that the adsorption curve is the significant curve for the present study, values for the co-operative index, C.I. ($=c_1 G_{11} + 1$), i.e. the number of H_2O/cluster, were taken from Starkweather's Fig. 6 (with some others, for intermediate values of w, further determined by his method of calculating slopes) up to $w = 0.221$, the highest regain given in Starkweather's paper, on the adsorption curve and plotted on Fig. 1. It is very difficult to get values for C.I. for $w > 0.221$ in Starkweather's Fig. 6. He states that at higher values of w, the data indicate 'indefinitely large clusters'. Yet there is a need for a value at saturation to complete the curve. Saturation was reported as 0.25 g H_2O/g cellulose.[10] Reasoning that at saturation water on adsorption behaves very much as if it were condensing on liquid water— c.f., studies, on enthalpies, entropies and free energies of condensation onto cellulose[10]—I adopted Némethy and Scherega's[7] value of 57 H_2O/cluster as an upper bound to apply at room temperature. It fits Starkweather's curve reasonably well. (The use of w/W on the top scale will be explained later.)

In this study, we need an average value for C.I. between $w = 0$ and saturation. From Fig. 1, an average $\overline{(C.I.)} = \overline{(c_1 G_{11} + 1)}$ was calculated for cellulose by graphical integration of the curve and dividing by 0.25. This gave $\overline{(C.I.)} = 6.71$.

The value of $\overline{(C.I.)} = 6.71$ will be used directly in deriving the equations connecting E with w for cellulosics.

2.4—The dependence of E on N, the effective hydrogen bond density per unit volume

The concepts involved here are extremely simple.[1, 11] They relate to randomly distributed microcrystals with disordered regions in between, to give sheets of hydrogen bond dominated papers, regenerated cellulose or similar polymers. (They do not apply to highly oriented materials like cotton, where the covalent bonds of the cellulose chain are significant contributors to E.) Then if the total effective number of hydrogen bonds, N_T bonds/cm^3, uniformly distributed in all directions, are subjected to uniaxial stress, they are equivalent at small stresses and strains to $N = (N_T/3)$ hydrogen bonds all oriented parallel to the stress vector. It is then shown that $E = kN^{1/3}$. The constant k ($\simeq 8 \times 10^3$ dyne/cm for cellulose) is derivable from thermodynamic parameters of the hydrogen bond, but its exact value is not important for the present studies. It will be assumed to be a known constant.

Fig. 2 illustrates the fact that N is proportional to E^3, even though its purpose in this study transcends this simple fact. In Fig. 2 are plotted three different types of results, but all performed in the same laboratory under
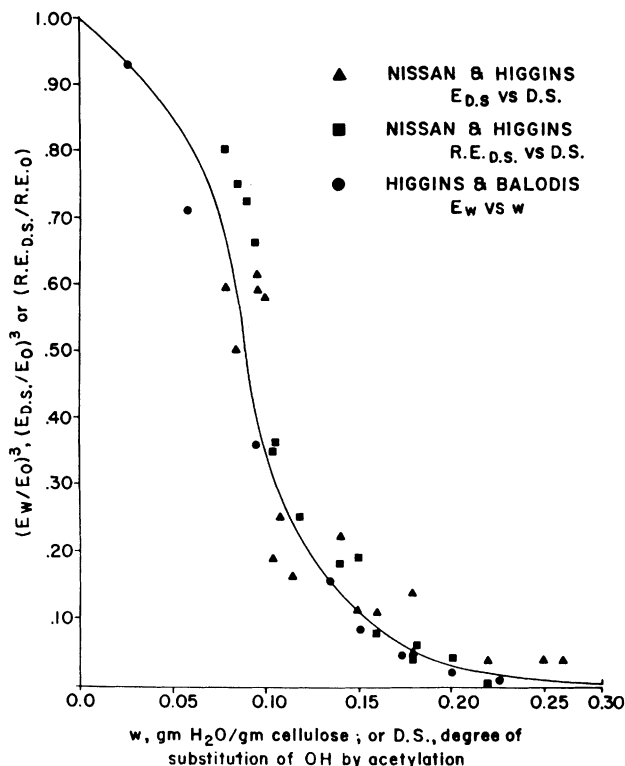
Fig. 2—The dependence of E^3 on w and on D.S. and of R.E.
on D.S.

similar conditions and by similar procedures. The first set of points are those reported by Nissan and Higgins[12] referring to $E_{D.S.}^3$ and R.E.$_{D.S.}$ *vs* D.S. In these experiments, a pulp sample was beaten and then different portions of it were acetylated to different degrees of substitution, D.S. Sheets were made and two quantities were measured, the modulus $E_{D.S.}$ at the particular D.S. and also the 'rupture energy' R.E.$_{D.S.}$, or the area under the stress strain curve up to rupture. If the total energy to rupture consists of N bonds, each storing, on average, one packet of energy, R.E., then the fact that $E_{D.S.}^3$—rather than $E_{D.S.}$ itself—falls on the same curve as R.E.$_{D.S.}$ for a given D.S. implies that E^3 is a measure of N to the same extent and in the same manner as R.E.$_{D.S.}$ is a measure of N, i.e. $(E_{D.S.}/E_0)^3 = (E.R._{D.S.}/R.E._0) = (N_{D.S.}/N_0)$.

The third set of points, by Higgins and Balodis,[14] shows E_w^3 (the cube of the modulus at regain w *vs* w as determined on regular unsubstituted

paper in the same laboratory run by Dr Higgins) falls on the same curve when converted to $(E_w/E_0)^3$. This fact is of crucial significance to our studies, but its interpretation will be discussed later in deriving our theory connecting E_w with w.

3—The dependence of E on w

In the theory being advanced here, two regimes of bond breaking *via* water adsorption are postulated: regime (1) and regime (2) designated by suffix (1) and suffix (2) respectively in the appropriate equations.

It is necessary to clarify the phrase 'bond breaking' in the context of the present study. Infrared absorption by cellulose, throughout the range $0 < w <$ saturation, shows no free hydroxyls; i.e. no 'broken' hydrogen bonds. All hydrogen bonds are 'made' both when cellulose is bone-dry and when it is saturated with water and in all stages in between.

Consider a bond between the primary OH of a glucose unit of one chain and the ring oxygen of another chain, i.e.,

$$\left[-C\,H_2OH - - - O\diagup \diagdown \right], \quad . \quad . \quad . \quad . \quad . \quad \text{(I)}$$
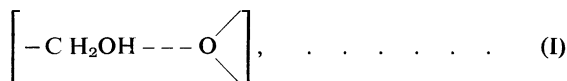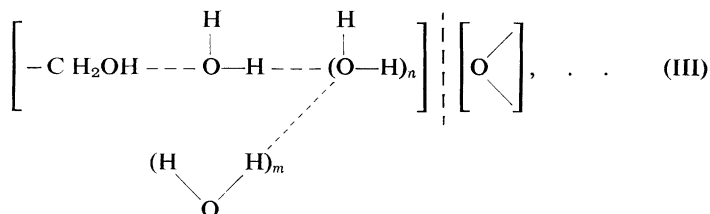
This bond, if in the disordered or paracrystalline portion of the cellulosic network and 'accessible', will contribute to the resistance offered by the network to a tensile stress and will, therefore, be counted in N. If a water molecule intervenes and gives

$$\left[-C\,H_2OH - - - O\diagup^{H}\diagdown_{H} \right]\left[O\diagup \diagdown \right], \quad . \quad . \quad . \quad \text{(II)}$$
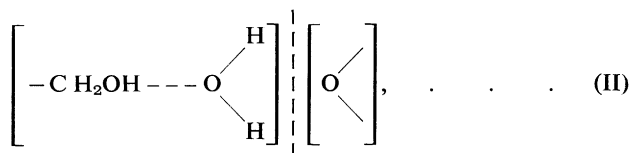
the bond is clearly 'broken' since the ring oxygen of the second chain, as well as the sixth carbon on the first chain now have enhanced degrees of freedom to move away from each other without constraints.* Furthermore, we can see that one water molecule 'broke' one hydrogen bond; I will say of this reaction that it is 'unimolecular'. Similarly, if this water molecule was itself the site for adsorption of further water, we still have a broken hydrogen bond insofar as the cellulose is concerned in exhibiting a resistance to stress

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* The fact that I.R. absorption still shows no free OH is explainable by postulating the H_2O molecule forms hydrogen bonds between its hydrogens and oxygens on the same chain which contains the $-C_6H_2OH$.

