Equation (3) fits much of the data in a quite satisfactory manner. Its essential applicability was indicated by the fact that, unlike several other possible equations, the same values of the constants were found whether starting with fumarate or with *l*-malate as substrate. In Fig. 3, the lines were drawn from this equation with values of α and β as follows: *p*H 5.97, $\alpha = -27{,}800$, $\beta = 2040$; *p*H 8.46, $\alpha = 35{,}700$, $\beta = 570$. Considering the great uncertainties in the processes involved in the fumarase reaction, however, the exact meaning of α and β is questionable, and equation (3) can be regarded as little more than an empirical expression that fits observed data. Thus, there is no indication in these data as to which of the three assumptions above may be correct, nor whether the real mechanism may not be in fact much more complicated than any of those here visualized.

Summary

The initial rate of the forward reaction in the system

$$\text{fumarate} + H_2O \overset{\text{fumarase}}{\rightleftharpoons} l\text{-malate}$$

bears no obvious relation to the initial rate of the reverse reaction. This was shown to be due to the reaction being composed of a series of steps of which the rate-controlling step was of the zero order. The effect on the system of temperature, *p*H, and enzyme and substrate concentrations was studied, and an equation derived which described the data obtained.

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[CONTRIBUTION FROM INSTITUTE OF POLYMER RESEARCH POLYTECHNIC INSTITUTE OF BROOKLYN]

Rate of Exchange of Cellulose with Heavy Water

BY V. J. FRILETTE,[1a] J. HANLE AND H. MARK

Introduction

The interchain structure of cellulose has aroused considerable interest in recent years. As with other polymers, there is reason to believe that the physical and chemical properties of cellulose are strongly influenced by the supermolecular texture that exists in a given sample. A generally accepted hypothesis concerning the texture of cellulose is[1b] that individual chain molecules having average extended lengths of several thousand Ångströms pass successively through regions of lower and higher lateral order. These ordered and disordered domains are not sharply distinguished and separated from each other but may be connected by areas of intermediate order. They are usually as a matter of convenience referred to as amorphous and crystalline constituents. One could expect different portions of a chain in such a structure to have different degrees of reactivity with small reagent molecules, for the behavior of an individual chain segment would depend upon how tightly it is bound laterally to its nearest neighbors. The reacting groups in the most disordered regions of a sample would be expected to be most easily accessible, while they would be inaccessible in the areas of high lateral order. Consequently, one would expect hydroxyl groups or glucoside bonds in amorphous regions to be most susceptible to reactions so that if the rate or extent of a particular reaction is followed quantitatively, it may be interpreted in terms of structural accessibility.

Until now, three chemical reactions have been used to characterize the reactivity of cellulose samples. Goldfinger, Siggia and Mark[2] measured the rate of periodate oxidation of various cellulose samples and established the existence of a rapid and a slow reaction. Assaf, Haas and Purves[3] treated cellulose with thallous ethylate in different solvents and found that only a fraction of the existing hydroxyl groups were converted to the thallium salt. Finally, Nickerson[4] and Conrad and Scroggie[5] studied the oxidative hydrolysis of cellulose to carbon dioxide and water. The rate of carbon dioxide evolution, which at first is rapid, gradually decreases to an almost constant value. It is claimed that by an analysis of the rate curves an estimate can be made of the amount of easily accessible (amorphous) cellulose originally present in the sample.

In this paper we shall describe a fourth reaction suitable for characterizing cellulose. It was first observed by Bonhoeffer[6] that the hydroxyl groups of cellulose react with heavy water. Champetier and Viallard,[7] who made a more systematic study of this effect, reported that a moderately slow reaction occurred and that practically all of the hydroxyl groups exchanged. The curves reported by these investigators showed little promise of yielding any information on accessibility, but a careful reading of the paper revealed that the cell in which the reaction was conducted had been

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(1a) The material for this paper was abstracted in part from the thesis of V. J. Frilette, submitted to the Faculty of the Graduate School of the Polytechnic Institute in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1947.

(1b) O. Kratky, *Z. angew. Chem.*, **53**, 153 (1940).

(2) Goldfinger, Siggia and Mark, *Ind. Eng. Chem.*, **35**, 1083 (1943).

(3) Assaf, Haas and Purves, THIS JOURNAL, **66**, 59 (1934).

(4) Nickerson, *Ind. Eng. Chem.*, **34**, 85 (1942).

(5) Conrad and Scroggie, *ibid.*, **37**, 592 (1945).

(6) Bonhoeffer, *Z. Elektrochem.*, **40**, 469 (1934).

