H-Bond Dissociation in Hydrogen Bond Dominated Solids

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ABSTRACT: Hydrogen bond dominated solids are those for which the mechanical properties are controlled primarily by the number of H bonds per unit volume N and the properties of such a bond and only to a minor extent by contributions from conformational entropy or other bonds. Young's modulus for such materials is related to N by $E = kN^{1/3}$ where k is determined by H-bond parameters. For such solids: (1) E decreases drastically on wetting; (2) under constant strain, stress decreases indefinitely. Here, these phenomena are related to corresponding decreases in N. Thus, rheological problems are translated into problems of chemical kinetics of the dissociation of H bonds in one of three regimes. Regimes 1 and 2 are manifested on wetting; regime 3 in stress relaxation. In regime 1 dissociation takes place singly; in regimes 2 and 3, a number of bonds appear to break cooperatively. Another distinction exists between regime 2 and 3: In regime 2, a single bond breaks unimolecularly but triggers a number of other bonds to break apparently "simultaneously". In regime 3, truly polymolecular reactions of high orders in N take place. Equations are derived for each regime and are checked against all data available to the author. Regimes 1 and 2 are discussed in part I and regime 3 in part II.

The class of solids under study is that of hydrogen-bonded solids, the mechanical properties of which are predominantly controlled by the number of such bonds per unit volume and the characteristics of such bonds. Contributions from conformational entropy or covalent, ionic, or van der Waals' bonds are of only minor significance. The prototype is, of course, ice, but the thrust of this study is toward understanding some of the mechanical behavior of fibers or sheets made of cellulose, e.g., paper, regenerated cellulose in rayon fibers and viscose sheets, and to a certain extent natural cellulose fibers like cotton, of unstretched and low stretch Nylon and (again to a certain extent) wool. Reservations are made about cotton, highly stretched rayon fibers, and viscose sheets or Nylon fibers because in these well-ordered materials the covalent backbones of the molecules contribute significantly in taking up the load. Similarly, reservations exist about wool because the disulfide bonds of cystine, in parallel with the hydrogen bond, take an active part in resisting, say, a tensile load. But even with these materials, cotton, ramie, Nylon 66 at high stretch, and wool, the reversible loss and gain in Young's modulus on wetting and drying respectively is expected, and found, to be primarily a function of the number of hydrogen bonds per unit volume of the material.

In previous publications,[1] Young's modulus E was shown to be related to the number of *effective* hydrogen bonds per unit volume, N, by the simple equation

$$E = kN^{1/3} \qquad (1)$$

If E is measured in dyn/cm^2 and N in number of bonds per cm^3, k for cellulose turns out to be equal to 8×10^3, approximately. In an isotropic, H-bond dominated solid of a total number of bonds per cm^3 N_T, available for taking up a load and which are of random orientation in space, it is shown that N calculated from eq 1, on the basis of a tensile experiment in one-dimensional stretching, is equal to $(N_T/3)$. By "available for taking up a load" is meant that they are not sterically hindered or otherwise protected from participating in resisting a stretch imposed on the material.

Two major rheological characteristics of these materials are: (1) a reversible loss, often drastic, in magnitude of E on wetting (paper which has not been especially treated to resist the effects of water looses almost all of its stiffness when wet and regains it completely on drying); (2) continuous stress relaxation at constant stretch with time. In the previous publications mentioned,[1] it was postulated that the observed losses were due to the break-up of hydrogen bonds on wetting or under stress, i.e., an actual diminution in N. This hypothesis and eq 1 then convert the rheological experiments of measuring E at different moisture contents, or of stress relaxation under constant stretch, into problems of the chemical kinetics of H-bond dissociation since E is a simple and direct measure of N, the number of H bonds per unit volume.

In the present paper, it will be shown that hydrogen bonds dissociate in one of three modes or regimes. Regimes 1 and 2 take place on wetting H-bond dominated solids while regime 3 appears in stress relaxation experiments. However, while regimes 2 and 3 manifest cooperative phenomena which are absent in regime 1,they do so in totally different manners.

I. Effects of Water on E

Before deriving the equations describing the relationships of E, Young's modulus, and w, the regain or water content in grams of H_2O per gram of solid for H-bond dominated solids, it will be found useful to summarize briefly two concepts:

(1) Frank and Wen's flickering cluster concepts of the behavior of hydrogen bonds, particularly in water.

(2) What is meant by "bond-breaking" when, say, cellulose adsorbs water.

Frank and Wen[2] considered the nature of the hydrogen bond and concluded 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' ".

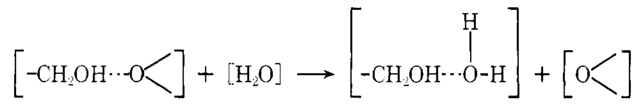
In the present paper I postulate that hydrogen bonds break down cooperatively in accordance with Frank and Wen's concepts: one bond breaking and triggering others to break to a total of $(\overline{\text{C.I.}})$ bonds breaking cooperatively where $(\overline{\text{C.I.}})$ is the average cooperative index.

Second, 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., structure I below.

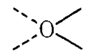
This bond, if in the disordered or paracrystalline portion of the cellulosic network and "accessible", will contribute to the resistance offered by the network to a tensile stress and will, therefore, be counted in N. If a water molecule intervenes and gives structure II, the bond is clearly "broken" 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. The fact that ir absorption still shows no free OH is explainable by postulating that the H_2O molecule forms hydrogen bonds between its hydrogens and oxygens on the same chain which contains the CH_2OH. Furthermore, we can see that one water molecule "broke" one hydrogen bond; I will say of this reaction that it is "unimolecular".

Thus, 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 I, i.e.,



I II

Because of the action of Frank and Wen's postulated mechanism in bond breaking, both in regime I and in regime II, 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, the BET monomolecular layer. 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 one-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 cooperative index C.I. The average C.I. for the whole range of $w_c \leqslant w \leqslant w_{\text{saturation}}$ 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.

Regime 1 will operate when $0 \leqslant w \leqslant w_c$, where w_c is postulated to be equal to w_m. Before deriving the equations for regimes 1 and 2, we need to define two quantities: N_0 and W. N_0 is the number of effective hydrogen bonds in the material at $w = 0$. W is the hypothetical quantity of water required to provide one molecule for each OH on the cellulose molecule (and similar potentially H-donating groups on other H-bonding polymers). For cellulose, six molecules of H_2O (mol wt = 18) are necessary for each repeating cellobiose unit (mol wt = 324), i.e.,

$$W = (6 \times 18)/324 = \tfrac{1}{3} \tag{2}$$

Let the effective number of H bonds per cm^3 be N at regain w. N and w can be normalized by dividing by N_0 and W respectively, so that (N/N_0) moves from 1 toward 0 as (w/W) changes from 0 toward 1. In regime 1 we postulate a unimolecular reaction according to

$$\mathrm{d}(N/N_0)_1 = -(N/N_0)_1 \mathrm{d}(w/W) \tag{3}$$

where the suffix 1 denotes "regime 1". Thus

$$\ln (N/N_0)_1 = -w/W + A \tag{4}$$

Since, when $(w/W) = 0$, $\ln (N/N_0)_1 = 0$, then $A = 0$. Hence,

$$\ln (N/N_0)_1 = -w/W \tag{5}$$

But from (1) $N = (E/k)^3$

$$\ln (E/E_0)_1 = -\tfrac{1}{3}(w/W) \tag{6}$$

Equation 6 is the general equation for regime 1 for all H-bonded fibers and sheets. Specifically, for cellulose, $W = \tfrac{1}{3}$ and eq 6 simplifies to

$$\ln (E/E_0)_1 = -w \tag{7}$$

Regime 2 will operate when $w \geqslant w_c$. In this regime we will invoke Frank and Wen's dictum ". . . when one bond breaks, then typically, a whole cluster will 'dissolve'." Thus, eq 3 is changed to eq 8, where $(\overline{\text{C.I.}})$ is the average cooperative index denoting, on average, the total number of H bonds breaking, including the trigger, when one such bond triggers others by breaking itself. The reaction is still first order in (N/N_0):

$$\mathrm{d}(N/N_0)_2 = -(\overline{\text{C.I.}})(N/N_0)_2 \, \mathrm{d}(w/W) \tag{8}$$

with initial condition that at $w = w_c$, eq 5 gives:

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

The suffix "2" denotes "regime 2", and the suffix "w_c" denotes "at $w = w_c$". Hence,

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

with

$$A = (w_c/W)\,[(\overline{\text{C.I.}}) - 1] \tag{11}$$

or

$$\ln (N/N_0)_2 = (w_c/W)[(\overline{\text{C.I.}}) - 1] - (\overline{\text{C.I.}})(w/W) \tag{12}$$

This is the general equation for regime 2 for all H-bonded fibers and sheets. For cellulose, specifically, $W = \tfrac{1}{3}$ and eq 12 simplifies to

$$\ln (N/N_0)_2 = (3w_c)[(\overline{\text{C.I.}}) - 1] - 3(\overline{\text{C.I.}})w \tag{13}$$

Using eq 1 yields, again for cellulose specifically,

$$\ln (E/E_0)_2 = w_c[(\overline{\text{C.I.}}) - 1] - (\overline{\text{C.I.}})w \tag{14}$$

Thus, in general,

$$\ln (E/E_0)_2 = A - Bw \tag{15}$$

where

$$A = \tfrac{1}{3}(w_c/W)[(\overline{\text{C.I.}}) - 1] \tag{16}$$

and

$$B = \tfrac{1}{3}(\overline{\text{C.I.}})/W \tag{17}$$

Thus, from a plot of $\ln (E/E_0)$ vs. w the slope B can be used, with knowledge of W to calculate $(\overline{\text{C.I.}})$, which in turn can be combined with the intercept A to calculate w_c. It is, however, more satisfying if these two parameters could be predetermined from nonrheological data or, at least, related to such data.