contributing to E, i.e.,

$$\left[-C\,H_2OH \,\text{---}\, \overset{\overset{\displaystyle H}{|}}{O}\text{---}H \,\text{---}\, (\overset{\overset{\displaystyle H}{|}}{O}\text{---}H)_n \right]\left[O\!\!\diagdown \right], \quad . \quad . \quad \text{(III)}$$

$$(H\diagdown_{\diagup}H)_m$$
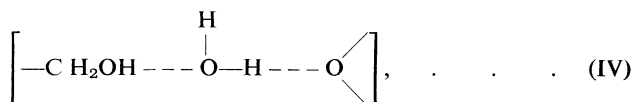$$O$$

The first H_2O molecule would have broken the bond by a unimolecular reaction; the second, third, etc., would contribute nothing to bond-breaking. In our regime (1), we envisage events of these types taking place leading to structures (II) or (III). Symbolically, at least a portion of the water adsorbed yields a reaction:

$$\left[-C\,H_2OH \,\text{---}\, O\!\!\diagdown \right] + [H_2O] \longrightarrow \left[-C\,H_2OH \,\text{---}\, \overset{\overset{\displaystyle H}{|}}{O}\text{---}H \right] + \left[O\!\!\diagdown \right]$$
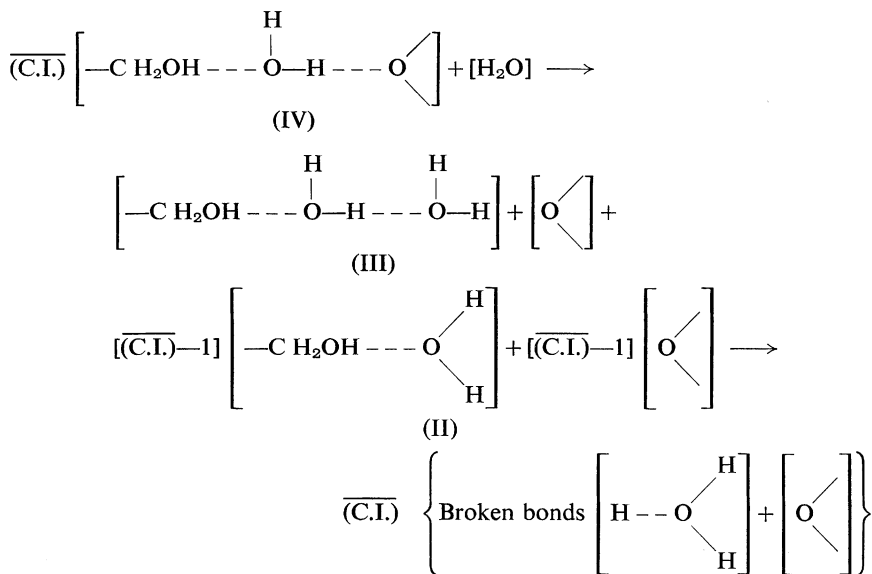$$\text{(I)} \qquad\qquad\qquad\qquad\qquad\qquad \text{(II)}$$
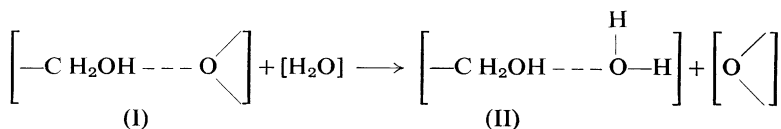
Another portion leading to structure III would result in no bond breaking.

Now consider an alternative situation. Consider that the water molecule acts as a bridge between the primary OH on the sixth carbon of one chain and the ring oxygen of a neighbouring chain, i.e.,

$$\left[-C\,H_2OH \,\text{---}\, \overset{\overset{\displaystyle H}{|}}{O}\text{---}H \,\text{---}\, O\!\!\diagdown \right], \quad . \quad\quad . \quad\quad . \quad \text{(IV)}$$

In this situation, the resistance to stress exhibited by the cellulose is either unimpaired or only slightly impaired since the volume expansion, tending to reduce N, is counteracted by the added new hydrogen bonds. Thus, the effect of adsorbing H_2O in this mode results in no bond breaking and is the same as if the water molecule had settled on another molecule as in structure (III)— i.e., (IV) is equivalent to (III) and could be an alternative mechanism to that provided by (III) for the non-bond breaking adsorption of H_2O. Now, further consider other H_2O molecules being adsorbed by the cellulose network. In regime (1) we envisage a fraction of these new arrivals equal to (N/N_0) will break bonds by the mechanism yielding structure (II) and a fraction $(N_0 - N)/N_0$ yielding structure (III). Then, of Δw adsorbed, $(N/N_0)\Delta w$ will be effective in breaking bonds in a 'unimolecular' mode; the rest, $(1 - N/N_0)\Delta w$, will be ineffective in breaking bonds but will be stored in structures like (III) or its equivalent (IV).
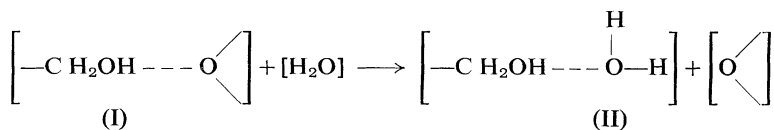
Next, consider a network of structure (IV) type of hydrogen bonds side by side. Although they are on different glucose units, electronically they are continuously in contact with each other and, therefore, subject to Frank and Wen's dictum, 'when one bond breaks, then, typically, a whole cluster will "dissolve".' To one member of this group of co-operative hydrogen bonds in structure (IV), let another H_2O be added changing that particular member from structure (IV) to structure (II)—i.e., 'breaking' that particular bond 'unimolecularly'. Frank and Wen's theory then predicts that the other members of the network will also break into structure (II). Thus, a number of bonds would break co-operatively. This number, like Starkweather's number of H_2O/cluster, will vary but will have an average number, $\overline{(C.I.)}$, i.e.,

$$\overline{(C.I.)}\left[-CH_2OH ---\overset{\overset{\displaystyle H}{\displaystyle |}}{O}-H---O\diagdown\right] + [H_2O] \longrightarrow$$

$$(IV)$$

$$\left[-CH_2OH---\overset{\overset{\displaystyle H}{\displaystyle |}}{O}-H---\overset{\overset{\displaystyle H}{\displaystyle |}}{O}-H\right] + \left[O\diagup_{\diagdown}\right] +$$

$$(III)$$

$$[\overline{(C.I.)}-1]\left[-CH_2OH---O\diagup^{\diagup H}_{\diagdown H}\right] + [\overline{(C.I.)}-1]\left[O\diagup_{\diagdown}\right] \longrightarrow$$

$$(II)$$

$$\overline{(C.I.)}\left\{Broken\ bonds\left[H--O\diagup^{\diagup H}_{\diagdown H}\right] + \left[O\diagup_{\diagdown}\right]\right\}$$

Thus, we see in this type of bond breaking one H_2O results in $\overline{(C.I.)}$ bonds breaking simultaneously, even though it actually participates, initially and in its own right, in breaking only one bond. Here of Δw, the fraction $(N/N_0)\Delta w$ will still be the triggering agency for breaking bonds, but the effect is the same *as if* there were $\overline{(C.I.)}$ times that number of bond breaking agents. This regime of multiple bond breaking I call regime (2).

There is another mechanism for regime (2). When one H_2O molecule alights on one OH group of a row as in structure (I)—i.e. all still forming H-bonds, it can break it by changing it from structure I to structure II by the

unimolecular reaction of regime (1) already discussed, i.e.

$$\left[-C\ H_2OH\ ---\ O\diagdown\diagup\right] + [H_2O] \longrightarrow \left[-C\ H_2OH\ ---\ \overset{\overset{\textstyle H}{|}}{O}-H\right] + \left[O\diagdown\diagup\right]$$

$$\qquad\qquad\text{(I)}\qquad\qquad\qquad\qquad\qquad\qquad\qquad\text{(II)}$$

Both in regime (1) and in regime (2), this reaction immediately triggers off further spontaneous H-bond breaking in the immediate vicinity of the first OH – – – O broken, but with a significant difference between the two regimes. In regime (1) there is a paucity of H_2O molecules as $w < w_c$, a critical moisture content of the order of w_m. But when w exceeds this particular w_c, the water molecules available provide three further sites for H-bonds. (In water and in ice, the

provides two sites and the two H's further two sites, i.e. each H_2O takes part in four H-bonds, each, of course, of half the strength of a bond.) Thus, in regime (1), those OH groups which have been triggered to break have little opportunity to remain broken and quickly are 're-made'. In regime (2), they latch onto adjoining oxygens of H_2O molecules and, because of the greater flexibility of the molecule, onto each other intramolecularly, and thus remain broken insofar as cellulose-cellulose bonding is concerned. The total number —i.e. the initial one broken by H_2O and the others triggered off by Frank and Wen's mechanism—will vary, but will average to a number, the co-operative index C.I. The average C.I. for the whole range of $w_c \leqslant w \leqslant w_{sat.}$ will be called $\overline{\text{(C.I.)}}$.

