# The Institute of Paper Chemistry

Appleton, Wisconsin

## Doctor's Dissertation

# The Degradation of Cellulose in Oxygen and Nitrogen at High Temperatures

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June, 1958

# THE DEGRADATION OF CELLULOSE IN OXYGEN AND NITROGEN AT HIGH TEMPERATURES

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of The Institute of Paper Chemistry
for the degree of Doctor of Philosophy
from Lawrence College,
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June, 1958

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# THE PROBLEM

Cellulose is degraded by heat, but various investigations in the past have not given us a complete insight into the nature of the degradation. Much information has been obtained, however, which demonstrates the complexity of the degradation and the importance of the reaction conditions.

Although cellulose is an important factor in our economy, its use in many applications is limited by its thermal instability. The development of a more heat-resistant form of cellulose would permit a wider utilization of cellulose, and allow the various segments of the cellulose industry to defend themselves better against the inroads of the synthetic polymer industry. A better understanding of the nature of the reactions taking place during the heat degradation[1] of cellulose is basic to the development of heat-resistant forms of cellulose.

The complexity of the heat degradation of cellulose precludes a complete investigation of all phases of the degradation. Of the three general classes of reactions which have been suggested by past investigations as contributing to the heat degradation of cellulose (oxidation, hydrolysis, and pyrolysis)[2], oxidation is the most easily

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[1] Heat degradation is defined here as the deterioration of cellulose under any conditions in which heat is a factor, and implies no specific mechanism.

[2] Oxidation refers to any oxidative reaction with cellulose, including subsequent chain scission as a result of oxidation. Hydrolysis refers to the hydrolytic scission of β -1,4 bonds in the cellulose, and produces materials chemically identical with the original cellulose except for the degree of polymerization. Pyrolysis is defined as the transformation of cellulose into other compounds through the action of heat alone.

identified and measured. Moreover, the effects of hydrolysis can be minimized by using a dry reaction system, while the effects of pyrolysis can be measured as a "blank" by running parallel degradation reactions in both an oxygen and an oxygen-free inert atmosphere. Thus, while the results would not be expected to be applicable to all heat degradations of cellulose, a study of this nature leads to conclusions which can be traced back to one general type of reaction.

The purpose of this thesis, then, was to make a thorough study of one phase of the heat degradation of cellulose in order to obtain an insight into the fundamental characteristics of the degradation. More specifically, the object was to determine whether oxidation is the primary reaction under the selected conditions of temperature, moisture, and gaseous environment.

## LITERATURE SURVEY

Most previous investigations in this field have dealt with the loss of strength during heating, and thus do not give a very complete picture of the degradation reaction. Other more fundamental studies have been made, using the change in various physical and chemical properties as a measure of degradation. In general, these investigations showed that the degradation reaction may be oxidative, hydrolytic, pyrolytic, or a combination of these, depending upon the conditions of reaction. Some of the more important investigations are discussed in the following paragraphs.

### STUDIES OF THE HEAT DEGRADATION OF CELLULOSE

Waller, Bass, and Roseveare (1) studied the degradation of cotton and rayon tire yarn heated in sealed tubes in the presence of air and moisture at 150 to 170°C. They found that the degradation, as measured by the loss in tensile strength, was proportional to both the temperature and the amount of moisture present; the presence of degradation products increased the strength loss. Both the consumption of oxygen and the formation of aldehyde groups increased as the humidity of the surrounding air increased, but the presence of moisture had no effect upon the carboxyl content of the degraded material. These authors suggested that the degradation under the conditions used was due to the formation and subsequent decomposition of oxidized cellulose.