It has already been stated that w_c is postulated to equal w_m, the monomolecular layer adsorption of water as calculated by BET equations. Since many polymers, and cellulose in particular, show hysteresis when adsorption curves are compared with desorption, w_c should be taken to be w_m on the adsorption curves as breakdown of H bonds takes place on wetting and bonding occurs on drying.

To get a predetermined value for $(\overline{\text{C.I.}})$, appeal is made to Starkweather's studies on the clustering of water molecules on cellulose.[3] Starkweather calculated the number of H_2O molecules per cluster as they adsorbed on polymers, e.g., cel-

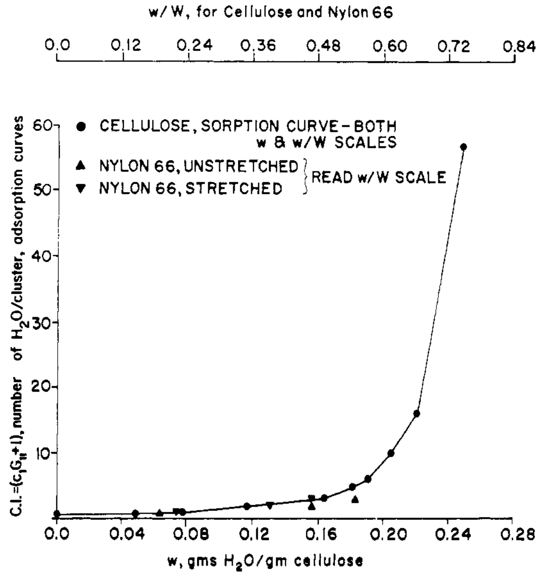


Figure 1. Number of H_2O/cluster as calculated by Starkweather[3] for cellulose, up to $w = 0.212$, and by Némethy and Scheraga[5] for liquid water, assumed the same for saturation value of $w = 0.25$, and for both cellulose and Nylon 66 vs. w/W.

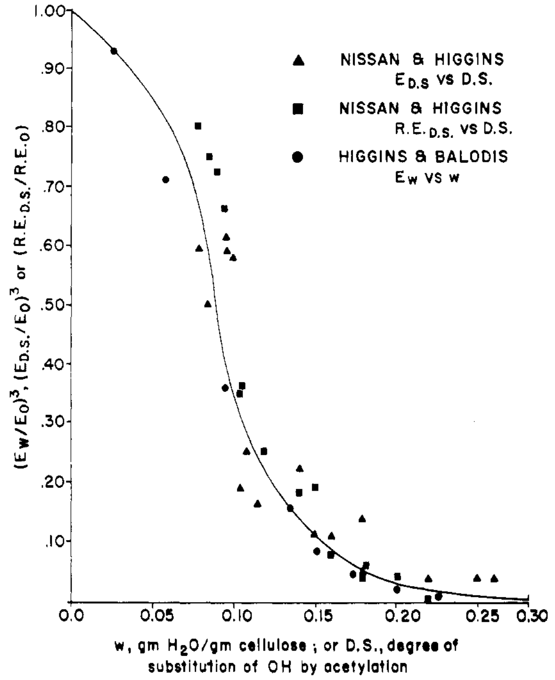


Figure 2. The relationships of E^3 with w and D.S. and of R.E. on D.S.

lulose, for different values of regain w. In Figure 1, I have replotted Starkweather's calculations for cellulose vs. w up to $w = 0.221$. It is very difficult to get values for the number of H_2O/cluster for higher regains. He states that at higher values of w, the data indicate "indefinitely large clusters". There is need to plot a number for w at saturation which, for the cotton cellulose studied by Starkweather, was reported by the experimenters[4] to be 0.25 g H_2O/g cellulose. Reasoning that at saturation water on adsorption behaves very much as if it were condensing on liquid water, I adopted Némethy and Scheraga's[5] value of 57 H_2O/cluster for water in bulk as an upper bound to apply at room temperature. Starkweather's curve extrapolates smoothly to this figure at $w = 0.25$.

In order to correlate the number of H_2O molecules per cluster for Nylon 66, it was found that a plot against w/W gave a reasonable fit for both Nylon 66 and cotton cellulose. (W for cellulose = $\frac{1}{3}$; W for Nylon 66 = 0.1593.) The significance of this plot will appear later when Nylon 66 data are analyzed.

Figure 1 gives the number of H_2O molecules per cluster, whereas we need an average number of H bonds on the cellulose acting cooperatively. The following was used to obtain $(\overline{\text{C.I.}})$ from Starkweather's calculations shown in Figure 1.

Starkweather's numbers of H_2O/cluster could describe one of several situations: (a) a number equal to $(\overline{\text{C.I.}})$ molecules of water clustered around and anchored to one OH group of cellulose in a "piggyback" formation; (b) a number of OH groups equal to $(\overline{\text{C.I.}})$, each with one H_2O molecule attached as in structure II, act cooperatively in adsorbing water from or releasing water to the atmosphere; (c) any one of many intermediate forms between (a) and (b). Experiments reported by Nissan and Higgins[6] coupled with experiments by Higgins and Balodis[7] reported from the same laboratory on paper and similar experiments by others indicate that (b) is probably the situation.

In the experiments reported by Nissan and Higgins, a sample of pulp was acetylated to different degrees of substitution (D.S.), made into handsheets of paper, and the modulus $E_{\text{D.S.}}$ as well as its rupture energy $\text{R.E.}_{\text{D.S.}}$ were measured at two different temperatures. (Rupture energy is the area, up to failure, under the tensile stress–strain curve.) A plot of $(E_{\text{D.S.}}/E_0)$ vs. D.S. fell on the same plot of $(\text{R.E.}_{\text{D.S.}}/\text{R.E.}_0)$ vs. D.S. indicating that N [measured by R.E. = N(r.e.) where r.e. = the rupture energy of a single H bond] is the same as measured by R.E. and by E^3. This fact was important in developing the theory connecting E^3 with N. What is of more importance to the present study is a later determination of the modulus E_w at regain w for regular paper by Higgins and Balodis gave a plot of $(E_w/E_0)^3$ vs. w which fell on the same curve. Other plots of (E_w/E_0) vs. w for cellulosics by other laboratories also fall on the same curve. The loss in E^3 and in R.E. follows regime 1 up to w or D.S. of approximately 0.05. Beyond this value for w or D.S., regime II breakdown of H bonds is observed where the cooperative phenomena described take charge. Thus, whether the OH of cellulose is broken by water or blocked by acetylation, the same cooperative mechanism which gives the loss in E applies. In other words, it is not solely the fact that water is the molecule of concern but the OH groups themselves which are breaking and which determine the cooperative phenomena in regime 2.

Thus, Figure 2 encouraged the author to take Figure 1 to give not only the number of H_2O/cluster but *also* the number of H bonds breaking cooperatively. A graphical integration of the curve on Figure 1 between $w = 0$ and $w = 0.25$ and dividing by 0.25 gave the mean $(\overline{\text{C.I.}}) = 6.71$.

Hence, it is postulated that in eq 15 $(\overline{\text{C.I.}})$ for cellulose and Nylon 66 = 6.71 and $w_c = w_m$. The following values of w_m have been reported as applicable to cellulose, hemicellulose, lignin (all components of paper):[8] cotton cellulose, 0.03 g H_2O/g solid; holocellulose, 0.06; sulfite pulp, 0.04; lignin, 0.05; rayon and other regenerated cellulose, 0.06; wood, 0.04–0.05. Thus, values for paper will be 0.04–0.06, depending on the pulp used and the proportions of cellulose, hemicellulose, and lignin in the paper; 0.05 g H_2O/g paper is probably the best value to be expected.

Inserting $w_c = 0.05$ and $(\overline{\text{C.I.}}) = 6.71$ in eq 14 for cellulosics, specifically, we get

$$\ln (E/E_0)_2 = 0.286 - 6.7w \qquad (18)$$

Equation 18 can only give the *average* behavior of cellulosic papers and fibers or sheets; individual samples will vary according to their individual composition.