It seems reasonable then, that regime (2) will not be initiated until a critical amount of water has been adsorbed, say, w_c. Thus, w_c will constitute the transition parameter for change from regime (1) to regime (2). I postulate in this theory that $(w_c/w_m) = 1$, although I am prepared to find and accept another critical number. As will be shown in the 'Discussion', an empirical determination of (w_c/w_m) from the data so far available to me on E vs w yields (w_c/w_m) of order (1). As was indicated in a previous section, this is not the first time that B.E.T. mathematical construct, w_m, appears to be physically significant in adsorption phenomena.

With this explanation of the term 'bond breaking', let us derive our basic equations for regimes (1) and (2). Tentatively, we shall assume that regime (1) ends and regime (2) begins at $w = w_c$, i.e. for regime (1), $0.0 < w/w_c \leqslant 1.0$ and for regime (2), $1.0 \leqslant w/w_c < w_{sat.}/w_m$.

3.1—*Regime (1)*

We define two quantities: N_0 and W. N_0 is the number of effective hydrogen bonds per unit volume at $w = 0$. W is the quantity of water required to provide one molecule each for every OH on the cellulose molecule. This quantity is six molecules of water of molecular weight 18 per cellobiose unit of molecular weight 324, i.e.

$$W = \frac{6 \times 18}{324} = \frac{1}{3}$$

Let the number of effective hydrogen bonds per cm^3 of the cellulosic sheet be N at regain w. We normalise our quantities by dividing N by N_0 and w by W, so that (N/N_0) moves from 1 to 0 as (w/W) changes from 0 to 1. A fraction $d(w/W)$ of new water molecules approaching the cellulose in regime (1) will find a fraction of bonds (N/N_0) still intact and available for breaking and a fraction $(1 - N/N_0)_1 \simeq w/W$ already covered with water molecules. To a first approximation, then:

$$d(N/N_0)_1 = -(N/N_0)_1 \, d(w/W) \qquad . \qquad . \qquad . \qquad (1)$$

or $\ln (N/N_0)_1 = -w/W + A.$

But since $\ln (N/N_0)_1 = 0$ at $w/W = 0$ $\therefore A = 0$ and

$$\ln (N/N_0)_1 = -w/W. \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

But $N = (E/k)^3, \qquad . \qquad . \qquad . \qquad . \qquad (3)$

$$3 \ln (E/E_0)_1 = -w/W. \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

Since, for cellulose, $W = \frac{1}{3}$,

$$\ln (E/E_0)_1 = -w \qquad . \qquad . \qquad . \qquad . \qquad (5)$$

or, in regime (1),

$$E_1 = E_0 \exp (-w). \qquad . \qquad . \qquad . \qquad (6)$$

This simple expression applies only to cellulose where $W = \frac{1}{3}$; for other polymers, equation (4) has to be used—e.g., for Nylon 66, $W = 0.1593$. In terms of (w/w_c), we have

$$\ln (N/N_0)_1 = -w/W \qquad - \qquad - \qquad - \qquad - \qquad (7)$$
$$= -(w_c/W)(w/w_c).$$

We shall use equation (7) as an initial condition for regime (2).

3.2—*Regime (2)*

When $w \geqslant w_c$, we invoke Frank and Wen's principle for co-operative bond breaking. The total number broken by the adsorption of one further H_2O molecule is the co-operative index C.I. We need a number for the average C.I. for the whole range $w_c \leqslant w < w_{sat.}$, i.e. for $(\overline{C.I.})$.

Starkweather's number of H_2O/cluster could mean one of several situations: (a) a number equal to C.I. molecules of water clustered around and anchored to one OH group of cellulose in a 'piggy-back' fashion; (b) a number of OH groups equal to C.I., each attached to a water molecule, act co-operatively in adsorbing water from, or releasing water to, the atmosphere; (c) any one of many intermediate forms between (a) and (b).

As has been mentioned already and shown in Fig. 2, the study by Nissan and Higgins,[12] the OH groups of cellulose pulp were blocked by acetylation. Papers made from these pulps showed Young's modulii which decreased as the degree of substitution, D.S., increased. The important point to note here is that a plot of $(E_{D.S.}/E_0)_3$—or $(N_{D.S.}/N_0)$—vs D.S. for these papers falls directly on a plot of (E_w/E_0)—or (N_w/N_0)—vs w for another, normal and unsubstituted paper reported from the same laboratory.[14] In other words, the OH groups blocked by acetylation behave the same way as those broken, or blocked, by H_2O in regime (2). Hence, I am persuaded that option (b)—i.e. a number of OH groups behave co-operatively to the extent of C.I. Thus, I *assume* that Starkweather's 'number of H_2O /cluster' also measures the 'number of OH groups/cluster' breaking up co-operatively. I take $\overline{(C.I.)}$, the average number under the curve of Fig. 1 taken from Fig. 6 of Starkweather's paper[6] and supplemented by Némethy and Scheraga's[7] value for liquid water—57 H_2O/cluster—at room temperature for $w = w_{sat}$) $= 0.25$ g/g cellulose, to be equal to $\overline{(C.I.)}$ for regime (2). Hence, for $w_c < w \leqslant w_{sat.}$:

$$d(N/N_0)_2 = -\overline{(C.I.)}(N/N_0)_2\, d(w/W) \qquad . \qquad . \qquad . \qquad (8)^*$$

with initial condition that, at $w = w_c$, using equation (2) or (7)

$$\ln (N/N_0)_{1,\,c} = \ln (N/N_0)_{2,\,c} = -(w_c/W). \qquad . \qquad . \qquad (9)$$

Hence,

$$\ln (N/N_0)_2 = -\overline{(C.I.)}(w/W) + A. \qquad . \qquad . \qquad . \qquad (10)$$

But since at $w = w_c$

$$\ln (N/N_0)_{1,\,c} = -(w_c/W) = \ln (N/N_0)_{2,\,c} \qquad . \qquad . \qquad (9)$$

$$= -\overline{(C.I.)}(w_c/W) + A. \qquad . \qquad . \qquad (11)$$

$$A = (w_c/W)[\overline{(C.I.)} - 1] \qquad . \qquad . \qquad (12)$$

or

$$\ln (N/N_0)_2 = (w_c/W)[\overline{(C.I.)} - 1] - \overline{(C.I.)}(w/W). \qquad . \qquad . \qquad (13)$$

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* We do not write $d(N/N_0)_2 = -d(w/W)(N/N_0)_2^{\overline{(C.I.)}}$ because we use Frank and Wen's concept that the reaction is still unimolecular with respect to N, but the rate is multiplied by $\overline{(C.I.)}$ due to the triggering action of the first bond to break.

But

$$\ln (N/N_0)_2 = 3 \ln (E/E_0)_2. \qquad \qquad \qquad (14)$$

Hence,

$$\ln (E/E_0)_2 = (\tfrac{1}{3})\{(w_c/W)[\overline{(C.I)}-1]-\overline{(C.I.)}(w/W)\} \qquad . \qquad (15)$$

Since $W = \tfrac{1}{3}$ for cellulose,

$$\ln (E/E_0)_2 = w_c[\overline{(C.I.)}-1]-\overline{(C.I.)}w \qquad . \qquad . \qquad (16)$$

or

$$E_2 = E_0 \exp \{w_c[\overline{(C.I.)}-1]-\overline{(C.I.)}w\} \qquad . \qquad . \qquad (17)$$

for cellulose. For other hydrogen-bonded solids, equation (15) has to be used with appropriate value for W (see Nylon 66 below).