Farquhar, Pesant, and McLaren (2) heated raw unextracted cotton

in atmospheres of air and nitrogen at temperatures of 75 to 220°C. and for reaction times of four and twenty-four hours. Neither the method of heating nor the amount of moisture present was given. Carboxyl content, hydroxyl content, fluidity, and weight loss increase with temperature and time of heating. For any given time and temperature, degradation was greater in air than in nitrogen, although in some cases the results were erratic. These authors measured the susceptibility of the heated cotton to enzymatic hydrolysis; in all cases the hydrolysis was less for the heated material than for the raw cotton. For cotton heated in air the hydrolysis decreased gradually with increasing temperature, while for cotton heated in nitrogen the hydrolysis decreased immediately, but was unaffected by time or temperature (75-200°C.). The authors suggested that a decrease in accessibility, due possibly to the formation of ether links or recrystallization, was responsible for the decreased hydrolysis. However, no explanation was offered for the difference in response to enzymatic hydrolysis between oxygen-heated and nitrogen-heated cotton. Farquhar et al. concluded that "heat alone accounted for only a part of the degradation of cellulose", and that "oxidative action began at lower temperatures and accelerated thermal decomposition at higher temperatures."

The thermal stability of manila insulation paper was studied extensively by Clark (3). The paper was submerged in oil, in a sealed container, with the surface of the oil in contact with air or nitrogen. Tensile strength was used as a measure of degradation. Clark found that the manila paper gradually lost its strength on heating, even in a

dry nitrogen atmosphere, although not as rapidly as when heated in a dry oxygen atmosphere. He also found that the paper went through a "dormant period" on heating, during which no gases were evolved. Moisture was found to have an accelerating effect upon the loss of strength when the paper was heated in glass containers; in this case, moisture appeared to have a more degrading effect than oxygen. Air and moisture accelerated the increase in copper number; the complete loss of tensile strength occurred at a higher copper number when moisture was present than when air was present. Clark also found that the pH of the aqueous extract of the paper decreased with time and temperature, and that the presence of oxygen and water increased the rate of decrease.

Clark concluded that both oxidation and hydrolysis could play a part in the heat degradation of paper, with hydrolysis due partially to the presence of acidic noncellulosic components in the paper (which might not be present in cotton linters). The relative importance of hydrolytic and oxidative degradation, he suggested, depended upon the conditions of heating. Under any conditions, pyrolysis was felt to be the important degrading mechanism during prolonged heating.

Elmquist and Downey (4) exposed cotton sheeting to high temperatures (145-334°C.) in a commercial mangle, varying the time (0-60 seconds) and the pressure (1.3-4.0 p.s.i.) used. They found that an increase in time, pressure, or temperature produced decreases in reflectance at 435 millimicrons, methylene blue absorption, and breaking

strength, and increases in fluidity and copper number. The changes in methylene blue absorption and copper number were considered indicative of the formation of a reducing-type oxidized cellulose, which they postulated was responsible for the degradation.

Agster (5) suggested that several reactions occur during the degradation of cellulose, and that the temperature of the degradation determined the type of degradation. Working with viscose rayon, he concluded that hydrolysis was the primary reaction below 140°C., air oxidation the primary reaction from 140 to 160°, and "cracking" the predominant reaction at temperatures greater than 160°. Haas (6) also postulated a change in reaction with a change in temperature. He suggested that for cotton, the degradation is chiefly oxidative above 200°C., and primarily hydrolytic below 180°.

Orr, Weiss, Humphreys, Mares, and Grant (7) studied the effects of heating in air at various relative humidities on the tensile strength and degree of polymerization of cotton fibers. At constant temperature and humidity both the strength loss and calculated number of chain breakages increased linearly with time; the degradation increased with increasing temperature and relative humidity. Using cotton tire cord, and heating in a range of 110 to 150°C. at 40% relative humidity, Conrad, Tripp, and Mares (8) obtained essentially the same results as Orr and co-workers. On the basis of the behavior in cuprammonium solution of heat-degraded and dilute acid-hydrolyzed cotton, they concluded that the heat degradation was oxidative rather than hydrolytic in nature.