(7) Champetier and Viallard, *Bull. soc. chim.*, [5] **33**, 1042 (1938).

opened for each density measurement made on the water, thus introducing the possibility that exchange with moisture vapor from the air may have occurred. While the errors thus introduced would not affect the over-all shape of the exchange curve, the calculated extent of the reaction would be too high. We felt, therefore, that a few more experiments along these lines would be of interest and observed, in fact, that the exchange is not of moderate speed, but very fast; to properly follow it, one must introduce some device for agitating the cellulose.

The mild conditions under which the cellulose–heavy water reaction can be carried out is a very advantageous feature from the point of view of characterization, for there is hardly a question but that the investigated sample remains chemically and physically unchanged during the course of the reaction.

Experimental

Treatment of Samples.—Through the courtesy of Drs. Conrad and Scroggie of the Rayon Department, E. I. du Pont de Nemours and Company, a variety of cellulose samples were obtained which had already been characterized for accessibility by the Nickerson method as modified by Conrad and Scroggie.[5] In addition to these samples, two native cottons which exhibited the normal X-ray fiber patterns were analyzed.

All of the samples were air-dried and contained considerable amounts of moisture (6–13%). It was not considered desirable to dry at elevated temperatures the samples which were actually to be used for the exchange reaction, since such a procedure might change the accessibility. As an alternative, about 100–200 g. of each cellulose was kept in a screw-cap jar for one week in order to ensure that all parts of the gross sample had achieved moisture equilibrium. Small portions of the conditioned gross sample were then used for the exchange reaction, while another portion was used to determine the moisture content. The latter analysis was made in duplicate by drying in an air oven at 110° in accordance with standard practice. To the experimentally determined values was added in all cases an arbitrary correction of 0.5%, since it is well known that cellulose dried under the conditions described tends to retain about this amount of water.[8]

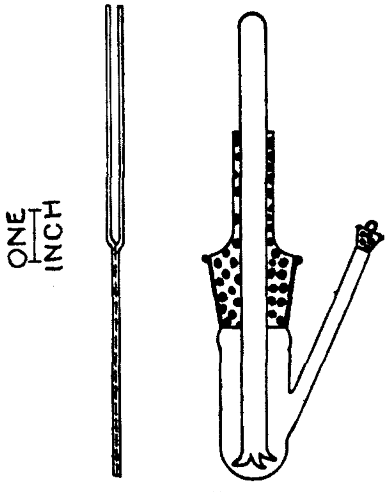

Fig. 1.—Reaction cell and micropipet.

Apparatus and Techniques.—The reaction cell is shown in Fig. 1. It was designed to permit intermittent agitation and the removal of microsamples of water without exposing the contents to air.

Approximately 2 g. of the conditioned sample was quickly weighed into the tared reaction cell, and 8 to 10 g. of heavy water of known specific gravity added. During transfer and weighing, the obvious precautions were taken to minimize changes in the moisture content of the cellulose as well as changes in the specific gravity of the heavy water.

When the weighings were completed, the glass stopper (not shown) was removed from the reaction cell and the ground-glass stirring assembly inserted in its place, where it remained until the run was completed. The cellulose was alternately loosened and compressed for about twenty minutes by manually manipulating the glass rod. After this initial period it was found sufficient to loosen and compress the wet cellulose only two or three times every half hour. The efficiency of the recommended agitation may be judged by the fact that if no agitation at all is used, one obtains what is apparently a very slow reaction which requires twenty-four to thirty-six hours to achieve maximum exchange,[7] but with the cell described above, if one breaks up and compresses the cellulose just once, a process requiring about three minutes, is found that exchange has proceeded to within a few per cent. of the value found after one or two hours. In other words, the reaction is diffusion-controlled, and is such a fast reaction that with a slight amount of agitation it goes practically to completion within a matter of minutes.

In order to follow the reaction, samples of water were removed and purified at intervals, and specific gravity measurements then were made. Purification was necessary in order to remove the buffer salts, suspended cellulose particles, and also any traces of impurities that might have been extracted from the cellulose. Before taking a sample of the free water, the reaction cell was tilted and the stirring rod pressed into the cellulose in such a way that a drop of water would run into the narrow sidearm to form an air-lock. To obtain the sample, the capillary pipet shown in Fig. 1, fitted with a medicinal dropper bulb (not shown), was inserted through the sidearm of the reaction cell and a sample drawn up from the cellulosic mass. The capillary was then removed and wiped dry with hard filter paper.