In the previous section, we derived a value for $\overline{(C.I.)}$ from Starkweather's curve plus Némethy and Scheraga's value for liquid water and found $\overline{(C.I.)} = 6.71$. Furthermore, I have postulated that $w_c = w_m$. For cellulosics w_m has a range of 0.03 up to 0.07 g H_2O/gm cellulose. Thus, equation (17) is an explicit equation for E_2 in terms of E_0, once w_c and $\overline{(C.I.)}$ values are known from other sources. For example, for celulosic sheets and fibres, putting $\overline{(C.I.)} = 6.71$ and $w_c = 0.05$

$$\ln (E_w/E_0)_2 = 0.286-6.71w. \qquad . \qquad . \qquad . \qquad (18)$$

This can only be an average equation and will be somewhat different for different papers, rayons and other cellulosic samples, but it is of interest for this theory to test it against what is known of E vs w experimentally.

4—Discussion

4.1—Paper

THERE are several studies in the literature giving E vs w. I have either taken the data directly from tables, or read off points from graphs as the case was, for each study. E_0 was sometimes given, and this was used; otherwise, I have either extrapolated the curve on the graph or used equation (6) to estimate E_0 from the value of E_w at the lowest one or two values of w. Then I performed a regression of $\ln (E_w/E_0)_2$ on w for points with $w \geqslant 0.05$. Here are the results for each study:

(1) Andersson and Berkyto:[13]

$$\ln (E/E_0)_2 = 0.312-6.240w; \quad r^2 = 0.948. \qquad . \qquad (19)$$

(2) Higgins and Balodis:[14]

$$\ln (E/E_0)_2 = 0.345-8.207w; \quad r^2 = 0.965. \qquad . \qquad (20)$$

(3) Benson[15] reported on six papers of which I analysed four representing the boundaries for the range of curves:

    (*a*) Experimental Lake State, M.D.:

$$\ln (E/E_0)_2 = 0 \cdot 218 - 5 \cdot 967w; \quad r^2 = 0 \cdot 995. \qquad . \qquad . \qquad (21)$$

    (*b*) Commercial Southern, M.D.:

$$\ln (E/E_0)_2 = 0 \cdot 224 - 6 \cdot 071w; \quad r^2 = 0 \cdot 992. \qquad . \qquad . \qquad (22)$$

    (*c*) Experimental Lake State, C.D.:

$$\ln (E/E_0)_2 = 0 \cdot 248 - 6 \cdot 597w; \quad r^2 = 0 \cdot 991. \qquad . \qquad . \qquad (23)$$

    (*d*) Commercial Southern, C.D.:

$$\ln (E/E_0)_2 = 0 \cdot 294 - 7 \cdot 276w; \quad r^2 = 0 \cdot 975. \qquad . \qquad . \qquad (24)$$

    (*e*) All four 'papers', together:

$$\ln (E/E_0)_2 = 0 \cdot 244 - 6 \cdot 456w; \quad r^2 = 0 \cdot 993. \qquad . \qquad . \qquad (25)$$

(4) Riemen and Kurath:[16]

$$\ln (E/E_0)_2 = 0 \cdot 177 - 7 \cdot 595w; \quad r^2 = 0 \cdot 997. \qquad . \qquad . \qquad (26)$$

(5) The same but converted to a standard grammage of 100 g/m^2 o.d., by Dr J. P. Brezinski of the Institute of Paper Chemistry (Private communication):

$$\ln (E/E_0)_2 = 0 \cdot 162 - 6 \cdot 054w; \quad r^2 = 0 \cdot 995. \qquad . \qquad . \qquad (27)$$

(6) J. P. Brezinski:[17]

$$\ln (E/E_0)_2 = 0 \cdot 287 - 5 \cdot 680w; \quad r^2 = 0 \cdot 982. \qquad . \qquad . \qquad (28)$$

If equal weights are given to all these equations—but omitting equations (25) and (27) since they are represented by equations (21) through (24) and equation (26) respectively—we obtain an average for $\overline{(\text{C.I.})}$ (which is the coefficient for w in each equation) of $6 \cdot 704 \pm 0 \cdot 894$ (the latter is the standard deviation). The figure obtained from averaging Starkweather's data of Fig. 1 was $6 \cdot 71$.

Secondly, it is possible to calculate w_c from the intercept of each of these equations since $w_c = (\text{Intercept})/[\overline{(\text{C.I.})} - 1]$. The values so obtained for equations (19) through (28) are respectively: $0 \cdot 060$; $0 \cdot 048$; $0 \cdot 044$; $0 \cdot 044$; $0 \cdot 044$; $0 \cdot 047$; $0 \cdot 045$; $0 \cdot 027$; $0 \cdot 032$; $0 \cdot 061$. Again omitting the seventh figure for equation (25) and the ninth, equation (27), to avoid duplication, the average for w_c is obtained as $\overline{w_c} = 0 \cdot 047 \pm 0 \cdot 011$. For paper, the B.E.T. monomolecular layer w_m is given by Stamm as averaging $0 \cdot 04$.[8]

Thus, paper as reported appears to behave in accordance with the theory presented here. There are, however, two studies which do not appear to fit. The first has already been mentioned, i.e. that by Craver and Taylor.[2] I will be remembered that these authors gave data which fitted the equation for regime (1), i.e.

$$\ln (E/E_0)_1 = -w. \qquad . \qquad . \qquad . \qquad . \qquad (5)$$

The difficulty was that it fitted this equation for all values of up to 0·28 approximately, whereas it should have departed from it when $w \geqslant w_c$ of approximately 0·05. There does not appear a reasonable explanation for this deviation.

The second deviation from theory is work reported by Caulfield.[18] This work appears to fit the equation:

$$\ln (E/E_0)_2 = 0.000 - 3.4415w. \qquad . \qquad . \qquad . \qquad (29)$$

Again, why $w_c = 0·000$ and $\overline{(C.I.)}$ is approximately half those reported by others is not easy to explain.

A last reservation should be mentioned here. I owe these remarks to a private communication from my friend, Dr J. P. Brezinski, of the Institute of Paper Chemistry. It is not easy to check literature values for E reported for values of $w \leqslant 0·06$ to 0·07 against regime (1) equations, partly because there are very few data in this regime and partly because of a peculiar difficulty. Dr Brezinski points out that often in the literature a distinct break is observed at $w = 0·06$ to 0·07 in the plots of E_w vs w for paper. The explanation is in the method of changing relative humidity in these experiments. Usually, it appears, experimenters dry the sheet from saturation to 50 per cent relative humidity. Then they determine E_w vs w on a rising, or adsorption, values of relative humidity up to relative humidity = 90 per cent. Then the sheet is redried to below 50 per cent relative humidity for determination of E_w at $w \leqslant 0·07$. Hence, the drier sheets are measured on the desorption portion of the curve while the wetter sheets are on the adsorption curve with an attendant discontinuity and uncertainty in the curves.

Where such uncertainties did not exist—e.g., with the papers studied by Andersson and Berkyto,[13] the experimental results did fit equation (5) for $w \leqslant 0·05$.

4.2—Other cellulosics

Meredith[19] studied the effects of moisture on the modulus of torsional rigidity of ramie, mercerised cotton, Fortisan, viscose rayon, Nylon and wool. The first four fibres are all cellulosics. I shall assume here that the ratio of (G_w/G_0) for these fibres is equal to (E_w/E_0), where G_w is the torsional rigidity at regain w and G_0 is the rigidity at $w = 0·0$. For all the cellulose fibres, Meredith found that the empirical relationship, at 25° C,

$$\ln (G_w/G_{65}) = -0·82[(w/w_{65}) - 1] \qquad . \qquad . \qquad . \qquad (30)$$

gives a reasonable approximation to the relationship between G and w for the range of 0 to 90 per cent relative humidity in terms of these quantities

at relative humidity of 65 per cent. In terms of the present paper,

$$\ln (G_w/G_0)_2 = [0{\cdot}82 - \ln (G_{65}/G_0)] - (0{\cdot}82w_{65})w. \qquad . \qquad . \qquad (31)$$

The following gives the appropriate values from Meredith's paper:

TABLE 1

Material and condition	$\ln (G_{65}/G_0)$	w_{65}
Ramie		
Adsorption	−0·755	0·079
Desorption	−0·821	0·086
Mercerised Cotton		
Adsorption	−0·799	0·093
Desorption	−0·916	0·110
Fortisan		
Adsorption	−0·844	0·109
Desorption	−1·022	0·126
Viscose Rayon		
Adsorption	−0·799	0·137
Desorption	−0·942	0·157
Averages	−0·862	0·112
	±0·090	±0·027

Since Meredith's equation (30) deals with average parameters, average values are inserted in equation (31) to yield equation (32). Thus,

$$\ln (G_w/G_0)_2 = [0{\cdot}82 - (0{\cdot}862 \pm 0{\cdot}090)] - [0{\cdot}82/(0{\cdot}112 \pm 0{\cdot}027)]w$$
$$= [-0{\cdot}042 \pm 0{\cdot}09] - [7{\cdot}72 \pm 2{\cdot}7]w. \qquad (32)$$

Thus, $\overline{(\text{C.I.})} = (7{\cdot}7 \pm 2{\cdot}7)$, but w_c is indeterminate because of the spread of the data.