Demus (9) measured the change in viscosity with time when cotton was heated at 150°C.; the decrease in viscosity became slightly less rapid after fifty hours. The presence or absence of oxygen had almost no effect on the viscosity when viscose rayon was heated at 150°. However, Staudinger and Jurisch (10) found that the decrease in degree of polymerization (D.P.) was greater when cotton was heated in air (85-150°C.) than in a high vacuum. It was also found that the D.P. drop after heating in air at 150° was the same whether the cotton was heated two, four, or six days. No attempt was made to explain this effect, and the complete reaction conditions were not given.

Honold, Poynot, and Cucullu (11) heated cotton fabrics at 160°C. in various atmospheres and compared the loss in strength. After two days in dry nitrogen, dry air, water vapor, and air plus water vapor, the losses in breaking strength were, respectively, 24, 46, 82, and 83%. While fabric strength is not the best measure of degradation, the data illustrate the effect which water has in the degradation.

Both Waller and co-workers (1) and Tarkow (12) found that heat-degraded cellulose had a lowered moisture-regain capacity. Tarkow claimed this lowered hygroscopicity was due to the formation of additional hydrogen bonds in the amorphous region, and not to the formation of ether linkages. Since the loss in moisture-regain capacity occurred in both oxygen and nitrogen, he concluded it was not an oxidative effect.

## STUDIES OF THE PYROLYSIS AND DESTRUCTIVE DISTILLATION OF CELLULOSE

An appraisal of the literature cited above leads to the conclusion that the heat degradation of cellulose may be oxidative, hydrolytic, or pyrolytic in nature. Of the three, pyrolysis has been studied most intensively, although most of these studies have been made using vacuum distillations at temperatures above 200°C. Both Hurd (13) and Pigman and Goepp (14) state that levoglucosan (1,6-anhydroglucose) is the main product (40% yield) when cellulose is vacuum-distilled. McCloskey and Coleman (15) made a study of this reaction and concluded that a 1,2-anhydride is an intermediate, since the reaction was blocked by a methoxyl group in the two position. Heuser, in his book on cellulose chemistry (16), also discussed the production of levoglucosan. He suggested that, since the "destructive distillation" of levoglucosan yields compounds which normally form during the destructive distillation of cellulose, it is likely that levoglucosan is an intermediate for these compounds. The fact that levoglucosan is obtained during vacuum distillation suggests that it does not break down in a vacuum. The compounds which Heuser listed (17) as being formed during destructive distillation at temperatures over 200° are: acetic acid, formic acid, acetone, methyl ethyl ketone, phenols, carbolic acid, cresol, toluene, furfural, hydroxymethyl furfural, maltol, $\delta$-valerolactone, methyl furan, 2,5-dimethyl furan, benzene, and diphenyl. Hurd (13) mentioned many of these compounds, as well as carbon monoxide, carbon dioxide, methane, hydrogen, oxygen, water, $\lambda$-valerolactone, xylenol,

guaiacol, valeric acid, cyclopentanone, and various furan homologs. Some of these latter compounds were obtained from high-pressure distillations.

Madorsky, Hart, and Straus (18) made a kinetic study of the vacuum pyrolysis of cellulose. On the basis of their results they concluded that the degradation involved random dehydration along the chain and simultaneous thermal scission of the chain, yielding levoglucosan, water, carbon monoxide, and carbon dioxide. The breaking of the chain was assumed to occur primarily at C--O bonds, since these were stated to be less stable than C--C bonds to thermal breakdown.

Cellulose gives off various types of volatile materials when it is heated. The nature and amount of these materials has been the subject of several papers. Chêne and Rochet (19) used a continuously recording weighing apparatus to study the drying of cotton. They found that cotton retained 0.1% moisture at 105°C., and showed no marked loss in weight between 120 and 183°. However, above these temperatures volatile materials were given off, the evolution becoming very rapid in the range 220-230°. Araki and Iida (20), using a similar weighing device, subjected various forms of cellulose to heat degradation. They concluded that, in air, heat degradation of cellulose (as measured by weight loss) began at 140-150°C., gradually increasing to 180°; rapid loss of weight began at 260°, and burning at 300°. The rate, however, was affected by the surrounding atmosphere: in oxygen the weight decrease began at a lower temperature and burning occurred at

220°, while in nitrogen a rapid weight loss did not occur even at temperatures in the range of 300 to 350°C.