The pipets were calibrated to contain 0.1 cc. of water. Manipulation of the sample was facilitated by a small hole at the top of the rubber bulb which was closed and opened at will by the index finger.

The water sample in the pipet was then transferred to a microdistillation flask. In Fig. 2 the construction and use of the flasks are illustrated. The flask at stage (3) is ready to receive the sample. The pipet was inserted until it touched the back wall of the flask, and the sample was run into the bulb. The tip of the pipet was then rotated against the portion of the horizontal tube adjoining the bulb in order to remove any large excess of water, after which it was carefully withdrawn so as to avoid contaminating the "receiver" portion of the flask. The flask containing the sample was then evacuated to *ca.* 20 mm. and the neck quickly sealed off with a hand torch. By simply hanging the flask with the "receiver" portion in ice water, distillation to dryness is attained in about one-half hour.

Several precautions should be observed in using the described distillation technique. It is advisable, for example, to store the retorts (stage 3) in a desiccator to provide a dry atmosphere for the sample; otherwise, large errors may be incurred. Also, in the evacuation step, one must be careful not to distil off any appreciable quantity of water before the seal is made.

After complete distillation, the flask was removed from ice-bath. The tube, maintained in a vertical position, was dried and then cut; the "receiver" portion of the flask thus became a convenient microbeaker containing the purified water. The specific gravity was immediately determined by the falling-drop method. This analysis

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(8) Hermans, "Physics of Cellulose Fibers," Elsevier, 1946, p. 200.

required 9 cu. mm. of the sample, and provided an accuracy of 1×10^{-6} specific gravity units. The method is in principle the same as that described previously by D. Rittenberg, *et al.*,[9] with some modifications by the present authors.[10]

Calculation of Extent of Exchange.—To derive a simple expression for calculating the extent of the exchange reaction, it is desirable to make two assumptions. It is assumed that the moisture present in the cellulose sample very rapidly dilutes the heavy water. It is further assumed that all three cellulose hydroxyls are indistinguishable so far as rate of exchange is concerned.

Now, the following definitions are adopted

x = grams of cellulose used;
m = percentage moisture content of x (wet basis);
Σ = moles of water ($D_2O + H_2O$) added to cellulose;
ξ_0 = initial mole fraction of D_2O in heavy water;
ξ_t = mole fraction of D_2O in heavy water at time t;
F = extent of reaction; *i. e.*, number of cellulose hydroxyls which have exchanged D for H divided by the number of such groups which would exchange if all of them were in equilibrium with the water.

If we write the exchange equilibrium as

$$2/3R(OH)_3 + D_2O \rightleftarrows 2/3R(OD)_3 + H_2O$$

then, for complete reaction, the number of moles of D_2O consumed from an infinite excess of 100% D_2O is given by

$$\frac{(1 - 0.01m)x}{108.1} \qquad (1)$$

For a *finite* amount of *dilute* heavy water, the number of moles consumed at time t is given by

$$\xi_t F\left[\frac{(1 - 0.01m)x}{108.1}\right] \qquad (2)$$

By definition

$$\xi_t = \frac{\text{Moles } D_2O \text{ initially present} - \text{moles } D_2O \text{ consumed}}{\text{Total moles } (D_2O + H_2O)} \qquad (3)$$

The assumption made at the beginning of this derivation regarding the moisture in the cellulose permits us to write

$$\xi_t = \frac{\xi_0\Sigma - \xi_t F\left[\frac{(1 - 0.01m)x}{108.1}\right]}{\Sigma + \frac{0.01mx}{18.02}} \qquad (4)$$

Now, if W is the original weight of the heavy water added to the cellulose, it is evident that

$$W = 20.0\,\xi_0\Sigma + 18.0(1 - \xi_0)\Sigma \qquad (5)$$

and this equation may be used to eliminate Σ from equation (4).

To eliminate the mole fractions ξ_0 and ξ_t, let the corresponding specific gravities be S_0 and S_t. The relationship between ξ and the corresponding S may be written

$$\xi = (S - 1.00000)/0.1080 \qquad (6)$$

Consideration of equations (4, 5, 6) with appropriate transpositions leads to the final relationship for F in terms of the weights of materials used and the observed specific gravities