As an illustration of the less ordered fibres and because it is the prototype of hydrogen-bond dominated solids, the data on viscose rayon were analysed in detail with the following results:

Adsorption, $w \geqslant 0{\cdot}068$, $\ln (G/G_0)_2 = 0{\cdot}328 - 8{\cdot}658w$; $(r^2 = 0{\cdot}990)$.   (33)

Desorption, $w \geqslant 0{\cdot}046$, $\ln (G/G_0)_2 = 0{\cdot}312 - 8{\cdot}442w$; $(r^2 = 0{\cdot}984)$.   .   (34)

$\overline{(\text{C.I.})}$: Adsorption $\overline{(\text{C.I.})} = 8{\cdot}658$; Desorption $\overline{(\text{C.I.})} = 8{\cdot}442$;
      mean $\overline{(\text{C.I.})} = 8{\cdot}55 \pm 0{\cdot}15$.

w_c: Adsorption $w_c = 0{\cdot}042$; Desorption $w_c = 0{\cdot}042$; mean $\overline{w_c} = 0{\cdot}042$.

Another illustration, but of a more highly ordered fibre which yields a peculiar deviation, Meredith's data on ramie were also analysed in detail with the following results:

Adsorption, $w \geqslant 0{\cdot}04$, $\ln (G/G_0)_2 = -0{\cdot}236 - 6{\cdot}707w$; $r^2 = 0{\cdot}996$.   .   (35)

Desorption, $w \geqslant 0{\cdot}047$, $\ln (G/G_0)_2 = -0{\cdot}239 - 6{\cdot}701w$; $r^2 = 0{\cdot}970$.   .   (36)

It is seen that while $\overline{(\text{C.I.})}$ is in good agreement with the other values obtained for cellulosics, w_c is paradoxically negative.

4.3—*Nylon 66*

Another hydrogen-bonded fibre is Nylon 66. While its modulii are greatly influenced by the covalent bonds, it is hypothesised here that the effect of moisture on these parameters will be through the break-up of hydrogen bonds by the co-operative mechanism under study.

The primary repeating units in Nylon 66 are [—$CO(CH_2)_4CONH(CH_2)_6$-NH—]. If we consider 2 H-bonds per unit, then $W = (2 \times 18)/226 = 0.1593$ for Nylon 66. I do not have values for w_c, but it is likely to be very low as Nylon does not adsorb water to the same extent as the cellulosics.

Works by Meredith,[19] Adams[20] and by Quistwater and Dunell[21, 22] were analysed and gave the following results averaged for different frequencies used in the tests:

TABLE 2

Author	Property studied and conditions	ln $(Property_w/Property_0)$ $= A - Bw$	$\overline{(\text{C.I.})}$	w_c
Meredith [19]	G/G_0, 25° C	$A = 0.030$; $B = 15.254$	7.290	2.3×10^{-3}
Adams [20]	G/G_0, Undrawn	$A = 0.078$; $B = 20.263$	9.684	6.5×10^{-4}
	G/G_0, Drawn	$A = 0.089$; $B = 16.233$	7.758	9.3×10^{-4}
Quistwater & Dunell[21]	E/E_0, 35° C ($100\,s^{-1}$)	$A = 0.1371$; $B = 12.297$	5.877	4.0×10^{-3}
Quistwater & Dunell [22]	E/E_0, 9° C ($150\,s^{-1}$ and $20\,s^{-1}$)	$A = 0.1785$; $B = 7.2215$	3.4512	1.16×10^{-2}
	E/E_0, 60° C ($150\,s^{-1}$ and $20\,s^{-1}$)	$A = 0.1270$; $B = 12.843$	6.1377	-3.9×10^{-3}
	Averages		6.70 ±2.1	0.003 ±0.005

In Table 2, $\overline{(\text{C.I.})}$ was calculated in accordance with equation (*15*), which gives $B = -\overline{(\text{C.I.})}/3W$. For Nylon 66, $W = 0.1593$. Similarly, $A = (\frac{1}{3})$ $[\overline{(\text{C.I.})} - 1]w_c/W$, and having calculated $\overline{(\text{C.I.})}$, w_c was accordingly determined. It will be noted that once again the variability of data renders w_c indeterminate except that it is less than 0.01—a reasonable conclusion for Nylon 66. However, it is of particular interest that the average value of $\overline{(\text{C.I.})}$, (6.70 ± 2.1), puts it in the same range as $\overline{(\text{C.I.})}$ for cellulosics (6.704 ± 0.894). This fact suggests that the Starkweather number of H_2O/cluster for Nylon 66 should fall on the same curve obtained for cellulose. Since W for Nylon 66 is different from that for cellulose, the values available for Nylon 66 in Starkweather's Fig. 5 were plotted in Fig. 1 of the present paper, but on a scale of

w/W. Up to the limits of available data, the points for Nylon 66 fall on the curve for cellulose with reasonable coincidence. Thus, it appears that the co-operative breakdown of H-bonds on water adsorption in Nylon 66 is identical with that of H-bond breakdown in cellulosics, despite the great differences not only in the chemical structures of the two classes of polymers but also in the components of the H-bonds linking the molecules of the two classes. Again, this suggests that these phenomena are founded on the H-bonds themselves connecting the molecules and not only related to the properties of the water molecule.

4.4—*Wool*

The remaining hydrogen-bonded fibre studied by Meredith[19] was wool. Similar analyses made on his results gave the following: For adsorption, $0.078 \leqslant w \leqslant 0.33$,

$$\ln (G/G_0) = 0.7716 - 10.5019w; \quad r^2 = 0.980. \qquad . \qquad . \quad (37)$$

For desorption, $0.096 \leqslant w \leqslant 0.33$,

$$\ln (G/G_0) = 0.9044 - 10.9859w; \quad r^2 = 0.985. \qquad . \qquad . \quad (38)$$

There is a peculiar difficulty in calculating W for wool since its composition varies. It has many types of amino acid residuals which vary in nature and percentages from one type of wool to another. Consden and Howitt[23] discuss the chemical composition of wool and give the approximate residue frequencies for eighteen amino acids, ranging from a low of $1/206$ for histidine and methionine to a high of $1/9$ for cystine. They suggest 'an average residue weight of roughly 100', but Meredith himself assumes one hydrogen bond per molecular weight of 122.[19] Hence, $W = 0.1475$ g H_2O/g dry wool may be taken as a basis to begin with. These data yield: $\overline{(C.I.)}$ for adsorption, 4.647; for desorption, 4.861; mean $\overline{(C.I.)}$ 4.75. Also, w_c for adsorption, 0.0312; for desorption, 0.034; mean w_c, 0.033.

The values for w_c are reasonable when viewed against the points of inflection on the water adsorption curves for wool. The value of 4.75 for $\overline{(C.I.)}$ appears too low, since the adsorption curve for wool is not too far off the curve for, say, rayon. Whether this particular value is the lower bound for a range of values for wool and could fit in the range for cellulosics—i.e. (6.7 ± 0.9)—and Nylon 66—(6.7 ± 2.1)—if other samples of wool were tested cannot be stated in the absence of replicate experiments. It could, however, represent a real difference from cellulosics and Nylon 66, since the structure of wool keratin as a double spiral with rungs made up of both hydrogen-bonds and disulphide linkages could interfere with the co-operative break-up

of H-bonds and thereby reduce the average number. Furthermore, the proportions of different amino acids and other chemical and morphological constituents are different for different wools and, therefore, there must be a fairly wide range in the molecular weight of the repeating unit, and hence in W, for different wools.