A more thorough study of the gases evolved during the heat degradation of paper in vacuo was made by Murphy (21). He found that measurable amounts of gases were given off from paper even at temperatures as low as 100°C. The gases consisted essentially of water, carbon dioxide, and carbon monoxide. After prolonged heating, the molar proportions of these gases approached the ratio 10:2:1, as determined by a freezing-out procedure. It was also found that the rate of evolution of carbon dioxide increased after the paper was exposed to oxygen for several hours and then tested for evolution of gases in vacuo at a higher temperature. Exposure to carbon dioxide and nitrogen had no effect upon the subsequent evolution of gas. It was concluded that heat degradation in air would be substantially the same as that in vacuo, with the exception of rate differences.

Clark, in his study of manila insulating paper (3), also investigated the gases of decomposition. He found that there was an induction period, at any temperature, during which heated paper gave off no gases. The length of this "dormant period" depended inversely upon the temperature, the presence of oxygen, and the presence of moisture. The amount of gas obtained increased as the temperature of heating (in nitrogen) increased, and the composition of the evolved gas also changed with temperature. At 100°C. the predominant gas was oxygen; as the temperature increased to 200° and over, the predominant gases

were carbon monoxide and carbon dioxide, with a minor amount of unsaturated hydrocarbons. Clark attributed these gases to the decomposition of oxidized cellulose.

Puddington, in a study of the vacuum pyrolysis of cellobiose (22), found that the main reaction at 210-240° was dehydration. However, in following the evolution of gaseous products, he also determined the presence of carbon monoxide and carbon dioxide, and small amounts of acids, aldehydes, and volatile solids. The ratio water: carbon dioxide:carbon monoxide eventually reached the proportions 64:4:1, with approximately two moles of water for every mole of cellobiose. Perlin studied the thermal decarboxylation of uronic acids at 255°C. (23). At this temperature, the initial reactions were decarboxylation and dehydration, followed later by the formation of carbon monoxide and volatile acids. After 15 minutes, nitrogen dioxide-oxidized cellulose evolved carbon dioxide in amounts equivalent to the uronic acid content as determined by the 12% hydrochloric acid method. After this time, the production of carbon dioxide, carbon monoxide, and volatile acids was attributed to decomposition of the cellulose. Perlin also found that, under the conditions of heating used, reducing sugars gave 3% carbon dioxide in 15 minutes, while cotton cellulose and starch yielded only negligible amounts.

Stamm (24), in a study of the heat degradation of Douglas-fir wood components, measured the amounts of carbon monoxide, carbon dioxide, tar, and noncondensable volatiles evolved from several wood

fractions at 220°C. Hemicelluloses gave the greatest amounts of these materials, alpha-cellulose the next greatest, and lignin the least. Although Stamm found that alpha-cellulose produced carbon dioxide on heating while Perlin found cotton linters did not, differences in the techniques used by these authors probably account for the discrepancy. Smith and Howard heated cotton cellulose in nitrogen over a temperature range of 190 to 400°C. (25), and found that the gases from heating at 250° consisted of 74.6% carbon dioxide, 11.6% hydrogen, 12.1% carbon monoxide, and 1.6% hydrocarbons. They found that, as the temperature of heating was increased, the carbon content of the residue increased and the hydrogen and oxygen contents decreased. The effect was particularly pronounced at temperatures above 200°. Friedel and Queiser (26) confirmed this result by studying the infrared spectrum of cellulose heated under similar conditions. They found that the spectrum given by the brown char obtained at 190°C. was not significantly different from the spectrum of cellulose, whereas a radical change was found to take place when cotton was heated in the range 190-250°.

Many reactions given in Hurd's book on pyrolysis (13) show that the carbon dioxide, carbon monoxide, and water evolved from heated cellulose are probable products of the heat degradation. Among the many illustrations are the following:

1) Production of carbon monoxide from the pyrolysis of aldehydes, ketones, sucrose, cellulose, formic acid, and hydroxy acids.