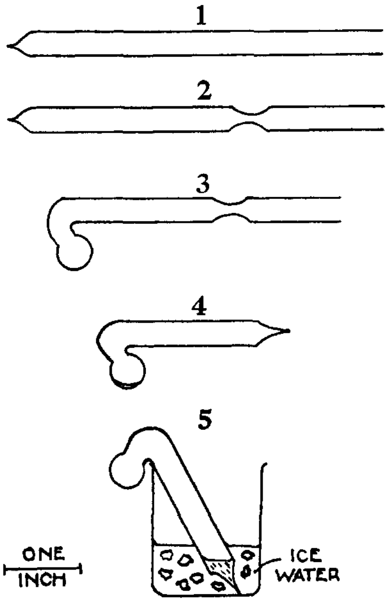

Fig. 2.—Preparation and use of microdistillation flasks.

$$F = A\left[\frac{S_0 - S_t}{S_t - 1}\right] - B \qquad (7)$$

where A and B are constants in any given reaction, and their equivalents are

$$\left.\begin{aligned} A &= \frac{108.1W}{(18.02 + 2\xi_0)(1 - 0.01m)x} \\ B &= \frac{1.081m}{18.02(1 - 0.01m)} \end{aligned}\right\} \qquad (8)$$

From a consideration of the quantities of cellulose and heavy water used, together with the precision attainable in the heavy water analysis,[10] it can be estimated that the value of F should be precise to within about (1 to 2) $\times 10^{-2}$; in terms of percentage of the hydroxyls exchanged, the precision should be about 1% over the entire range.

Results

Effect of *p*H and Temperature.—In order to choose the most advantageous reaction conditions rather than to adopt them arbitrarily, a set of experiments were run at different acidities and different temperatures.

For this study, sheeted, high-grade commercial cotton linters was used. The reaction was run at room temperature and 70°, both at *p*H 6. To adjust the *p*H, sufficient potassium dihydrogen phosphate was added to the water to give a 0.05*M* concentration; then, sufficient sodium hydroxide as a concentrated solution in water was added to achieve the desired *p*H. A Beckmann *p*H meter was used to determine acidity. For the 70° run, the cell was immersed in a thermostated bath and the water brought to temperature before adding the cellulose. The cell was not removed from the

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(9) Keston, Rittenberg and Schoenheimer, *J. Biol. Chem.*, **122**, 227 (1937).

(10) Frilette and Hanle, *Anal. Chem.*, **19**, 984 (1947).

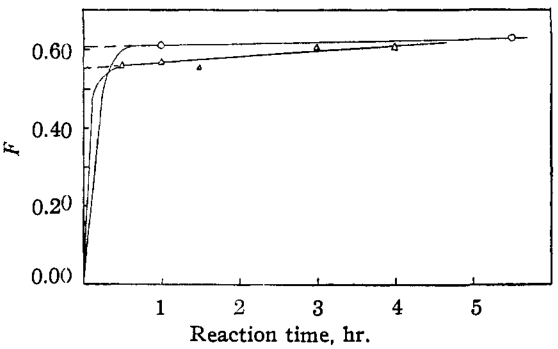

Fig. 3.—Effect of temperature on rate of exchange: O, cotton linters, *p*H 6, 70°; Δ, cotton linters, *p*H 6,25°.

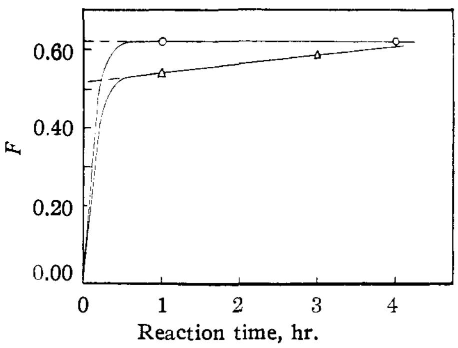

Fig. 4.—Effect of *p*H on rate of exchange: O, cotton linters, *p*H 3.9, 25°; Δ, cotton linters, *p*H 10.5, 25°.

bath until the run was completed. In this experiment, two triplicate samples were taken, the first set after one hour and the second after five and one-half hours. For the room temperature experiment, samples were taken singly but at more frequent intervals, and in addition a sample was taken after ten days of standing at room temperature. The results for both of these runs are plotted in Fig. 3; it can be seen that the influence of temperature is negligible over the range studied. The nature of the data obtained empirically in these two runs and its conversion into extent of exchange is illustrated by Tables I and II. In order to conserve space all other runs are summarized by the "characterization values" defined in the next section.

Table I

Exchange of Cotton Linters at 70°

Weight of cellulose, x = 2.060 g.; moisture content on wet basis, m = 5.7%; weight of heavy water used, W = 9.653 g.; initial mole fraction of D_2O in heavy water, ξ_0 = 0.22; calculated values, A = 29.13 and B = 0.363.