Verification. (1) Paper. In ref 1, data were presented to verify regime 1 for paper. There are not many data for giving E for $w < 0.05$, but all such data, except one, verified eq 7. The exception was one set of data by Craver and Taylor[9] which was embarrassingly too supportive. Measurements of E by a sonic method at different values of w yielded results in good agreement with eq 7, right up to saturations. Thus, while these experiments confirm the equation for regime 1, it is difficult to understand why the agreement goes up to saturation when, as we shall see presently, all other experiments (except one other set also measured sonically) show a sharp break into regime 2 at $w = 0.05 \pm 0.01$. We shall return to this point briefly later.

Many more data exist for regime 2. I have collected all I could in the form of tables or graphs. In some, E_0 was also given; otherwise, I either calculated E_0 from E at the lowest value of w by means of eq 7 or read it off the graphs by smooth extrapolation. Performing a regression analysis of ln (E/E_0) on w for $w \geqslant 0.05$ for all available data gave the following:

(1) Andersson and Berkyto[10]

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

(2) Higgins and Balodis[7]

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

(3) Benson[11] reported on six papers of which I analyzed four representing the boundaries for the range of curves: (a) Experimental Lake State, M.D.

$$\ln (E/E_0)_2 = 0.218 - 5.967w;\ r^2 = 0.995 \qquad (21)$$

(b) Commercial Southern, M.D.:

$$\ln (E/E_0)_2 = 0.224 - 6.071w;\ r^2 = 0.992 \qquad (22)$$

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

$$\ln (E/E_0)_2 = 0.248 - 6.597w;\ r^2 = 0.991 \qquad (23)$$

(d) Commercial Southern, C.D.:

$$\ln (E/E_0)_2 = 0.294 - 7.276w;\ r^2 = 0.975 \qquad (24)$$

(e) All four "papers", together:

$$\ln (E/E_0)_2 = 0.244 - 6.456w;\ r^2 = 0.993 \qquad (25)$$

(4) Riemen and Kurath[12]

$$\ln (E/E_0)_2 = 0.177 - 7.595w;\ r^2 = 0.997 \qquad (26)$$

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

$$\ln (E/E_0)_2 = 0.162 - 6.054w;\ r^2 = 0.995 \qquad (27)$$

(6) J. P. Brezinski[13]

$$\ln (E/E_0)_2 = 0.287 - 5.680w;\ r^2 = 0.982 \qquad (28)$$

If equal weights are given to all these equations, but omitting eq 25 and 27 since they are represented by eq 21 through 24 and eq 26, respectively, we obtain an average for $(\overline{\mathrm{C.I.}})$ of 6.704 ± 0.894 (the latter is the standard deviation). The figure obtained from averaging Starkweather's data of Figure 1 was 6.71.

Second, it is possible to calculate w_c from the intercept of each of these equations by eq 16. The values so obtained for eq 19 through 28 are respectively: 0.060; 0.048; 0.044; 0.044; 0.044; 0.047; 0.045; 0.027; 0.032; 0.061. Again omitting the seventh figure for eq 25 and the ninth, eq 27, to avoid duplication, the average for w_c is obtained as $\overline{w}_c = 0.047 \pm 0.011$ against an expected value of 0.05 ± 0.01 from BET equations giving the monolayer value.

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.[9]

The second deviation from theory is work reported by Caulfield.[14] This work also measures E sonically by measuring the speed of a stress pulse in the paper. This work appears to fit the equation:

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

Again, why $w_c = 0.000$ and $(\overline{\mathrm{C.I.}})$ is approximately one-half those reported by others is not easy to explain.

(2) Other Cellulosics. The effects of moisture on the torsional rigidity at regain w, G_w, of ramie, mercerized cotton, Fortisan, viscose rayon, Nylon, and wool are reported by Meredith.[15] Cellulose is the primary constituent of the first four fibers. If it is assumed that $G_w/G_0 = E_w/E_0$, Meredith's results can be analyzed here for verification of the equations for regime 2.

Meredith gave an empirical relationship linking (G_w/G_{65}) to w/w_{65} at 25 °C for all four cellulosic fibers:

$$\ln (G_w/G_{65}) = -0.82\,[(w/w_{65}) - 1] \qquad (30)$$

where the suffix "65" denotes "at 65% relative humidity". To render Meredith's empirical equation in terms of the present study, it is transformed to

$$\ln (G_w/G_0)_2 = [0.82 - \ln (G_{65}/G_0)] - (0.82/w_{65})w \qquad (31)$$

Values read off Meredith's paper for ln (G_{65}/G_0) and w_{65} for each of the four cellulosic fibers, for adsorption and desorption, were averaged [since eq 30 and 31 only use averages] and found to give ln $(G_{65}/G_0) = -0.862 \pm 0.090$; $w_{65} = 0.112 \pm 0.027$. Inserting these values into eq 31 yields

$$\ln (G_w/G_0)_2 = (-0.042 \pm 0.09) - (7.72 \pm 2.7)w \qquad (32)$$

Thus, $(\overline{\mathrm{C.I.}})$ for all cellulosics studied by Meredith is (7.72 ± 2.7) against the Starkweather average of (6.71) and the average for all papers studied of (6.7 ± 0.9). The value for w_c was indeterminate as the standard deviation was approximately twice the value of the mean.

As further examples, detailed regression analyses were performed on the data presented for viscose rayon (an example of regenerated, less ordered cellulose) and ramie (natural, highly ordered cellulose). The results were as follows. Viscose rayon $(\overline{\mathrm{C.I.}})$: adsorption = 8.658; desorption = 8.442; mean $(\overline{\mathrm{C.I.}}) = 8.55 \pm 0.15$. w_c: absorption = 0.042; desorption = 0.042; mean $w_c = 0.042$. For ramie $(\overline{\mathrm{C.I.}})$: adsorption = 6.707; desorption = 6.701; mean $(\overline{\mathrm{C.I.}}) = 6.70 \pm 0.00$. w_c: adsorption = negative; desorption = negative; mean = negative. Thus, while the values for $(\overline{\mathrm{C.I.}})$ are reasonable and w_c for viscose rayon is as predicted, the values for w_c for ramie obtained from the regression are paradoxically negative.

(3) Nylon 66. Another hydrogen-bonded fiber is Nylon 66. While its moduli are greatly influenced by the covalent bonds, it is hypothesized here that the effect of moisture on these parameters will be through the break-up of hydrogen bonds by the cooperative mechanism under study.

The primary repeating units in Nylon 66 are [$-\mathrm{CO(CH_2)_4CONH(CH_2)_6NH}-$]. 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,[15] Adams,[16] and Quistwater and Dunell[17,18] were analyzed and gave the results in Table I averaged for different frequencies used in the tests.

In Table I, $(\overline{\mathrm{C.I.}})$ was calculated in accordance with eq 17, which gives $B = -(\overline{\mathrm{C.I.}})/3W$. For Nylon 66, $W = 0.1593$. Similarly, $A = \frac{1}{3}[(\overline{\mathrm{C.I.}}) - 1]w_c/W$, and having calculated $(\overline{\mathrm{C.I.}})$,

Table I

Author	Property studied and conditions	ln (property$_w$/property$_0$) = $A - Bw$	($\overline{\text{C.I.}}$)	w_c	Eq No.
Meredith[15]	G/G_0, 25 °C	$A = 0.030$; $B = 15.254$	7.290	2.3×10^{-3}	33
Adams[16]	G/G_0, undrawn	$A = 0.078$; $B = 20.263$	9.684	6.5×10^{-4}	34
	G/G_0, drawn	$A = 0.089$; $B = 16.233$	7.758	9.3×10^{-4}	34
Quistwater and Dunell[17]	E/E_0, 35 °C (100 s^{-1})	$A = 0.1371$; $B = 12.297$	5.877	4.0×10^{-3}	35
Quistwater and Dunell[18]	E/E_0, 9 °C (150 s^{-1}, 20 s^{-1})	$A = 0.1785$; $B = 7.2215$	3.4512	1.16×10^{-2}	35
	E/E_0, 60 °C (150 s^{-1}, 20 s^{-1})	$A = 0.1270$; $B = 12.843$	6.1377	-3.9×10^{-3}	35
		Av	6.70 ± 2.1	0.003 ± 0.005	

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 Figure 5 were plotted in Figure 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 cooperative 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) **Wool.** The remaining hydrogen-bonded fiber studied by Meredith[15] was wool. Similar analyses made on his results gave the following: For adsorption, $0.078 \leqslant w \leqslant 0.33$,

$$\ln (G/G_0) = 0.7716 - 10.5019w;\ r^2 = 0.980 \qquad (36)$$

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

$$\ln (G/G_0) = 0.9044 - 10.9859w;\ r^2 = 0.985 \qquad (37)$$

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[19] discuss the chemical composition of wool and give the approximate residue frequencies for 18 amino acids, ranging from a low of $\frac{1}{206}$ for histidine and methionine to a high of $\frac{1}{9}$ for cystine. They suggest "an average residue weight of roughly 100", but Meredith himself assumes one hydrogen bond per molecular weight of 122.[15] Hence, W = 0.1475 g H_2O/g dry wool may be taken as a basis to begin with. These data yield: ($\overline{\text{C.I.}}$) for adsorption, 4.647; for desorption, 4.86; mean ($\overline{\text{C.I.}}$), 4.75. Also, w_c for adsorption, 0.0312; for desorption, 0.034; mean w_c, 0.033. If the molecular weight of the repeating unit was taken as 100, mean ($\overline{\text{C.I.}}$) would be (5.8 ± 0.2) and mean w_c 0.031.