2) Production of carbon dioxide from the pyrolysis of sucrose, cellulose, carboxylic acids, β-ketonic acids, and dibasic acids.

3) Production of water from many compounds, especially by the formation of lactones and anhydrides and as a by-product of oxidation reactions.

The conditions necessary for the formation of these gases, as well as the more complex products, naturally varied with the nature of the material undergoing degradation. Nevertheless, these reactions illustrate possible sources of some of the products obtained from heated cellulose.

## STUDIES OF THE HEAT DEGRADATION OF CELLULOSE DERIVATIVES

The degradation of cellulose derivatives by heat, in the presence of oxygen, has been the subject for several investigations. In some of these, the study was thorough enough to permit the authors to postulate a mechanism for the degradation.

In order to establish the mechanism for the oxidative degradation of ethyl cellulose, McBurney (27) measured the rate of oxygen absorption, as well as the ethoxyl, carboxyl, and peroxide content under controlled reaction conditions. The rate of oxygen absorption was found to vary with both time and temperature, but to be independent of the degree of substitution and chain length. An induction period was noticed, and found to be a function of the free aldehyde content of the derivative. On the basis of this and other information, McBurney concluded that the degradation was a peroxide-catalyzed chain reaction which was initiated at reducing end groups and aldehyde groups within the chain. The formation of carboxyl groups, loss of ethoxyl groups, and chain scission was attributed to the decomposition of ether hydroperoxides by a thermal mechanism.

Cellulose acetate is much more stable than ethyl cellulose, but at temperatures in the range above 160°C. oxidation occurs, as shown by loss in strength, increase in color, and solubility changes. Evans and McBurney made a study of this degradation (28), but were not able to deduce a specific mechanism for the reactions. The major products of the decomposition were found to be carbon monoxide, carbon dioxide, acetic acid, and water. The rate of oxygen consumption was similar to that of an auto-catalytic free-radical process, and showed an induction period followed by a zero-order reaction. This type of oxygen consumption was not found by Waller and co-workers (1) in their work with cotton yarn; the rate of oxygen consumption by the yarn was rapid at first, but diminished with time and appeared to approach zero after 24 hours at 150°C. The evolution of gaseous products from cellulose acetate was generally linear with the amount of oxygen absorbed; the change in intrinsic fluidity (a measure of chain breaks) was linear at first, then went through a rate change. This was considered indicative of a change from random attack to a specific attack, possibly on the chain ends. On the basis of the available information, no mechanism could be derived. It was noted, however, that oxidative degradation was accompanied by a purely thermal breakdown which undoubtedly contributed to the effects noted.

Hobbs and Wilson (29) also made a study of the accelerated aging of cellulose acetate film over a temperature range of 60 to 176°C., using moist and dry nitrogen and moist and dry oxygen as surrounding atmospheres. Although Clark (3) found that moisture had a far greater

effect than oxygen on the degradation of manila paper, Hobbs and Wilson concluded that moisture had only a minor influence on the heat degradation of cellulose acetate film. The principal degradation was found to be oxidative in nature, and the extent of degradation to be a function of the oxygen concentration. On the basis of Arrhenius plots (time to reach a given intrinsic fluidity vs. reciprocal temperature), they concluded that the degradation reaction was the same over the temperature range studied. This conclusion is contrary to Agster's findings (5) on the degradation of viscose rayon, and to Haas' work (6) with cotton. Further evidence for the oxidative nature of the degradation was obtained when Hobbs and Wilson found that the addition of antioxidants to the film held degradation to a negligible amount.

Several authors have shown (11, 30, 31) that materials made from cotton acetylated to a degree of substitution of approximately one are more resistant to heat degradation than materials made from unacetylated cotton. Honold and co-workers (11) found, for example, that after four days in air at 160°C. cotton fiber lost 70% of its breaking strength, while partially acetylated fiber lost only 20% of its breaking strength. Schreiber, Bullock, and Ward (32) made a study of the resistance of partially acetylated cellulose to nitrogen dioxide oxidation and hydrochloric acid hydrolysis. The partially acetylated material retained its strength and fluidity and developed essentially no carboxyl and carbonyl groups when subjected to the nitrogen dioxide treatment, and was more resistant than untreated cotton to acid hydrolysis.