5—*Summary*

THUS, it appears that H-bonds break on wetting under two regimes. In regime 1, a unimolecular reaction (of order 1 in N) takes place. In regime 2, the reaction is still first order in N, but the first bond breaking triggers the breakdown of $[\overline{(C.I.)} - 1]$ others so that a total of $\overline{(C.I.)}$ bonds break 'simultaneously'. The value of $\overline{(C.I.)}$ as predetermined from averaging Stark-weather's calculations for cotton cellulose and Nylon 66 of 'the number of H_2O/cluster', assumed also to indicate the number of H-bonds which act co-operatively is 6·71. Against this figure, paper samples in different labora-tories gave $6·7 \pm 0·9$ (with the exception of two sets of experiments using sonic methods); a group of cellulosic fibres gave $(7·72 \pm 2·7)$: Nylon 66 in four sets of experiments gave $(6·7 \pm 2·1)$ and wool gave $(4·8$ to $5·8)$ depending on the value to be taken for W. The grand mean for all papers, other cellulosics, Nylon 66 and wool $[\overline{(C.I.)} = 4·8]$ is 6·5. With $\overline{(C.I.)}$ for wool taken as 5·8, the mean for $\overline{(C.I.)} = 6·7$. Omitting wool, mean $\overline{(C.I.)} = 7·0$.

The values postulated for w_c were to be the values obtained for the mono-molecular adsorption of water as calculated by B.E.T. equations. For the different papers, Nylon 66 and wool, this expectation was reasonably satisfied. For cellulosics, it was not possible to be sure as occasional paradoxically negative values were obtained.

Finally, there is no acceptable explanation for the deviation of two sets of results (measured on paper by measuring the velocity of stress propagation) from the theory and from other experimental results.

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Discussion

Prepared discussion contribution by N. L. Salmén and Dr E. L. Back

Dr Nissan has in his article calculated the average co-operative index ($\overline{C.I.}$) and the critical moisture ratio w_c for a Nylon 66 at three different temperatures from measurements by Quistwater and Dunell (1, 2). Looking closely into these data, it is evident that the co-operative index increases with temperature while the critical moisture ratio decreases with temperature. Is this then a phenomenon which holds also for other hydrogen bonded materials?

We have recently carried out stress–strain measurements on kraft sack paper at different temperatures. The dependence of moisture content on the modulus of elasticity is shown in Fig. 1. Here the measurements at 20° C and 46° C are evaluated both in air and in an inert silicon oil giving the same results, while the measurements at −10° C only is evaluated in pre-thermostated silicon oil (3). In these measurements the modulus of elasticity is calculated on paper strip thickness at 20° C and 65 per cent R.H. and no correction is made for the change in thickness so far. Correction for the thickness variation will be made later. Apparently the measurements of Quistwater and Dunell do not include this correction either.

These data have been applied to the equation of moisture dependence of the modulus of elasticity, above the critical moisture ratio. As shown in Table 1, there exists just as for Nylon 66 an increasing co-operative index and a decreasing critical moisture ratio with temperature. So this temperature dependence seems to hold for paper as well.

TABLE 1.—MODULUS OF ELASTICITY

Dependence of modulus of elasticity, E_w, on moisture ratio, w, above the critical moisture ratio, w_c, and the average co-operative index ($\overline{C.I.}$) for a kraft sack paper at different temperatures. Evaluated from stress–strain measurements at a strain rate of $8 \cdot 3 \cdot 10^{-3}$/s.
The modulus of elasticity is calculated on paper strip thickness at 20° C and 65 per cent R.H.

Temperature °C	$\ln (E_w/E_0)_2$	Correlation r^2	$(\overline{C.I.})$	w_c
−10	0·375–5·75w	0·991	5·75	0·079
+20	0·420–6·55w	0·985	6·55	0·075
+46	0·382–7·46w	0·978	7·46	0·059

Under the chairmanship of B. W. Attwood
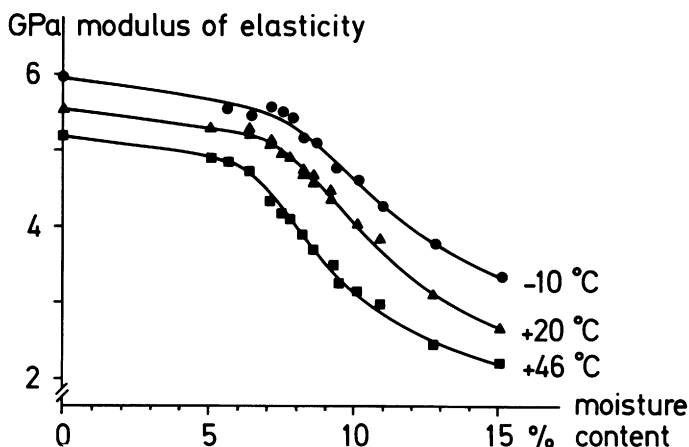
GPa| modulus of elasticity

Fig. 1—The modulus of elasticity versus temperature for kraft sack paper at three different temperatures. Evaluated by stress–strain measurements at a strain rate of $8 \cdot 3 \cdot 10^{-3}$/s. The modulus of elasticity is calculated on paper strip thickness at 20° C and 65 per cent R.H.

Dr Nissan, can this effect of temperature be explained by the present theory of reactions of hydrogen bonded solids to moisture and temperature?

Nissan Thank you for noticing something which passed me by completely. $\overline{CI}$ does seem to display a temperature regularity rather than remaining constant. I think that the prediction of this regularity lies in the quantum-mechanical treatment of hydrogen bonds, which is beyond my abilities.

Dr A. de Ruvo I seem to have a problem with scale when I talk about drying stresses. Page says it is micro-creeping, I explain it on the macroscopic scale, you on the other hand talk about breaking up hydrogen bonds. Are you talking about the loosening of the carbohydrate chain by the increase in the number of hydrogen bonds in the lattice? Surely, the softening of the polymer must go through the main chain?

Nissan I think that scale is a very important issue. I am here talking about the joining between cellulose chains not necessarily within the crystallites but in the para-crystalline portion and in the so called amorphous region of the cellulose. There is where I believe that the water takes effect. I believe

that paper behaves as discontinuous at the microfibrillar or lamellar level but as a continuum of hydrogen bonds at a larger scale.

Dr H. Corte   Mr Chairman, I have followed Dr Nissan's work since his first tentative publication in *Nature* in 1953 and I always found his models admirably constructed and stimulating. But I still cannot help feeling that they are really not concerned with paper at all but with a very simplified model of the material. I would like to make three points. One of the first mathematical concepts that were published, in 1957, was the fact that the load-elongation curve of paper can be described as a sum of a linear term and a square term in the strain. In the original publication this was derived from the Morse function of the potential well, now it is the Lennard-Jones function; and indeed, it does not matter what function you use, any curve can be described by a polynomial if enough terms are considered. It is fortuituous that commercial tensile testers have such an inertia that they smooth out the response to give a parabolic curve. If the sensitivity of the tester is high enough or if the sample is thin enough you will observe that the load-elongation curve is saw-toothed and not continuous at all. The second point is the new mathematical relationship Dr Nissan told us about, namely, the dependence of the modulus on the moisture content. The typical result here is that it is the logarithm of the modulus which depends linearly on the moisture content. This formula was based on the experimental results of three published papers. These authors plotted the modulus against the moisture content, not the logarithm of the modulus; but this again does not matter because the data cover such a small range that, strange though it may sound, a straight line is produced in either case. It merely means that any curve can be described by a straight line if the range is short enough. You cannot prove anything with it. Lastly, if you tear a piece of paper and look at the torn edges through a magnifying glass you will see fibres sticking out. These are the building blocks of paper, and any attempt to describe mechanical or any other properties of paper both rationally and in quantitative terms must start with a description of its fibrous structure. It would be very difficult using Dr Nissan's theory, to conclude that there is a difference between papers made from long fibres and papers made from short fibres; or from fibres with many fine particles and fibres with fewer fine particles, for example. The building blocks of paper are and will remain the fibres and not lamellae, microfibrils or hydrogen bonds. The similarity between paper and a hydrogen-bond dominated continuum is about the same as that between a cornfield and a cake.

Nissan   I prefer the cake to the cornfield. Dr Corte has not only followed my work but also my initial figure of 4·5 kcal/mole for hydrogen bond energy

was based on unpublished but privately communicated work which he did with Schascheck. So it is Dr Corte who was partially responsible for this model. Now turning to his specific remarks:

(1) The fact that most curves can be fitted by a polynomial is perfectly true, but if one or more of the parameters are derived from independent data then you can predict what some factors may or may not do to your curve. If you determine the coefficients empirically as you imply then you can indeed get a better fit to the data but this has no fundamental meaning.

Written after the event

(2) Your second point was the fact that for some data we can plot either $\ln (E/E_0)$ or (E/E_0) vs. w and get straight lines. This is true for (E/E_0) varying between $1 \cdot 0$ and say $0 \cdot 75$. Since my theory predicts a log relationship then, mathematically the natural scale plot is also predicted as an approximation. The differences are that my theory predicts linearity down to much lower values on log scales but not on natural scale.