Reaction time, t, hr.	Specific gravity, S	$\frac{S_0 - S_t}{S_t - 1}$	$A\left[\frac{S_0 - S_t}{S_t - 1}\right]$	Extent of exchange, F
	1.024220			
0	1.024216	0	0	0
	1.024218			
	1.023440			
1.0	1.023440	0.0333	0.969	0.61
	1.023433			
	1.023420			
5.5	1.023422	0.0341	0.992	0.63
	1.023417			

Table II

Exchange of Cotton Linters at 25°

Weight of cellulose, x = 2.200 g.; moisture content on wet basis, m = 5.7%; weight of heavy water used, W = 11.13 g.; initial mole fraction of D_2O in heavy water, ξ_0 = 0.23; calculated values, A = 31.37 and B = 0.363.

Reaction time, t, hr.	Specific gravity, S	$\frac{S_0 - S_t}{S_t - 1}$	$A\left[\frac{S_0 - S_t}{S_t - 1}\right]$	Extent of exchange, F
0	1.024533[a]	0	0	0
0.5	1.023818	0.0300	0.942	0.58
1.0	1.023818	.0300	.942	.58
1.5	1.023822	.0298	.935	.57
3.0	1.023788	.0313	.980	.62
4.0	1.023795	.0310	.974	.61
168	1.023770[b]	.0321	1.005	.64

[a] Average for three samples. [b] Average for two samples.

Two additional runs were made at room temperature, one at *p*H 3.9, the other at *p*H 10.5. The results of these two experiments were plotted in Fig. 4; these curves together with the room temperature run of Fig. 3 indicate that the influence of *p*H also is negligible.

General Character of the Exchange Curve.—The shape of the exchange *vs.* time curve is simple and essentially similar for all the cellulose samples which were studied. Its characteristics are: (1) a very steep rise which is substantially terminated after a fraction of an hour, and (2) a horizontal part with such a small slope that the exchange value even after one week differs only slightly from the value observed at one hour.

Since the curves for different cellulose samples are so consistent in shape, a generalized notation to represent the data may be adopted which is more concise and lends itself to comparison better than the original curves. Specifically, let the intercept of the horizontal portion of the curve extrapolated to zero time be called the *a* value; the magnitude of *F* at four hours, the *b* value; and

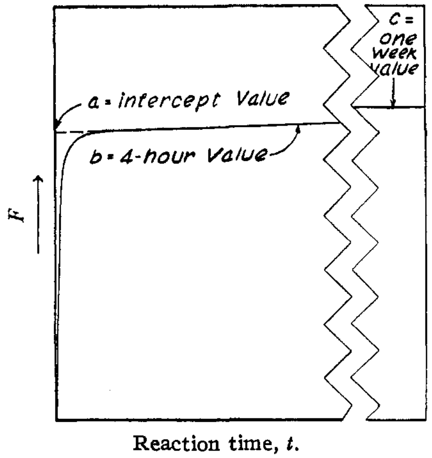

Fig. 5.—Generalized reaction curve and characterization values.

the magnitude of F at one week, the c value, all as indicated in Fig. 5. For convenience, these values collectively will be called the "characterization values" for the various samples.

Returning once again to the effect of temperature and pH on the exchange rate of a cotton linters sample, we may summarize the results by the characterization values as presented in Table III. It may be noted at this point that the four runs indicate an experimental precision that is about as good as that estimated in a previous section, especially if one considers the b value as the correct measure of accessibility. The average deviation of the a value is ± 0.025, which is poorer than expected; but the average deviation of the b value is ± 0.005, which agrees with the predicted value corrected for the multiplicity of the determinations.

TABLE III

EFFECT OF pH AND TEMPERATURE: COTTON LINETRS

	Reaction conditions		Characterization values		
Run	pH	°C.	a	b	c
1	6	70	0.61	0.62	..
2	6	25	.57	.61	0.64
3	3.9	25	.62	.62	..
4	10.5	25	.54	.61	..

It can be seen from the tables that many of the samples produce perfectly flat curves in the interval from the first to the fourth hour. Some of the samples, however, show a significant difference between the a and the b value. All samples appear to continue to exchange a small, but always a significant amount, in the interval from four hours to one week, and the extent of this exchange does not seem to be related to the magnitude of the difference between a and b. The reasons for the differences in magnitude of a, b, and c are under investigation at the present time; the results so far indicate that where b differs significantly from a, it may be attributed to a residual diffusion error. Accordingly, we shall tentatively assume the b value, *i. e.*, the value of F after four hours, to be the measure of accessibility.