Since Malm and co-workers (33) have shown that the primary hydroxyl groups are preferentially acetylated, it appeared that at a degree of substitution of one the large majority of primary hydroxyl groups were acetylated, and as a result were resistant to oxidation to carboxyl groups by nitrogen dioxide. However, preventing the oxidation of primary hydroxyl groups does not explain the heat resistance of partially acetylated cellulose, since oxidation restricted to primary hydroxyl groups would not result in chain cleavage. Schreiber et al. concluded that the resistance was probably due to the prevention of hydrolytic splitting in a manner not determined.

In another study of cellulose derivatives, Wolfrom and co-workers (34) studied the controlled heat degradation of cellulose nitrate. Among the products found were carbon dioxide, carbon monoxide, methane, hydrogen, formaldehyde, formic acid, glyoxal, water, nitrous oxide, nitric oxide, and nitrogen dioxide. It was postulated that the formaldehyde came from the $C_6$ carbon, and the glyoxal from the $C_1$-$C_2$ carbons, by a thermal breakdown of the ring structure.

## SUMMARY OF PREVIOUS WORK

Work by many investigators in the past has established that the conditions under which cellulose is degraded by heat have a major role in determining the nature and the extent of the degradation. The conditions which have been found to be important are the temperature, the amount of oxygen present, the amount of moisture present, the pressure, and the time of reaction.

A great many changes have been found to take place when cellulose is degraded at high temperatures. The carboxyl, carbonyl, and hydroxyl group contents increase, and various gases are released. The D.P. decreases, as do the moisture-regain capacity, susceptibility to enzymatic hydrolysis, and pH of the residue. Based on a wide variety of heating conditions and methods of analysis, various investigators have suggested that the degradation is oxidative, hydrolytic, or pyrolytic, or a combination of these.

No single reaction appears to predominate under a given set of conditions. Clark (3), for example, felt that both oxidation and hydrolysis occur during the early stages of degradation, but that pyrolysis is by far the main reaction after a relatively short time. Agster (5) suggested that the primary reaction changed from hydrolysis to oxidation to "cracking" with increasing temperature; Haas (6) also felt that the temperature governed the type of reaction, but suggested that oxidation predominates in the temperature range for which Agster postulated "cracking" as the primary reaction. This lack of agreement is also apparent when studies to determine the effect of moisture are compared; although it has generally been found that the presence of moisture accelerated the degradation, Hobbs and Wilson (29) found that moisture had little effect on the heat degradation of cellulose acetate. One point at which general agreement has been reached is that pyrolysis occurs at high temperatures, i.e., greater than 200°C. It was also concluded that this reaction occurs to a much lesser extent at lower temperatures.

The relative importance of oxidation and hydrolysis under a given set of reaction conditions is far from established. That oxidation occurs can be shown by the formation of carboxyl groups. Clark (3), however, discounts the importance of oxidation as a degrading mechanism since, as he suggests, the oxidation of the primary hydroxyl group in cellulose would not be expected to reduce the chain length or the tensile strength of cellulose fiber. McBurney (35), on the other hand, concluded that oxidation was the primary reaction, and that chain cleavage was a result of thermal decomposition of the oxidized cellulose. The occurrence of hydrolysis cannot be shown as easily as oxidation, and must be inferred from such effects as lowered viscosity and increased carbonyl content (which could also be a result of oxidation). The increased degradation, which occurs in an inert atmosphere as the amount of moisture present is increased, also points to a hydrolytic reaction. However, because of the difficulties in separating effects, there is still a lack of agreement over the relative importance of oxidation and hydrolysis when cellulose is degraded at high temperatures.