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 ($\overline{\text{C.I.}}$) 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 disulfide linkages could interfere with the cooperative 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 [($\overline{\text{C.I.}}$) − 1] others so that a total of ($\overline{\text{C.I.}}$) bonds break "simultaneously". The value of ($\overline{\text{C.I.}}$) as predetermined from averaging Starkweather'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 cooperatively, is 6.71. Against this figure, paper samples in different laboratories gave 6.7 ± 0.9 (with the exception of two sets of experiments using sonic methods); a group of cellulosic fibers gave (7.72 ± 2.7); Nylon 66 in four sets of experiments gave (6.7 ± 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 [with ($\overline{\text{C.I.}}$) = 4.8] is 6.5. With ($\overline{\text{C.I.}}$) for wool taken as 5.8, the mean for ($\overline{\text{C.I.}}$) = 6.7. Omitting wool, mean ($\overline{\text{C.I.}}$) = 7.0.

The values postulated for w_c were to be the values obtained for the monomolecular adsorption of water as calculated by BET 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.

II. Cooperative Phenomena in Stress Relaxation

In stress relaxation experiments, a sample of length l is stretched by a fixed amount δl and kept so stretched for the duration of the experiment under constant temperature and relative humidity. The force F_t at time t is observed. Dividing the force F_t by the constant area of the sample gives the stress σ_t at time t for constant stretch δl or constant strain $\epsilon = \delta l/l$. It is found that for paper and other cellulosic materials σ_t decreases with time continuously, even for small values of the constant strain.

For purposes of the present study, we need N_t, the values of N at time t, vs. t. Thus, there are two sets of arithmetical operations which should be understood before the theory of cooperative H bond breaking under stress can be utilized:

(1) σ_t has to be transformed to E_t, the modulus at time t.

(2) transforming E_t to N_t at any temperature used for the experiment.

(1) **Transforming σ_t to E_t.** The method to be used depends on the magnitude of the strain ϵ. For $\epsilon < 0.005$, E_t can simply be taken as equal to (σ_t/ϵ). For higher strains, allowance must be made for the intrinsic curvature of the stress–strain plot for H-bond dominated solids. This curvature in the stress–strain relationship is intrinsic and reversible, over and above any curvature due to irreversible creep or stress relaxation taking place during the experiment. In ref 1, the relationship of stress to strain in terms of N and the characteristics of the H bond is derived, and it is shown that for moderate strains, up to, say, $\epsilon = 0.01$, an approximation may be used:

$$\sigma = E\epsilon - 1.2 \times 10^{12}\epsilon^2 \tag{38}$$

when σ is measured in dyn/cm². Thus,

$$E_t = (\sigma_t/\epsilon) + 1.2 \times 10^{12}\epsilon \tag{39}$$

Equation 39 takes into account only the first two terms of an infinite series. If $\epsilon > 0.01$, it is necessary to use the full eq 40 by means of which E can be calculated by reiteration. Generally, two or three reiterations are sufficient.

$$\sigma_t = 1.22 \times 10^{-12}E_t^{\,2}[1 - \exp(-8.19 \times 10^{11}\epsilon/E_t)] \times [\exp(-8.19 \times 10^{11}\epsilon/E_t)] \tag{40}$$

Although eq 40 yields values for E_t from somewhat large strains, perhaps a warning against using large strains for the purposes of studying the kinetics of H-bond breaking is in order. Equations 39 and 40 assume that the strain remains constant at its original value at $t = 0$. This is more nearly the fact the smaller the strain is. At higher strains, creep and molecular ordering may render analysis less rigorous.

Another reservation should be made clear at this point. Since σ_t decreases continuously with t, then eq 39 and 40 indicate that E_t decreases continuously with time. Yet, if at time t the sample is released from the strain originally imposed at $t = 0$ and E is measured immediately it may be found very much higher than E_t calculated (by, say, eq 40) at the instant of stress release. [Another way is to measure E dynamically, i.e., $(E_t)_D$ while the $(E_t)_s$ is being independently calculated from σ_t which is recorded statistically, under the constant strain ϵ. $(E_t)_D$ will be found larger than $(E_t)_s$ and may, in fact, be a constant with time.] This apparent paradox is explainable by visualizing the H bonds breaking under stress to yield a continuously decreasing E_t but immediately rebonding in new positions carrying no stress to yield a high $(E_t)_D$ or a high E for the sample when released from stress and its modulus remeasured, since in this new measurement all bonds will be subjected to stress (i.e., those remaining intact and those which broke and rebonded) while E_t measures only those bonds which were originally subjected to stress and which are still intact at time t.

2. **Calculating N_t from E_t.** Equation 1 was derived from the H-bond parameters at room temperature to yield a value for k:

$$N_t = (E_t/7780)^3 \tag{41}$$

This value may be used at 20–25 °C. For relaxation experiments performed on cellulosic materials at greatly different temperatures $E_t^{\,20°\mathrm{C}}$ should first be calculated from $E_t^{\,T°\mathrm{C}}$; $N_t^{\,20°\mathrm{C}}$ is then calculated and retransformed to $N_t^{\,T°\mathrm{C}}$ as follows:[1]

$$E_t^{\,20°\mathrm{C}} = \exp[\ln E_t^{\,T°\mathrm{C}} - 35(20 - T°\mathrm{C})\,\mathrm{d}\ln L/\mathrm{d}T] \tag{42}$$

where $(\mathrm{d}\ln L/\mathrm{d}T)$ is the linear thermal expansion coefficient for the specimen. If this parameter is not known

$$E_t^{\,20°\mathrm{C}} = \exp[\ln E_t^{\,T°\mathrm{C}} - 4 \times 10^{-3}(20 - T\ °\mathrm{C})] \tag{43}$$

Then, eq 41 can be used to calculate $N_t^{\,20°\mathrm{C}}$ from $E_t^{\,20°\mathrm{C}}$ so calculated. Then

$$N_t^{\,T°\mathrm{C}} = N_t^{\,20°\mathrm{C}}(\rho^{T°\mathrm{C}}/\rho^{20°\mathrm{C}}) \tag{44}$$

$$= N_t^{\,20°\mathrm{C}}[1 + (20 - T\ °\mathrm{C})\,\mathrm{d}\ln L/\mathrm{d}T]^3 \tag{45}$$

$$= N_t^{\,20°\mathrm{C}}[1 + (20 - T\ °\mathrm{C})(1.14 \times 10^{-4})]^3 \tag{46}$$

where $\rho^{T°\mathrm{C}}$ is the density at T °C.

As we shall see presently, since most of the analyses utilize the ratios (E_t/E_0) and (N_t/N_0), where the suffix 0 denotes "at time $t = 0$", eq 41 to 46 are only infrequently used to determine N_0.

3. **The Kinetics of H Bond Breaking under Stress.** The basic assumption in the theory under discussion is that σ_t, and consequently E_t, decrease with time because N_t decreases with time as H bonds break under stress cooperatively. The number of bonds breaking together, i.e., the "cooperative index", is designated α to distinguish it from the other cooperative index (C.I.) since in stress relaxation the kinetics are of reactions of order α and not unimolecular as with the breakdown on wetting.