(3) Finally, with reference to short and long fibres, my theory states that whether you use short or long fibres you have to accumulate the same number of H-bonds per cm^3 to attain a given modulus; the art and difficulty involved in accumulating such numbers will be different with the two types of fibres but that is the field of papermaking and not of rheology of paper.

Back I would like to refer to the critical moisture content, w_c, and its temperature dependence. What do you think of the following proposal: the critical moisture content is the moisture content at a given temperature, where the glass transition occurs. This means that the critical moisture content w_c will decrease with increasing temperature and regime 1 in your approach will disappear at $220°$ C. Thus w_c is the moisture content where segments of the amorphous cellulose chain can start to rotate. This is how Quistwater interpreted his data and the way in which we have tried to do it.

Nissan That is most interesting, but I have no comment at present.

Mr K. Ebeling I cannot accept the idea advocated by Dr Nissan during the past 20 years that typical paper can be visualised and—what is even more dangerous—seriously described as a continuum of only hydrogen bonds. I presented at the 1973 Cambridge symposium results of a thermodynamic study of dry paper structure that, at least to me, clearly showed that the structure of typical paper is not that of a hydrogen bond continuum but a heterogeneous structure of definite structural elements. One could see that

when the total number of hydrogen bonds at the dry condition N_0 was constant, the corresponding modulus of elasticity (related to E_0) was greatly dependent on the history to which the paper structure and its elements were subjected during the consolidation process and phases preceding it. Similarly it was not observed that the elastic load-elongation behaviour of these dry paper samples would be curved as proposed by Dr Nissan. Instead, as soon as the load-elongation curve showed curvature, a pronounced irreversible structural change was observed. It seems to me that the basic values of key parameters in Dr Nissan's paper are very questionable. Dr Goring told in his paper earlier in this symposium that the present concept of clusters does not include clusters with tens of water molecules in them. Recent work at the Institute of Paper Chemistry by Professor Swanson and his students have shown that the old BET specific surface areas for paper have to be multiplied by a factor of about 3 to obtain the 'true' specific surface area of cellulosic materials. I would like to know how the observed 'curve fitting accuracy' in Dr Nissan's paper is changed when the referred changes in the key constants are taken into account?

Nissan I am not familiar with how you measured N_0 and found it constant even though E_0 was varying. I will be happy to study this however and see its effects. You also alluded to Némethy and Scheraga's figures for the size of the clusters. What they did in the 1972 paper was that they recalculated the cluster sizes on the assumption that there should not be a greater number than 9 or 10 and they calculated a spectrum from several parameters. This number has been reported by different people at different times and it varies from the low of seven or so for Némethy and Scheraga up to about 300 by Frank and others. An interesting independent determination of this is by low angle X-ray scattering of water which gives a co-ordination number of 4·4. But signals are very strong from 3 shells of water, and if you calculate the number involved, depending on whether you stop at 3 shells or 4 you get somewhere between 30 and 80 molecules. Therefore this figure is not quite clearly known. The figure for the amount of water clustering around cellulose at saturation is still in doubt. Assuming for the moment that there is no connection between that figure and what you get from the rheological figure, you can still use the rheological figure itself to give CI without dependence on other sources. When you do that for an unknown system such as lignin and use the rheological data themselves you get a figure for the number of hydrogen bonds per repeating unit in that material which comes out to be in the same parish as the structural formula for lignin provides. It is the accumula-

tion of such data that will prove the utility, not only the validity, of the theory. I would be very interested to read your contribution, however.

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Dr Nissan studied the literature quoted by Dr Ebeling and the following exchange was received after the event.

Nissan (1) You stated that you measured E_0 and N_0 independently from each other for papers and found that papers having the same N_0 had different E_0 values. I failed to find these independent measurements in your paper. As I said at the Conference, I cannot see how you can do that for paper. N_0 is the effective number of H-bonds per cm^3 resisting strain and for isotropic paper reaches a maximum of one-third the total H-bonds per cm^3. But not all H-bonds are available as steric hindrance may protect some; in paper, 1 have demonstrated that not *all* H-bonds are effective. In non-isotropic paper, N is different in different directions. In a machine-made paper, N_0 in the MD is different from N_0 in the CD since E_0 values in the two directions are different. Indeed, this is the explanation for having E in MD greatly different from E in CD for machine-made papers dried under strain when fibre orientations, as seen under the microscope, show no great anisotropy: Much smaller elements than the fibres will be pulled in MD so that the effective number of H-bonds resisting strain in MD is greater than those in CD. This is no new concept: In crystallites, the number of H-bonds in the 101 plane exceeds the number in, say, the 002 plane. Hence, the crystallites are anisotropic precisely for this reason. Similarly, anisotropic paper has different E values and, hence, N values in different directions.

Please let me know: Where did you demonstrate that you had measured N_0 *independently* of E_0 and found N_0 constant while E_0 varied?

(2) You stated that, in your paper of four years ago, you found paper to behave differently from regenerated cellulose and, therefore, your observations contradicted my theory. Looking at your Figs 1, 6 and 7, I find the following statements are true: For strains ranging from 0·000 up to a critical strain, specific for each material (i.e. *ca.* 0·003 for Fig. 1, 0·002 for regenerated cellulose and 0·001 for Al foil), the slope of rate of work input (and of stress) with respect to strain is positive while the slope for the 'Heat Flow' is negative.

This is the region which my theory discusses. In this region, all three materials behave in the same way and their behaviour is reversible. Thus, in this region they behave as members of one class of materials. At the critical strain for each of the three materials, the slope of 'Heat Flow' curve changes from negative to positive indicating new heat generating phenomena are initiated, or at least are accelerating to such an extent that they overwhelm the heat absorption taking place on storing strain energy in the bonds. You interpret these new, or accelerating phenomena, as due to reversible and irreversible bond breaking and remaking. Beyond the critical strain—where irreversible phenomena are observed rheologically as well as thermodynamically—the three materials may behave differently. (I say 'may' because I do not know what the curves in Fig. 6 would have looked like, if you did not finish or stop cycle 1 at a strain of 0·015 but continued to, say, 0·020; would the heat flow curve have crossed the zero line as the curve in Fig. 1 did at a strain of 0·007? If so, Fig. 6 and Fig. 1 would have looked the same.) But, Dr Ebeling, events beyond the critical strain are very clearly beyond the province of my theory which specifically studies E, at zero strain, and ventures slightly beyond that (see below) in the reversible region but with loud warnings not to exceed 'small', i.e. reversible region, strains. So what is your purpose in discussing phenomena of irreversible and reversible bond breaking through strain energy outside the domain of my theory and stating that they contradict my theory, when, in fact, as your own Fig. 1 and Fig. 6 show that where my theory is applicable (below the critical strain) paper and regenerated cellulose do behave as members of the same class? I am completely at a loss to understand this confusion of regimes.

Let me explain my difficulties in understanding your statements by an example. Suppose you came across the following, as if it were a new discovery: 'When a fluid is in the laminar regime—i.e. with Reynolds number less than 2,000—the velocity profile in a straight, long circular pipe is parabolic.' Would you test this statement by deliberately measuring the profile in a pipe when the flow is turbulent at Reynolds number of, say, 10^5? And if you did do so and found the profile was not parabolic, would you publish a paper or make a public statement to the effect that you had found the proposed theory contradicted by your experiments? I cannot imagine that you would. Then why do you do with the rheology of paper what you would not do in the example? Why do you dwell on differences in rates of bond breaking and remaking in paper and cellophane to state that a theory on Young's modulus—i.e. stress–strain ratio at zero strain or very low strains—is contradicted by your observations?

Please, do try to explain your purpose in making these statements.