Wood Pulp Samples.—Since the rate of exchange was not noticeably influenced by the variables studied, all of the experiments which follow were made at room temperature and pH 6.

Wood pulp samples previously studied by Drs. Conrad and Scroggie were used after the described one-week conditioning. The practice in this instance was to take frequent single samples rather than triplicate samples at widely spaced intervals. The data are summarized in Table IV.

TABLE IV

CHARACTERIZATION VALUES FOR WOOD PULPS

		Characterization values		
Run	Sample description	a	b	c
5	Wood pulp from beech	0.53	0.54	0.68
6	Same, from southern pine	.48	.55	.57
7	Same, from western hemlock	.54	.55	.67
8	High alpha wood pulp from southern pine	.68	.68	.73
9	Wood pulp treated with caustic of approx. 10% concn.	.68	.74	.81

Regenerated Cellulose Samples.—Four different regenerated cellulose fibers were studied by the same methods as described above. The results are shown in Table V. In addition to these samples, two native cotton fibers were run; for one of these a b value of 0.41 was found, and for the other 0.46. These values are the lowest found for any of the samples studied and indicate that native cotton has a relatively small fraction of accessible chain segments.

TABLE V

CHARACTERIZATION VALUES FOR VISCOSE RAYON FIBERS

		Characterization values		
Run	Sample description	a	b	c
10	"Cordura" high tenacity viscose rayon	0.86	0.86	0.89
11	Fiber G, high tenacity viscose rayon	.67	.67	.74
12	Textile viscose rayon	.66	.68	.75
13	Special viscose rayon spun without appreciable tension	.78	.81	.90

Discussion

If it is assumed that cellulose is composed of easily accessible (amorphous) and more difficultly accessible (crystalline) domains, it is probable that the rapid, limited exchange with D_2O involves all of the hydroxyls in the amorphous regions together with those in the surface of the crystalline arrays. One cannot ignore the contribution of the surface hydroxyls to the extent of the exchange reaction in estimations of crystallinity, for experimental evidence indicates that the areas of high lateral order are very small and, as a consequence, a large fraction of their hydroxyl groups are arranged in the surface. If this factor is taken into account, the relationship between the amount of crystalline material in a cellulose sample and the extent of the exchange reaction may be written

$$F' = \sigma\alpha + (100 - \alpha),$$

where

F' = $100F$, *i. e.*, the percentage of all of the hydroxyls which react rapidly with D_2O

σ = the fraction of the hydroxyls of the crystalline domains which are in the surface and accessible to D_2O

α = the per cent. of crystalline material in the sample

Solving for α

$$\alpha = \frac{100 - F'}{1 - \sigma}$$

In order to arrive at estimates of α for the samples which were studied, it is first necessary to assign a value to σ. To arrive at this value, it may be assumed that the effective surface development of the crystalline regions is represented by an infinitely long, square prism with a base of between

50 and 100 ångströms on edge.[11,12] A cross-section of such a prism would contain approximately twenty rows of cellulose chains, each row in turn consisting of ten chains. Now, if one takes a volume element of the idealized prism by passing through it two parallel planes which are perpendicular to the long edges of the prism, the surface development may be computed readily. In particular, if the transecting planes are spaced so that the element contains 200 anhydroglucose units, it is evident that 20 of these units will lie in the hydroxyl-rich surfaces, and 36 (edgewise) in the other two faces. Thus, for every 100 anhydroglucose residues in a crystalline domain, 28 lie in the surface. Assuming now that all hydroxyls attached to the latter are reactive, we arrive at $\sigma = 0.28$. This value was used to calculate the values for α shown in Table VI; values derived from a different method are shown for comparison.

TABLE VI

CRYSTALLINITY AS ESTIMATED FROM D_2O EXCHANGE AND NICKERSON DEGRADATION

		Accessibility		Crystallinity	
Run	Sample description	From D_2O exchange, F' (%)	Nickerson method[b] (%)	From D_2O exchange,[a] α (%)	Nickerson method,[c] %
..	Cotton	41	..	82	..
..	Cotton	46	..	75	..
1 to 4	Cotton linters	61	5	54	95
5	Wood pulp, beech	54	12	64	88
6	Wood pulp, pine	55	10	63	90
7	Wood pulp, hemlock	55	9	63	91
8	Wood pulp, pine	68	8	44	92
9	Wood pulp, pine	74	15	36	85
10	"Cordura" rayon	86	30	19	70
11	Fiber "G"	67	15	46	85
12	Textile rayon	68	27	44	73
13	Special rayon	81	..	26	..