The kinetics of cooperative dissociation of H bonds under stress are developed in ref 1 and fully elaborated by Sternstein.[20] Here, the equations will be given without elaborate explanations and then will be used to analyze new, extensive data on the relaxation of regenerated cellulose published by Haughton and Sellen in 1973.[21]

It has been shown[1] that once relaxation has proceeded to the extent that (E_t/E_0) is, say, less than 0.9, a single parameter α_1, which I call "the principal cooperative index", controls the dissociation of the H bonds:

$$-\mathrm{d}(N/N_0)/\mathrm{d}t = k(N/N_0)^{\alpha_1} \tag{47}$$

The suffix t is dropped henceforth for simplicity of notation. Equation 47 yields, when $(N/N_0)^{1-\alpha_1} \gg 1$ and $\alpha > 1$,

$$\mathrm{d}\log(N/N_0)/\mathrm{d}\log t = 1/(1 - \alpha_1) = \beta \tag{48}$$

Equation 48 was found to describe the behavior of relaxation of regenerated cellulose reported by Meredith as a composite or "master" curve for 16 decades of time in seconds.[1] Sternstein[20] elaborated these ideas to cover the full range of relaxation from $t = 0$ up to indefinitely large times. He found a much more complex behavior to govern the full curve, involving an infinite series of polymolecular reactions, each with order α_i and reaction rate constant k_i, but which quickly degenerated to the single polymolecular reaction with principal cooperative index α_1. Thus, Sternstein found two basic sets of equations: (a) in the integrated (empirical form), and (b) in differential form (analytical). The two equations are interconnected as follows: (a) Integrated form, empirical

$$(N/N_0)^{1-\alpha} - 1 = k(\alpha - 1)t^m \tag{49}$$

or

$$\log[(N/N_0)^{1-\alpha} - 1] = \log k + \log(\alpha - 1) + m\log t \tag{50}$$

Thus, by plotting the lhs of (50) vs. $\log t$, for various assumed values of α, the best straight line is determined from which the basic parameters α and m are determined. (In the present analysis, the best value of α is determined analytically in three ways to give the "best fit" for a straight line. This will be discussed below.) (b) Differential form, analytical: differentiating (49) yields

$$-\mathrm{d}(N/N_0)/\mathrm{d}t = kmt^{m-1}(N/N_0)^{\alpha} \tag{51}$$

$$= k'(N/N_0)^{\alpha}[(N/N_0)^{1-\alpha} - 1]^{(m-1)/m} \tag{52}$$

where

$$k' = m[(N_1/N_0)^{1-\alpha} - 1]^{1/m}/(\alpha - 1) \tag{53}$$

and $N_1 = N$ at $t = 1$ s. When eq 51 is expanded in a Taylor series, we get:

Table II
Relaxation Parameters for Sternstein Experiment No. 1

Temp, °K	314
Strain, ϵ	0.0071
Initial stress, σ_0, dyn/cm^2	6.06×10^8
Initial modulus, E_0, dyn/cm^2	9.38×10^{10}
Initial hydrogen bond concentration, N_0, bonds/cm^3	1.75×10^{21}
c_0, mol/l.	2.92

$\alpha = 3.0$	$\alpha_1 = 4.4$	$k_1 = 11.8 \times 10^{-3}$
$m = 0.59$	$\alpha_2 = 6.4$	$k_2 = 8.20 \times 10^{-3}$
$k' = 0.0118\ \mathrm{s}^{-1}$	$\alpha_3 = 8.4$	$k_3 = 6.95 \times 10^{-3}$
	$\alpha_4 = 10.4$	$k_4 = 6.24 \times 10^{-3}$
$N_A/1000N_0 = 0.343$	$\alpha_i = 4.4 + 2(i-1)$	$k_i/k_{i-1} \rightarrow 1.0$ as $i \rightarrow \infty$

		Per mole clusters	Per mole H bonds
$K_1 = 3.10 \times 10^{-4}$	$\Delta F_1 =$	23.3 kcal	5.3 kcal
$K_2 = 2.54 \times 10^{-5}$	$\Delta F_2 =$	24.9 kcal	3.9 kcal
$K_3 = 2.53 \times 10^{-6}$	$\Delta F_3 =$	26.3 kcal	3.1 kcal
$K_4 = 2.67 \times 10^{-7}$	$\Delta F_4 =$	27.7 kcal	2.7 kcal
$K_i/K_{i-1} \rightarrow 0.118$ as $i \rightarrow \infty$		$\Delta F_i - \Delta F_{i-1} \rightarrow 1.33$ as $i \rightarrow \infty$	

$$\frac{-\mathrm{d}(N/N_0)}{\mathrm{d}t} = \sum_{i=1}^{i=\infty} k_i (N/N_0)^{\alpha_i} \tag{54}$$

to give

$$\frac{-\mathrm{d}(N/N_0)}{\mathrm{d}t} = k' \Bigg[(N/N_0)^{\alpha_1} + \frac{1-m}{m} (N/N_0)^{\alpha_2} + \frac{1-m}{2!m^2} (N/N_0)^{\alpha_3} + \frac{(1-m)(1+m)}{3!m^3} (N/N_0)^{\alpha_4} + \ldots + \frac{(1-m) \prod_{q=0}^{q=i-3} (1+qm)}{(i-1)!m^{(i-1)}} (N/N_0)^{\alpha_i} \Bigg] \tag{55}$$

or

$$\frac{-\mathrm{d}(N/N_0)}{\mathrm{d}t} = k_1 (N/N_0)^{\alpha_1} + k_2 (N/N_0)^{\alpha_2} + \ldots k_i (N/N_0)^{\alpha_i} \tag{56}$$

In this simplified form then:

$$\alpha_1 = (m + \alpha - 1)/m \tag{57}$$

$$\alpha_2 = (m\alpha + \alpha - 1)/m \tag{58}$$

$$\alpha_3 = [m(2\alpha - 1) + \alpha - 1]/m \tag{59}$$

$$\alpha_4 = [m(3\alpha - 2) + \alpha - 1]/m \tag{60}$$

$$\alpha_i = \frac{m[(i-1)\alpha - (i-2)] + \alpha - 1}{m} \tag{61}$$

$$k_1 = k' \tag{62}$$

$$k_2 = [k'(1-m)]/m \tag{63}$$

$$k_3 = [k'(1-m)]/2!m^2 \tag{64}$$

$$k_4 = [k'(1-m)(1+m)]/3!m^3 \tag{65}$$

$$k_i = \frac{k'(1-m) \prod_{q=0}^{i=3} (1+qm)}{(i-1)!m^{(i-1)}} \tag{66}$$

This, then, appears to be the general relaxation equation for hydrogen-bonded networks. A few explanatory comments are necessary. First, note that the Taylor series is really a two-parameter equation in only α and m. These are the two fundamental constants or parameters controlling the change of N or (N/N_0) with time at constant extension. Second, from these two parameters α and m we get a series of α_i's and k_i's denoting the orders of the reaction, i.e., how many hydrogen bonds break down cooperatively in a unit relaxation jump, and the rates of reaction, respectively. The calculations for α_i and k_i from α and m are as given above. Fortunately, these calculations can be simplified. By a little arithmetic we get

$$\alpha_1 = (m + \alpha - 1)/m$$
$$\alpha_2 = \alpha_1 + (\alpha - 1) \tag{67}$$
$$\alpha_i = \alpha_1 + (i-1)(\alpha - 1)$$

Please note that while α_1 is a function of both m and α, the differences between successive α_i's are all equal to $(\alpha - 1)$; m does not appear in them. Thus, the calculation of the different α_i's is extremely simple.

This analysis shows that the relaxation process is controlled by a spectrum of mechanisms, not by one relaxation mode. In this spectrum, α_1, the principal cooperative index is the minimum number of cooperating hydrogen bonds involved in relaxation. Initially, when N/N_0 is close to 1.0, reactions with a number of group sizes are taking place since the rate constants do not drop off rapidly as the group size increases. As N/N_0 becomes significantly less than 1.0, however, the rates of breakdown in larger groups drop off much more rapidly since the rates are proportional to $(N/N_0)^{\alpha_i}$, and this function decreases much more rapidly as α_i becomes larger. Thus, at long times the breakdown is dominated and controlled by the smallest group size, α_1. That is why for relatively low values of N/N_0 the whole equation degenerates into one with d log (N/N_0)/d log t being equal to a negative constant β and

$$\alpha_1 = \frac{\beta - 1}{\beta} = \frac{m + \alpha - 1}{m} \tag{68}$$

For this reason, α_1 was named "The Principal Cooperative Index". (It is interesting to note that this α_1 is, indeed, identical with the α of the original simpler rate eq 47 and 48.)