## MATERIALS

Acetate-grade cotton linters were used throughout the experimental program. These linters, obtained through the courtesy of the Buckeye Cellulose Corporation, were labeled as follows: "Buckeye Cotton Oil Co., Cellulose and Specialties Division, BUKIPULP. Acetate Grade Cotton Linters Pulp Type 1:AY:500, for Dr. Kyle Ward, Jr." Before use in the thesis work the linters were run through a Wiley Mill with no screen to break up lumps. They were then stored in a covered container until needed.

The linters were analyzed to determine the characteristics of the raw material. The results of these analyses are given in Table I.

TABLE I

ANALYSIS OF ORIGINAL COTTON LINTERS

| | |
|---|---|
| Carboxyl content | 0.42 meq./162 g. |
| Uronic acid content | 3.47 meq./162 g. |
| Carbonyl content | 2.85 meq./162 g. |
| Intrinsic viscosity (nitrate) | 17.50 |
| Degree of polymerization | 1775 |
| Ash content | 0.01% |
| Wax content | 0.21% |

The D.P. value was almost identical to that calculated from the cuprammonium and cupriethylenediamine viscosities which were supplied by the Buckeye Cellulose Corp. for this lot. The calculation was made using the nomograph and equations suggested by Gloor and Klug (36).

It should be noted that the uronic acid content was considerably higher than the value for total carboxyl. This, however, was not

unexpected, since small amounts of carbon dioxide are evolved gradually even from many sugars and polysaccharides which contain no uronic acid groups. In view of this fact, Browning (37) stated: "...amounts of carbon dioxide in the range of 0.2 to 0.4% cannot be considered definite evidence of the presence of uronic acid groups." The value of 3.47 meq. per 162 grams of linters is equivalent to slightly less than 0.1% carbon dioxide.

The gases used in the degradation runs were obtained from the Matheson Company. The oxygen was "extra-dry", with a minimum purity of 99.6%. The nitrogen was "prepurified", with a minimum purity of 99.996% and a maximum oxygen content of 8 parts per million.

The majority of the solvents and chemicals used were reagent grade. The acetone and the ethanol were c.p. grade, and the calcium sulfate and n-pentane were technical grade. The Hopcalite catalyst and the Ascarite absorbent were commercial products of unknown purity. The ethylenediamine tetraacetic acid was obtained as "Titra-Ver", the disodium-dihydrogen-dihydrate, from the Hack Chemical Co., and was designated "highest purity." The anhydrous sodium borohydride was obtained from Metal Hydrides, Inc., and labeled 98+%.

# APPARATUS AND METHODS

## CLOSED SYSTEM

The reaction apparatus designated as the closed system was designed so that the cotton linters were heated in a closed, circulating atmosphere. Provision was made for absorbing any water, carbon dioxide, and carbon monoxide which was evolved.

Neither the volume measurement nor the absorption train functioned properly. As a result, the closed system was used only for a few preliminary degradation runs to find a convenient operating temperature. The majority of the degradation runs were made in an open system, which will be described in the next section.

The design of the closed system was based upon the apparatus used by Evans and McBurney (28) in their study of the oxidation of cellulose acetate. A complete description of the closed system and its operation is given in the Appendix.

## OPEN SYSTEM

### DESCRIPTION

The open-flow, or noncirculating, system was used for the large majority of the degradation runs. A diagram of this system, as used for runs in oxygen, is shown in Figure 1. The reaction oven was made of Transite with insulated double walls, and had a small door in front to provide access to the reaction vessel during runs. A steady flow