[a] Crystallinity estimated from D_2O exchange, $\alpha = (100 - F')/(1 - \sigma)$. [b] Values in this column determined by Nickerson method as modified by Drs. Conrad and Scroggie; these data were supplied through the courtesy of these investigators. [c] Crystallinity estimated from the Nickerson degradation by subtracting from 100 the per cent. accessibility to $FeCl_3$:HCl.

It might be well to mention at this point that while the accessibility, F, is an exact empirical value, the crystallinity, α, is only an approximation. How close α approaches the true value for crystallinity depends in part on the validity of σ and in part on the magnitude of the accessibility. For a sample in which all but 10% of the hydroxyls are accessible the magnitude of α would vary only from 14 to 23% if the value of σ were doubled; on the other hand, if one were to consider a much more crystalline sample, *e. g.*, cotton with 41% of the hydroxyls accessible, then the value for α would vary from 82% for $\sigma = 0.28$ to 100% for $\sigma = 0.41$, a much larger change in α for a much smaller change in σ. Since the computation of σ is based on two methods for estimating crystallite size,[11,12] it is not likely that it is in error by the magnitudes just discussed. In fact, if one compares the averaged values of Table VI with the estimates of crystallinity arrived at by Hermans[13] through a study of the density of various types of cellulose, it is noted that a fairly good agreement exists. The average values for crystalline content reported by Hermans are 60% for ramie and cotton, 50% for wood pulp and 25% for regenerated cellulose.

In contrast to the density method of Hermans, it is interesting to point out that the accessibility of cellulose to heavy water is in all cases distinctly greater than that observed with the Nickerson method, as is shown in Table VI. A possible explanation is that additional crystallization occurs in the early stages of the reaction. During hydrolysis, cellulose chains in the easily accessible areas are broken and new, free, chain ends are produced; this process removes constraints on these chains and makes their segments more easily mobile. They will now be able to arrange themselves in a higher degree of lateral order under the influence of the strong intermolecular forces between the chains, and part of the material which was disordered before will undergo crystallization. It has been pointed out previously by several observers[14] that, for the same polymer, low molecular weight fractions have a greater tendency to crystallize than those of higher molecular weight; also, Ingersol[15] has recently reported that treating cellulose fibers with hydrochloric acid sharpens their X-ray patterns. The increased density[16] and decreased moisture regain[17] of cellulose fibers upon prolonged treatment with the Nickerson reagent also points to the fact that additional crystallization occurs while glucosidic bonds are hydrolyzed in the easily accessible areas. It is therefore understandable that the D_2O exchange method indicates larger amounts of disordered material than the Nickerson method. Similar reasoning will also hold for the oxidation method[2] mentioned in the introduction, for it was carried out at a low *p*H and partial hydrolysis with subsequent crystallization was bound to occur in the easily accessible arrays.

The thallation method of Assaf, Haas and Purves[3] leads to lower accessibilities than any of the other procedures; this is probably due to the fact that it is carried out in an anhydrous system. It tests the texture of the sample in the bone-dry state and indicates only those domains as accessible that can be approached by an organic (hydrophobic) solvent. The ingenious extrapolation to zero molecular volume eliminates the volume re-

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(11) Hengstenberg and Mark, *Z. Krist.*, **69**, 271 (1928).

(12) Kratky and Mark, *Z. physik. Chem.*, **B36**, 129 (1937).

(13) Hermans, "Physics of Cellulose Fibers," Elsevier, 1946, p. 71.

(14) Baker, Fuller and Pape, THIS JOURNAL, **64**, 776 (1942).

(15) Ingersol, *J. Applied Phys.*, **17**, 924 (1946).

(16) Tessler, Woodberry and Mark, *J. Polymer Sci.*, **1**, 437 (1946).

(17) Nickerson, *Ind. Eng. Chem.*, **34**, 1480 (1942).

quirements of the solvent and probably leads to a true value of accessible hydroxyl groups for a non-swelling reagent. In an aqueous medium, swelling takes place and a number of weak (van der Waals) bonds between hydroxyl groups of adjacent chains are opened and hitherto inaccessible areas are made penetrable by the reagent. One should, therefore, expect that all methods using aqueous systems should indicate higher degrees of accessibility, which is in fact the case. The highest proportions of disordered areas should be given by X-rays, by density considerations,[13] and by the heavy water exchange method; the figures deduced from these three methods should also agree numerically. Table VII contains the accessibilities as reported by all methods and shows, indeed, that the thallation method gives the lowest values whereas the two "destructive methods" in aqueous media, involving hydrolysis and oxidation, give higher figures for the disordered areas and agree with each other to a first approximation. Finally, the non-destructive methods of X-ray diffraction, density evaluation and heavy water exchange lead to the highest figures for the accessible domains; these methods, too, agree with one another reasonably well.