(3) You stated that in the reversible portions of your curves for paper, you did not find the effects predicted by my 'second coefficient of elasticity, K'. In other words, you stated that the stress–strain curve was 'straight' until the yield point (or critical strain) when irreversible phenomena appeared, whereas my theory predicts a curvature in the reversible initial portion for H-bond dominated solids. But, Dr Ebeling, I give *quantitative* predictions, not simply qualitative ones. Let us see what my theory states. It states $\sigma = E\varepsilon - 1\cdot1 \times 10^7\varepsilon^2$ when σ is measured in N/cm². In your Fig. 1, you studied a *dry*, 100 per cent rag paper of high E without previous mechanical conditioning. The critical strain was approximately 0·003 and $\sigma \simeq 2\,500$ N/cm². Thus, $2\,500 = 0\cdot003E - 1\cdot1 \times 10^7(0\cdot003)^2 = 0\cdot003E - 99$. Thus, $0\cdot003E = 2\,500 + 99 = 2\,599$ N/cm². In other words, the effect of the second coefficient of elasticity, K, of my theory on this particular paper is approximately as 99:2 500 or 4 per cent. This means that a tangent at zero strain would be 99 N/cm² above the observed curve at $\varepsilon = 0\cdot003$, if the paper were mechanically conditioned. But your Fig. 1 shows a slight heel at zero strain, and I infer that you did not mechanically condition your paper. As Steenberg showed thirty years ago, if you do not do that, small adventitious bonding sites are irreversibly broken at the first cycle and paper shows an irreversible (NOT reversible) first portion in its stress–strain curve due to a pseudo-work hardening—i.e. the tangent at zero strain lies below the observed stress–strain curve. Dr Ebeling, for whatever reasons, you neglected to 'mechanically condition' your papers before testing. Therefore, the initial portions of your curves contain an 'irreversible' component of the order of magnitude and of opposite sign to the contribution of my K. How do you propose to analyse your curves to extract the irreversible component first and then to test for the validity of my K? By neglecting this elementary precaution, you had no truly reversible portion within the precision required to study second-order phenomena.

Since K is independent of E, its influence is more noticeable with papers of low E rather than the high E paper you tested. That was why the extensive measurements by Andersson and Berkyto confirmed my predictions: They were over a wide range of E and had a large, statistically significant number of observations. But the fatal flaw in the initial portion of your curves is due to the adventitious irreversibility you did not choose to eliminate.

Do you not think, Dr Ebeling, that when you set out to confirm or refute a theory you should take all the necessary precautions demanded by the tests?

(4) None of the above had anything to do with the subject of my contribution, which was the effect of water on E. However, you did raise one question which indirectly dealt with the subject paper. You raised the question of

surface area measurements by BET applied to cellulose and stated that at the I.P.C. they found a correction and asked if that would change the 'correlations' I found. Dr Ebeling, my paper did not deal with surface areas. It simply stated that there was a critical *moisture content*, W_c, separating Regime (1) from Regime (2). I then postulated that W_c could be the same as W_m—the value obtained for water content of paper when its adsorption isotherm is analysed by the standard BET manner. I made it clear that this is an interesting but peripheral further postulate which is not essential to the theory but was very interested to find that, in fact, W_m was probably equal to W_c. The regressions I made gave W_c, not W_m. If you could care to read my paper, you will find the following clear statement: 'I postulate in this theory that $(W_c/W_m) = 1$, although I am prepared to find and accept another critical number.' So, Dr Ebeling, what was it exactly you wished to know about the 'correlations'?

(5) Finally, Dr Ebeling, you warned that my theory was 'dangerous'. This is a grave and serious charge to make in the field of ideas. You will remember that it was precisely this charge which brought the hemlock to Socrates' lips. Therefore, I believe it is your duty either to substantiate or to withdraw it. Since the charge was publicly made, I believe justice demands that—if not substantiated—the withdrawal should be made publicly, too. Otherwise, you may find yourself considered not to have met the reasonable but strict scientific criterion of objectivity. That, believe me, would sadden me because I do believe we need younger scientists like you to take over from the Nissans, the Steenbergs and the Cortes before long. I think it is necessary to do so by sticking strictly to scientific objectivity and not make unfounded charges in the heat of debate; otherwise you will lose credibility with serious scientists.

Ebeling I will be specific with the 5 points raised by Dr Nissan.

1. I stated that when the total number of hydrogen bonds N_0 under absolutely dry conditions (not the same N_0 as in Dr Nissan's paper) was kept constant, the corresponding tensile modulus of the handsheets could be varied greatly, depending for instance on the drying history of the handsheets. There was no need to introduce steric hindrance to account for the observed difference.

Instead, the present knowledge of the structure of the swollen cell wall and its behaviour during the consolidation process of the paper structure will account for the observed differences. Besides, it will give the practical papermaker a more powerful tool to predict and to understand the structural behaviour of paper than the hydrogen bonded continuum model of Dr Nissan can ever be.

2. The original experimental data included in the dissertation[1] lead to the conclusion that the behaviour of structural elements in paper is different from that of cellophane. A conclusion was made—based on results of the heat phenomenon, on the sharpness of the apparent yield point and on the stress relaxation—that the structural behaviour of paper during straining is closer to that of aluminium foil than to that of cellophane. The hydrogen bonds connecting the results indicated that the structural elements respond to straining in a different manner in the case of paper than in the case of cellophane. In other words, if one accepts that cellophane perhaps might be approximated as a hydrogen bonded continuum, this same reasoning is not applicable to paper.

3. Dr Nissan is absolutely correct when he states that I did not 'mechanically condition' my paper samples before running the experiments in the microcalorimeter. The point I was trying to make in my first contribution was that even after the 'mechanical conditioning' (see for instance the second straining in Fig. 1 of ref.[2] there was no evidence of clear curvature of the specimen in the elastic regime.

As soon as one observed the curvature, an irreversible structural phenomenon also appeared. Thus I am not refuting Dr Nissan's theory of 'a second coefficient of elasticity'. All I am pointing out is that it does not seem to have any practical significance at all. This is actually quite natural because paper is not a hydrogen bonded continuum, where one can define various fundamental phenomena to be specific only to certain strain levels. On the contrary —because of the distinct structural elements of the consolidated cell wall— one has different types of strain related structural phenomena going on at any level of strain.

4. Dr Nissan states that the BET construct w_m, designating monolayer coverage, is the critical moisture content where regime (*1*) ends and regime (*2*) begins. What I wanted to find out was the physical significance attached to w_m. If it is interpreted as a monolayer coverage, the recently obtained results of the surface area of cellulosic fibres, which suggest that the old BET areas smaller by a factor of 3, would increase the moisture content of monolayer coverage by a factor of 3 and seriously mix up the boundary between Dr Nissan's regimes (*1*) and (*2*). However, as pointed by Dr Nissan, consideration of surface areas and monolayer coverages is not at all necessary for the derivation of Dr Nissan's theory of E vs. w.

In my thesis work paper samples were also tested at 11 per cent r.h. and at 48 per cent r.h. The corresponding moduli values are 7, 1 kN/cm² and 5,9 kN/cm². The modulus at 0 per cent r.h. (dry nitrogen) was 7·6 kN/cm². The corresponding moisture contents were about 2 per cent (estimated) and 5 per

cent. Using Dr Nissan's equation (*6*) one obtains for the predicted values $E_{11\%} = 7\cdot45$ and $E_{48\%} = 7\cdot32$. I am not in a position to comment on the significance of these differences.

However, it seems to me that the selection of the value for w_c is very critical for the value of the correlation coefficient between observed and predicted results in case one is not using the correlation between the logarithms of the dry and moist moduli.

One interesting point that was observed during the referred thesis work was that paper was adsorbing moisture from the surrounding gas phase during straining. For the elastic regime the amount of water adsorbed was about 0·1 per cent. During destraining this adsorbed water was desorbed. The fact that the moisture content of the paper sample was not constant during the straining makes also questionable Dr Nissan's H-bond continuum treatment of the elastic modulus vs. moisture content.

In my thesis, I reasoned that the adsorbed moisture during straining, amounting from 0·1 to 0·2 per cent is not related to a bulk sorption phenomenon. Instead—it was postulated—it is related to coverage of surface area made accessible by straining. However, it was not possible to state whether all these areas became accessible due to the breakage of interfibre bonds or whether part of it became accessible because of separation of surfaces that were in very close contact but not molecularly bonded before the straining.

This experimental observation does not agree with the 'static' assumption of the moisture content made by Dr Nissan. It is also questionable whether one can use the 'elastic modulus' of hydrogen bonds in such a case, where a strain induced increase in the moisture content of the paper sheet is actually affecting the local contribution of the structure (not a continuum) to the overall elastic modulus.

5. The word 'dangerous' in my first contribution is not used to state that Dr Nissan's theory is able or likely to inflict injury. I used the work as a synonym to the word 'risky', i.e. it is possible that by concentrating solely on the role of hydrogen bonds when explaining the behaviour of paper one is not passing beneficial and directly applicable information on the coming generations of paper scientists and practical papermakers. For fear of not seeing the forest for the trees, let us not concentrate too much on the hydrogen bonds!

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