Now each cooperative index α_i is associated with a reaction rate constant k_i. As we have seen, k_i is a constant multiple of (k_{i-1}), the multiplier being independent of α, but is a function of i and m only. Thus,

$$\frac{k_i}{k_{i-1}} = \frac{i-3}{i-1} + \frac{1}{(i-1)m} \tag{69}$$

As a preliminary illustration in the present study, calculations are presented in Table II where, in addition, use is made of Eyring's absolute reaction rate equation to obtain the free

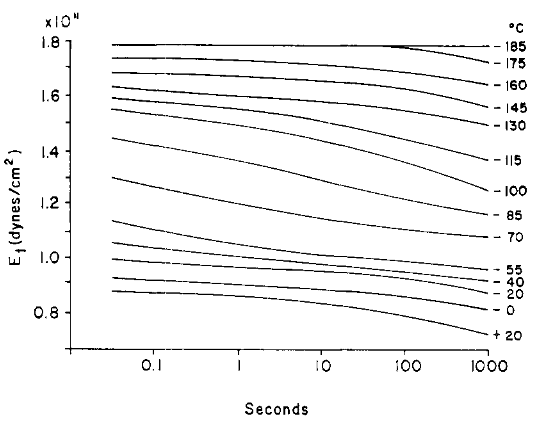


Figure 3. Stress relaxation curves for dried regenerated cellulose at 0.3% strain by Haughton and Sellen.[21]

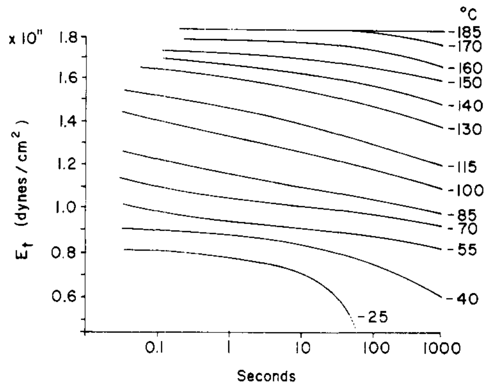


Figure 4. Stress relaxation curves for 75% rhs regenerated cellulose by Haughton and Sellen.[21]

energy of activation from these reaction rate constants, on one of Sternstein's experiments, i.e., Experiment No. 1. This calculation involves conversion of the k's to units based on hydrogen bond concentrations in moles/liter instead of bonds per cubic centimeter. This conversion consists of setting up a rate equation similar to eq 56 for $-\mathrm{d}c/\mathrm{d}t$, where c is molar concentration of hydrogen bonds. The rate constants in this case are K_i's, and it can be shown that K_i equals $k_i(N_A/1000N_0)^{\alpha_i-1}$ where N_A is Avogadro's number. I am not sure whether my use of Eyring's absolute rates is legitimate for reactions of such high order. Nevertheless, I have included in Table II the figures obtained for ΔF per mol of reacting hydrogen bond group and per mole of effective hydrogen bonds as well as the corresponding K's or rate constants based on moles/liter for illustrative purposes.

As can be seen here, the K's decrease by a factor of about 10 for each step to higher α's or to higher reaction orders. Thus, for instance, when the hydrogen bond concentration, c, has gotten down from the original 2.92 to 1.0, the contributions of the various terms to the total reaction rate is directly proportional to the K_i values. Thus, here the α_1 term is responsible for 90% of the reaction rate. At other concentrations, the relative contributions of the various reaction modes are strongly influenced by multiplication of the K_i by the concentration raised to the α_i. For example, at the beginning the higher terms have a much more significant contribution with α_2, for instance contributing 70% as much as α_1. When the concentration gets down to small values, terms above α_1 become vanishingly small.

The table also shows that the free energy is 23.3 kcal/mol of cooperating bond clusters for the α_1 reaction mode and increases gradually for higher modes. This amounts to 5.3 kcal/mol of hydrogen bonds which decreases gradually for the higher modes.

Table III
Determination of Values of N_0 at the Temperature of Experiments of Sternstein and of Haughton and Sellen

Source	Temp, °C	10^{11} $E_0^{20\,°\mathrm{C}}$	10^{22} $N_0^{20\,°\mathrm{C}}$	10^{22} $N_0^{T\,°\mathrm{C}}$
Sternstein 1	41	1.013	0.2208	0.2192
Sternstein 2	36	1.088	0.2735	0.2720
Sternstein 3	30	1.062	0.2544	0.2535
Sternstein 4	57	1.160	0.3315	0.3273
Sternstein 5	50	1.178	0.3471	0.3436
Sternstein 7	37	1.403	0.5865	0.5831
Sternstein 8	27	1.240	0.4049	0.4039
Av		1.163		
Standard deviation		± 0.130		
H & S, dry	20	0.8951	0.1523	0.1523
	0	0.8614	0.1357	0.1376
	−20	0.8600	0.1351	0.1370
	−40	0.8459	0.1285	0.1312
	−55	0.8604	0.1353	0.1388
	−70	0.9256	0.1684	0.1736
	−85	0.9612	0.1886	0.1955
	−100	0.9721	0.1951	0.2032
	−115	0.9383	0.1754	0.1836
	−130	0.9040	0.1569	0.1651
	−145	0.8803	0.1449	0.1532
	−160	0.8515	0.1311	0.1393
	−170	0.8415	0.1265	0.1349
Av		0.892		
Standard deviation		± 0.045		
H & S, 75% rhs	−25	0.6791	0.0665	0.0675
	−40	0.7230	0.0803	0.0820
	−55	0.7610	0.0936	0.0960
	−70	0.8187	0.1165	0.1201
	−85	0.8500	0.1304	0.1351
	−100	0.9058	0.1578	0.1644
	−115	0.9050	0.1574	0.1648
	−130	0.9128	0.1615	0.1699
	−140	0.8960	0.1528	0.1613
	−150	0.8791	0.1443	0.1529
	−160	0.8751	0.1423	0.1512
	−170	0.8597	0.1349	0.1439
Av		0.839		
Standard deviation		± 0.078		

The theory will now be applied to analyze very extensive data reported by Haughton and Sellen.[21]

Haughton and Sellen's data covered the very wide range of −170 to +20 °C on dry and "wet" cellulose samples. The graphical method for determining α and m, developed by Sternstein, proved tedious and occasionally gave equivocal results. Accordingly, three different computerized methods of determining the best straight line for log $[(N/N_0)^{1-\alpha} - 1]$ vs. log t were developed for calculating the "best" α and m values. These methods are denoted by (r^2), (LES), and (TPM), respectively, and are described in the Appendix.

Having obtained the three different values for α and m, a further check was made on the appropriateness and utility of the analysis. Using average values of α and m, from the three estimates, E_t was calculated from t and checked against the tables supplied by Haughton and Sellen. Some results were rejected where the agreement was not good enough, but all results are shown in the following. They will be discussed below.

These methods were applied to the data obtained by Sternstein[20] as well as those by Haughton and Sellen.[21] Figures 3 and 4 are reproductions of Haughton and Sellen's data. All of the following calculations were made on tabulated data from these authors and from Sternstein's thesis.

Table IV
Determinations of Values of α, m, and α_1 from the Measurements of Sternstein and of Haughton and Sellen

Source	Temp, °C	α			m			α_1		
		r^2[a]	LES	TPM	r^2	LES	TPM	r^2	LES	TPM
Sternstein 1	41	(2.9)	(2.9)	(2.3)	(0.57)	(0.572)	(0.489)	(4.33)	(4.32)	(3.66)
Sternstein 2	36	(3.7)	(2.6)	(2.7)	(0.695)	(0.531)	(0.545)	(4.88)	(4.01)	(4.12)
Sternstein 3	30	(3.1)	(3.0)	(2.4)	(0.579)	(0.565)	(0.487)	(4.63)	(4.54)	(3.87)
Sternstein 4	57	2.4	2.3	2.3	0.51	0.495	0.495	3.75	3.63	3.63
Sternstein 5	50	3.2	3.1	2.6	0.66	0.641	0.569	4.33	4.28	3.81
Sternstein 7	37	3.5	3.3	2.5	0.653	0.625	0.522	4.83	4.68	3.87
Sternstein 8	27	3.4	3.3	3.0	0.595	0.582	0.544	5.03	4.95	4.68
H & S, dry	20	6.2	5.8	7.1	0.525	0.509	0.561	10.90	10.43	11.87
	0	11.5	10.4	21.9	0.598	0.570	0.889	18.56	17.49	24.51
	−20	10.3	7.9	10.1	0.508	0.445	0.502	19.31	21.00	19.13
	−40	23.0	1.1[c]	24.4	0.964	0.226	0.959	23.82		25.40
	−55	51.9[c]	1.1[c]	N.S.[b]	2.41	0.212	N.S.[b]			
	−70	51.9[c]	16.0	N.S.[b]	2.86	0.886	N.S.[b]	18.82	17.93	
	−85	11.9	7.1	12.2	0.780	0.531	0.796	14.97	12.49	15.07
	−100	11.2	9.3	5.9	0.700	0.604	0.443	15.57	14.74	12.06
	−115	11.9	11.0	14.6	0.60	0.572	0.692	19.17	18.48	20.65
	−130	21.9	19.4	18.0	0.585	0.540	0.515	36.73	35.07	34.01
	−145	1.1[c]	1.1[c]	N.S.[b]	1.000	1.000	N.S.[b]			
	−160	20.3	13.6	N.S.[b]	0.567	0.493	N.S.[b]	35.04	26.56	
	−170	(7.6)	(1.1[c])	N.S.[b]	(0.376)	(0.341)	N.S.[b]	(18.55)		
H & S, 75% rhs	−25	(1.1[c])	(1.1[c])	(6.0)	(0.456)	(0.456)	(1.951)			(3.56)
	−40	(1.1[c])	(1.5)	(2.8)	(0.292)	(0.317)	(0.417)		(2.58)	(5.32)
	−55	8.0	5.2	6.5	0.476	0.358	0.411	15.71	12.73	14.38
	−55	8.0	5.2	6.5	0.476	0.358	0.411	15.71	12.73	14.38
	−70	51.8	11.0	N.S.[b]	2.887	0.603	N.S.[b]	18.60	17.58	
	−85	26.7	14.5	26.8	1.795	0.965	1.802	15.32	14.99	15.32
	−100	10.7	10.1	10.1	0.795	0.755	0.755	13.20	13.05	13.05
	−115	9.8	9.5	10.5	0.701	0.685	0.740	13.55	13.41	13.84
	−130	10.6	10.3	12.4	0.647	0.636	0.715	15.84	15.62	16.94
	−140	14.0	13.0	19.3	0.692	0.662	0.856	19.79	19.13	22.38
	−150	31.9	30.9	4.6	0.900	0.882	1.135	35.33	34.90	39.41
	−160	9.9	8.5	40.4	0.596	0.581	0.998	15.93	13.91	40.48
	−170	1.1[c]	1.1[c]	N.S.[b]	0.439	0.439	N.S.[b]			

[a] r^2: r^2 method; LES: least error squared; TPM: three point method. [b] N.S.: no solution found for $1.1 \leq \alpha \leq 51.9$. [c] Reached the search limit of $1.1 \leq \alpha \leq 51.9$.