TABLE VII

ORDER OF ACCESSIBILITY FOUND BY DIFFERENT METHODS

Method	% Accessible or amorphous Cotton	Cotton linters	Wood pulp	Rayon
Thallation[3]	..	0.4[c]	..	...
Nickerson oxidation[5a]	..	5.3	10	24
Periodate oxidation[2]	1–2	6.0	..	7–19
Density[11]	40	...	50	75
Heavy water exchange[b]	21	46	46	66
X-Ray densitometry[5]	..	...	..	81

[a] Data supplied through courtesy of Drs. Conrad and Scroggie. [b] Values averaged from Table IV. [c] Unswollen samples.

Summary

It has been found that cellulose reacts very rapidly with heavy water, provided sufficient agitation is used; the rapid reaction is of limited extent, and is succeeded by a much slower reaction which persists for days. In none of the cases studied were all of the hydroxyls exchanged, even at the end of one week. The techniques used and the calculations involved are outlined.

The extent of the rapid reaction is a measure of the accessibility of the cellulose sample, and from the accessibility an estimate is made of the amount of amorphous material present in each of the samples studied. The average amounts found for different types of cellulose were as follows: 21% for cotton, 46% for wood pulp and 66% for rayon.

The different accessibility values found for the same cellulose sample when different methods are used are discussed and compared. These methods fall into three classes. In the first class is the thallation method, where a non-swelling solvent is used, and with which the lowest values are found. In the second class are the two hydrolytic, aqueous methods, which give intermediate values for accessibility. In the last class are the physical, non-destructive methods which give the highest values.

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n-Alkyl Diselenides

BY GEORGE G. STONER AND ROGER W. WILLIAMS

In connection with a program[1] of research on selenium and its compounds, it was of interest to examine a number of *n*-alkyl diselenides. Of this particular homologous series, methyl,[2,3] ethyl,[2,4] propyl,[2,3,5] butyl[3] and dodecyl[6] diselenides are known, having been prepared by a variety of methods.

A convenient method of synthesis, based on the following three reactions,[7] and not previously applied to this series, was used to prepare butyl, amyl, hexyl, heptyl, octyl, and nonyl diselenides.

$$Se + K_2SO_3 = K_2SeSO_3$$

$$RX + K_2SeSO_3 = RSeSO_3K + KX$$

$$2RSeSO_3K + I_2 + 2H_2O = RSeSeR + 2KHSO_4 + 2HI$$

This sequence of reactions yields *n*-alkyl diselenides which are less likely to be contaminated than those prepared by the other methods,[2–6] and the yields are good (Table I). The offensive odors of the *n*-alkyl diselenides decrease considerably in intensity above hexyl in the homologous series.

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(1) Sponsored by the Selenium Development Committee.

(2) Beilstein, "Handbuch der organischen Chemie," 4th ed., Vol. 1, pp. 291, 349 and 360; and 2d supplement, pp. 278 and 357. Also, M. L. Bird and F. Challenger, *J. Chem. Soc.*, 570–574 (1942).

(3) H. J. Backer and W. van Dam, *Rec. trav. chim.*, **54**, 531–538 (1935).

(4) A. Baroni, *Atti accad. Lincei*, **14**, 28–32 (1931); *C. A.*, **26**, 1896 (1932).

(5) E. P. Painter, K. W. Franke and R. A. Gortner, *J. Org. Chem.*, **5**, 579–589 (1940).

(6) G. H. Denison, Jr., and P. C. Condit, U. S. Patents 2,398,414, 2,398,415, and 2,398,416 (April 16, 1946).

(7) This method was discovered by T. S. Price and L. M. Jones, *Proc. Chem. Soc.*, **24**, 134 (1908), and *J. Chem. Soc.*, **95**, 1729–1738 (1909), who used it in preparing benzyl and nitrobenzyl diselenides; *cf.* T. S. Price and D. F. Twiss, *J. Chem. Soc.*, **95**, 1489 (1909). Recently, H. P. Ward and I. L. O'Donnell, THIS JOURNAL, **67**, 883 (1945), used the same method to prepare two bis-(2-alkoxyethyl) diselenides, hydrogen peroxide having been used in place of iodine.