In Table III, $E_0{}^{20\,°\mathrm{C}}$ values were first calculated from $E_0{}^{T\,°\mathrm{C}}$ and $N_0{}^{20\,°\mathrm{C}}$ and $N_0{}^{T\,°\mathrm{C}}$ derived by means of the equations given above. These values of $N_0{}^{T\,°\mathrm{C}}$ will be used later in calculating K_1 values. Values of α and m as calculated by the "r^2", "least error squared" (LES), and the "Three Points" methods (TPM) are given in Table IV. Finally, k' and K_1 as calculated by the three methods are given in Table V.

Let us first examine Table III. I presume that $E_0{}^{20\,°\mathrm{C}}$ for the Sternstein samples and for Haughton and Sellen's data on dry and "wet" cellulose represent one value each, as the sample strips were presumably taken from one batch. There are at least four sources of variance giving rise to the standard deviations shown: (1) Assuming they do represent a single batch of manufacture in each set of experiments, there is the manufacturing and sampling variance. (2) Experimental errors in measuring E_t, the modulus at different times, at each temperature. (3) Extrapolation errors from E_t to E_0. (4) Theoretical approximations in our equations which were developed to calculate $E_0{}^{20\,°\mathrm{C}}$ from $E_0{}^{T\,°\mathrm{C}}$. The coefficients of variation for Sternstein's and Haughton and Sellen's data are 11.2, 5.04, and 9.30%, respectively. I am inclined to believe that they do represent a single batch in each case and that the results are satisfactory.

A second point emerges from Table III. Accepting the hypothesis that we are dealing with a single batch in each set, except for −25 °C for "wet" cellulose (which shows other aberrations as well), all values for $E_0{}^{20\,°\mathrm{C}}$ are within two standard deviations from the mean for the set; thus, all data are acceptable, excepting −25 °C for "wet".

Tables IV and V show the following. The first point to note is that these "objective" methods using r^2, LES, and TPM approaches do agree with the "subjective" graphical method used by Sternstein on his data. Sternstein had obtained $\alpha = 3.0$ and $m = 0.59$. The grand mean obtained by the three methods is 2.9 ± 0.3 for α and 0.58 ± 0.05 for m. They are, therefore, validated. But it can also be seen from Tables IV and V that the three methods do not always give the identical results, although on the whole they tell the same story. Furthermore, some of the relaxation curves of Haughton and Sellen did not yield "best fit" values for α and/or m by one or more of the three methods, i.e., no solution could be found at all. These are indicated by "N.S." in Table IV while others, at the limit of the search, have a footnote c designation.

Finally, E_t was recalculated for different values of t and compared with the original data. Using discrete values for t the following equations were used:

$$k = (k'/m)[(N/N_0)_{t=1}{}^{1-\alpha} - 1]^{(m-1)/m} \tag{70}$$

$$(N/N_0) = \{k(1-\alpha)t^m + 1\}^{1/(1-\alpha)} \tag{71}$$

$$(E/E_0) = (N/N_0)^{1/3} \tag{72}$$

and

$$E = (E/E_0)[\text{"expl"}\ E_0] \tag{73}$$

Unacceptably large deviations were found for the "wet" data of Haughton and Sellen at −25 and −40 °C and for the "dry" data at −170 °C. The shape of the curves for these three sets

Table V
Average Values of Relaxation Rate Parameters Determined by the Three Methods

Source	Temp, °C	α	m	α_1	k'	K_1
Sternstein 1	41	(2.70)	(0.544)	(4.10)	(8.99×10^{-4})	(1.39×10^{-5})
Sternstein 2	36	(3.00)	(0.590)	(4.34)	(1.76×10^{-3})	(7.85×10^{-6})
Sternstein 3	30	(2.83)	(0.544)	(4.35)	(6.75×10^{-4})	(4.54×10^{-6})
Sternstein 4	57	2.37	0.500	3.67	2.79×10^{-3}	3.01×10^{-5}
Sternstein 5	50	2.97	0.623	4.14	5.92×10^{-3}	2.30×10^{-5}
Sternstein 7	37	3.10	0.600	4.46	7.60×10^{-3}	2.61×10^{-6}
Sternstein 8	27	3.23	0.574	4.89	7.64×10^{-3}	4.55×10^{-6}
H & S, dry	20	6.37	0.532	11.1	4.68×10^{-2}	4.24×10^{-6}
	0	14.6	0.686	20.2	5.75×10^{-2}	1.90×10^{-8}
	−20	9.43	0.485	19.8	7.04×10^{-2}	1.85×10^{-8}
	−40	16.2	0.716	24.6	3.05	13.49×10^{-8}
	−55		1.31			
	−70	34	1.87	18.4	3.78	6.16×10^{-8}
	−85	10.4	0.702	14.2	7.18×10^{-1}	2.11×10^{-7}
	−100	8.8	0.582	14.1	2.51×10^{-1}	5.24×10^{-8}
	−115	12.5	0.621	19.4	1.48×10^{-1}	2.78×10^{-10}
	−130	19.8	0.547	35.3	1.85×10^{-1}	2.63×10^{-16}
	−145		1.00			
	−160	17.0	0.530	30.8	4.97×10^{-3}	5.51×10^{-13}
	−170	(4.35)	(0.359)	(18.5)	(1.42×10^{-4})	(1.01×10^{-10})
H & S, 75% rhs	−25	(2.73)	(0.954)	(3.56)	(5.45×10^{-1})	(4.07×10^{-1})
	−40	(1.80)	(0.342)	(3.95)	(1.19×10^{-2})	(3.15×10^{-3})
	−55	6.57	0.415	14.3	6.16×10^{-1}	1.09×10^{-3}
	−70	31.4	1.74	18.1	3.77	2.82×10^{-5}
	−85	22.7	1.52	15.2	6.37	6.56×10^{-5}
	−100	10.3	0.768	13.1	2.21	1.16×10^{-5}
	−115	9.93	0.709	13.6	4.83×10^{-1}	6.60×10^{-6}
	−130	11.1	0.666	16.1	1.29×10^{-1}	2.13×10^{-8}
	−140	15.4	0.737	20.4	5.48×10^{-2}	3.98×10^{-10}
	−150	35.8	0.972	36.5	2.60×10^{-2}	2.39×10^{-16}
	−160	19.6	0.725	23.4	3.08×10^{-3}	1.53×10^{-19}
	−170	1.1	0.439			

of data in Figures 3 and 4 would indicate that they were different in behavior from the others and, therefore, it was understandable to find them not conforming to the theory proposed. It was more puzzling to find Sternstein's Experiments 1, 2, and 3 also with somewhat large deviations. I believe they represent "learning curves" in the series of experiments as the following table of the mean absolute percentage deviation between experimental and recalculated E_t shows steady improvements with sequential number of the experiment:

Expt No.	1	2	3	4
Mean absolute % dev	9 ± 6	7 ± 4	11 ± 8	3 ± 2
Expt No.	5	7	8	
Mean absolute % dev	0.9 ± 0.4	0.5 ± 0.4	0.7 ± 0.5	

To illustrate the degree of concordance deemed acceptable in the analysis of Haughton and Sellen's data, Figure 5 gives typical results of calculations for −130 °C "wet" and −70 °C dry deemed "excellent", for −20 °C dry deemed "good", and for −40 °C dry deemed on the boundary of acceptability (r^2 for these last points was 0.968).

All analyses which are considered doubtful are enclosed in parentheses in Tables IV and V.

With these comments and reservations, first let us examine the values for m reported in Table V. The following conclusions appear to be reasonable:

(1) For dry cellulose m is independent of temperature. A value of $m = 0.55$ appears to apply to all data analyzed within the uncertainty of experimental and calculational errors.

(2) For "wet" cellulose m has values greater than 0.5, except for $T = -40$ °C (of doubtful significance) and $T = -55$ °C. I am inclined to take m for the "wet" cellulose experiments to be also independent of temperature and equal to 0.73. However, the results for −40 and −55 °C should alert us to difficulties in interpretation; they call for confirmation. As we shall see immediately below, there appears to be a secondary transition behavior in cellulose around these temperatures.

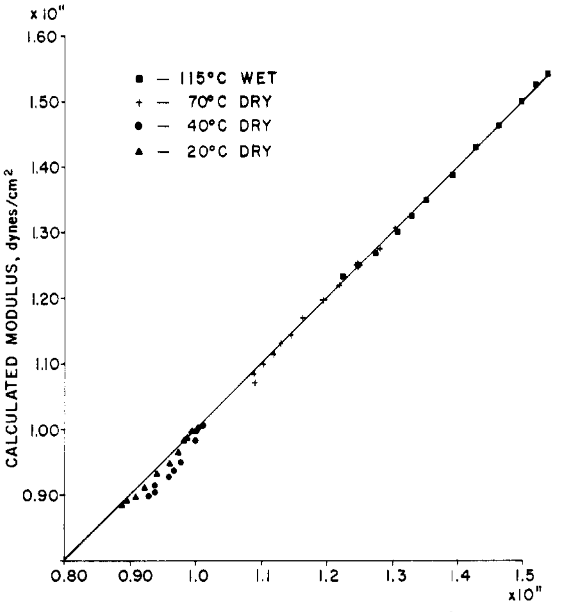


Figure 5. Calculated vs. experimental E_t for four temperatures.

(3) Nissan and Sternstein[22] have shown that a value of m between 0.5 and 1.0 was required for the kinetic equations used here to behave in a manner consistent with absolute rate theory and the continually relaxing strain free energy. It is,

therefore, gratifying to find that these extensive analyses of new data confirm this prediction, i.e., m is never less than 0.5.

The values for α_1 for dry and "wet" cellulose appear in Table V. It seems that α_1 is definitely temperature dependent, with interesting features. Thus, for dry cellulose maxima appear to exist at around −40 and −140 °C with a minimum around −100 °C. For "wet" cellulose the maxima appear at −70 and −150 °C with a minimum around −100 °C. It is unfortunate that the data for "wet" at −40 °C proved unanalyzable by the present method as this temperature may constitute a secondary transition temperature.

The average values calculated for K_1 for the data of Sternstein and of Haughton and Sellen are also shown in Table V with average values of the other parameters for comparison. As to be expected, a steady decrease appears, in general, as the temperature dropped. There is, however, considerable scatter to the data.

Thus, there appears the suggestion that temperatures of −40 to −70 °C, −100 °C, and −140 to −150 °C are of peculiar significance in cellulose structure and kinetics.

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Appendix. Methods of Straight Line Selection

Three techniques were applied by Rivkin, Lee, and Capers of Westvaco to the reiterative process for determining the values of α and m from the relaxation data. In one approach, an estimate of the parameters α and m was obtained by a direct search for the "best fit" straight line when $\log\,[(N/N_0)^{1-\alpha} - 1]$ was plotted against log time. The coarse search was carried out for values of α between 1.1 and 50.0 followed by a fine search of ±0.9 on either side of the best whole number value. The value of m was, of course, the slope of the "best fit" line and was determined by conventional regression formulas.[23] As a measure of the "goodness of fit", one can choose from a variety of statistics. Here we report that value of α as best which maximizes

$$r^2 = 1 - \Delta_r^{\,2}/\Delta_t^{\,2} \tag{74}$$

where the variances are defined as follows: let

$$y = \log\,[(N/N_0)^{1-\alpha} - 1] \tag{75}$$

then for each value of α in the search, a set of y_a and y_c are generated where: y_a = actual y associated with appropriate log t; y_c = calculated y using appropriate log t and regression equation; $\bar{y}$ = mean value of y_a; and

$$\Delta_r^{\,2} = \frac{1}{n-1}\sum_{i=1}^{n}(y_c - y_a)^2 \tag{76}$$

$$\Delta_t^{\,2} = \frac{1}{n-1}\sum_{i=1}^{n}(y_a - \bar{y})^2 \tag{77}$$

This is called "the r^2 method" in the discussion of the results.

A similar method is the use of the "least error squared" as a criterion for the "best fit" straight line. This is simply the line that minimizes $\Delta_r^{\,2}$. If the population of y's were the same for each trial value of α, this would be no different from r^2; however, one can see that the set of y's and hence $\Delta_t^{\,2}$ will change for each trial value of α. A merit of the "least error squared" criterion is its relation to the confidence limits for the estimate of the slope m when $\log\,[(N/N_0)^{1-\alpha} - 1]$ is regressed upon log t. These limits depend upon $\Delta_r^{\,2}$ and the variance in the independent variable, log t. During a search, the set of y's changes with changing α, but the set of log t's does not; hence, as the error squared decreases our confidence in the estimate of m increases.[23] This method is called the "least error squared" or LES method in the discussion of results.

We were not entirely satisfied with these approaches because of the relative insensitivity of r^2 to α, so other measures of "goodness of fit" were explored as well as more systematic search procedures such as the method of steepest descent. An alternative approach to estimating α, which is somewhat more direct, was developed by Dr. Hong Lee. The raw relaxation data (E vs. t) are smoothed. The smoothed values of (N/N_0) for $t = 0.1$, $t = 10$, and $t = 100$, respectively, are used to develop the parameters of a cubic equation which follows from the hypothesis.

$$\log\,[(N/N_0)^{1-\alpha} - 1] = m \log t + \text{intercept} \tag{78}$$

The equation resulting from setting equal the slopes of two contiguous segments is:

$$\begin{aligned}&[(N/N_0)_{t=10}{}^{1-\alpha} - 1]^3 \\ &\quad = [(N/N_0)_{t=100}{}^{1-\alpha} - 1]^2\,[(N/N_0)_{t=0.1}{}^{1-\alpha} - 1]\end{aligned} \tag{79}$$

This can be solved numerically to yield a value of α producing a straight line. This we call the "Three Points Method" or TPM in the discussion.

References and Notes

(1) A. H. Nissan, *Nature (London)*, **175**, 424–425 (1955); *Trans. Faraday Soc.*, **53**, 700–721 (1957); R. H. Marchessault and C. Skaar, Ed., "Surfaces and Coatings", Syracuse University Press, Syracuse, N.Y., 1967, pp 221–265.

(2) H. S. Frank and W-Y. Wen, *Discuss. Faraday Soc.*, **24**, 133–140 (1957).

(3) H. W. Starkweather, Jr., *Macromolecules*, **8**, 476–479 (1975).

(4) J. L. Morrison and M. A. Dzieciuch, *Can. J. Chem.*, **37**, 1379–1390 (1959).

(5) G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36 (12)**, 3382–3400 (1962).

(6) A. H. Nissan and H. G. Higgins, *Nature (London)*, **184**, 1477–1478 (1959).

(7) H. G. Higgins and V. Balodis, "Fracture", Osborn, C. J. Ed., University of Melbourne, Melbourne, Australia, 1965, pp 201–220.

(8) A. J. Stamm, "Wood and Cellulose Science", Ronald Press, New York, N.Y., 1964, Chapter 5, pp 142–166.

(9) J. K. Craver and D. L. Taylor, *Tappi*, **48 (3)**, 142–147 (1965).

(10) O. Andersson and E. Berkyto, *Sven. Papperstidn.*, **54**, 441–444 (1951).

(11) R. E. Benson, *Tappi*, **54**, 699–703 (1971).

(12) W. P. Riemen and S. K. Kurath, *Tappi*, **47**, 629–633 (1974).

(13) J. P. Brezinski, Doctor's Dissertation, Institute of Paper Chemistry, Appleton, Wisc., 1955.

(14) D. F. Caulfield, private communication.

(15) R. Meredith, *J. Text. Inst.*, **48**, T163–T174 (1957).

(16) N. Adams, *J. Text. Inst.*, **47**, T530–T540 (1956).

(17) J. M. R. Quistwater and B. A. Dunell, *J. Polym. Sci.*, **28**, 301–318 (1958).

(18) J. M. R. Quistwater and B. A. Dunell, *J. Appl. Polym. Sci.*, **1**, 267–271 (1959).

(19) R. Consden and F. O. Howitt, "The Structure of Textile Fibres", A. R. Urquhart and F. O. Howitt, Ed., The Textile Institute, Manchester, England, 1953, pp 75–90.

(20) S. S. Sternstein, Doctoral Dissertation, Rensselaer Polytechnic Institute, Troy, N.Y., 1961.

(21) P. M. Haughton and D. B. Sellen, *J. Phys. D:*, **6**, 1998–2011 (1973).

(22) A. H. Nissan and S. S. Sternstein, *Pure Appl. Chem.*, **5**, 131 (1962).

(23) O. L. Davies, "Statistical Methods in Research and Production", Hafner Publishing Co., New York, N.Y., 1971, Chapter 7.