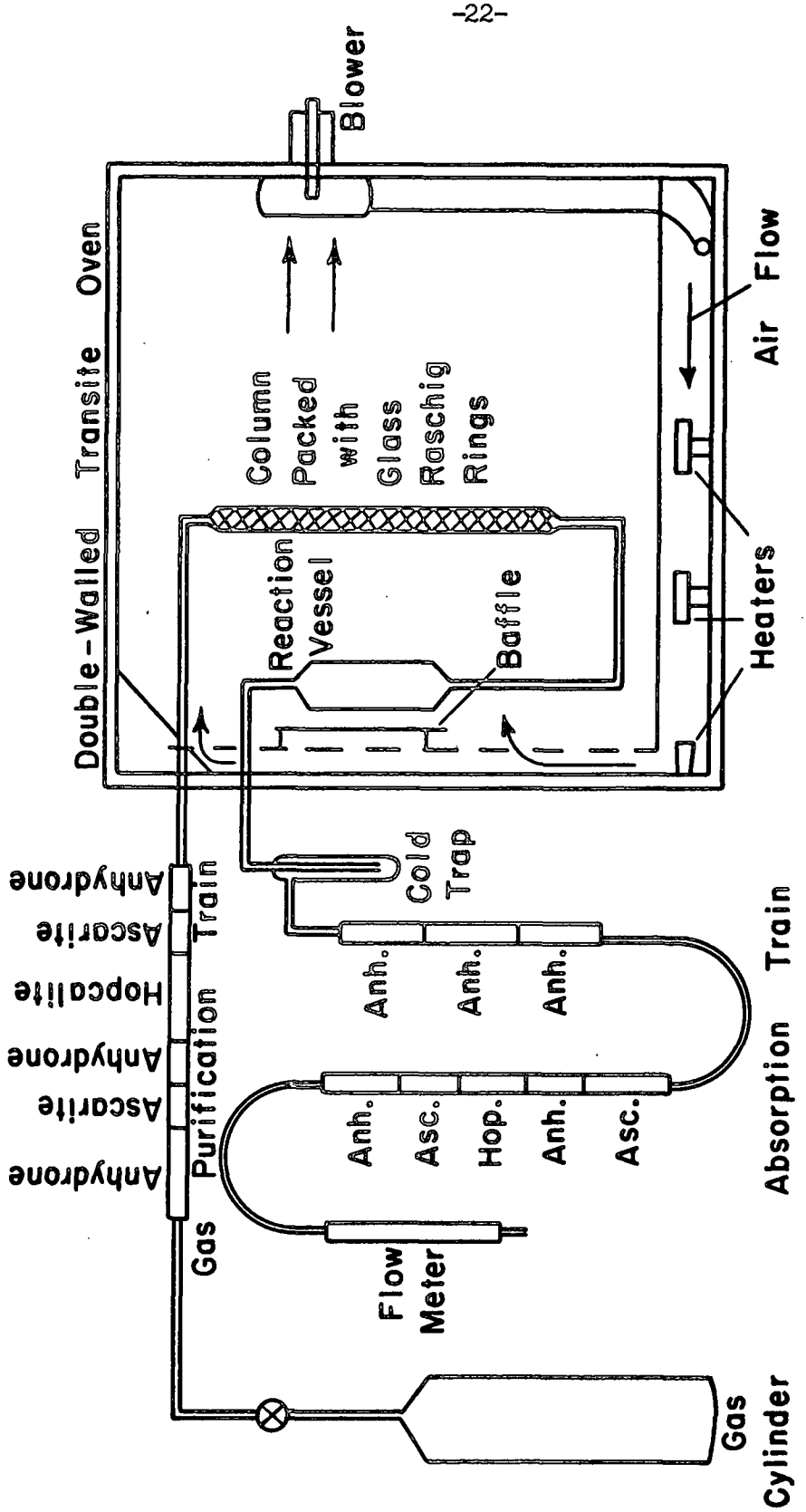


Figure 1. Open Reaction System for Runs in Oxygen

of oxygen (or nitrogen) was passed through the linters, after first passing through a purifying absorption train. The entire system, including the packed tower for preheating the gas, was made of glass, using semi-ball joints.

The two 750-watt fin heaters and the 600-watt cone heater were capable of heating the oven to temperatures in excess of 200°C. An American Instrument Co. "Quickset" bimetal thermoregulator, operating through an electronic relay, was used to maintain the oven temperature to within 1.0°C. by controlling one of the fin heaters. A turbine blower, with a capacity of 50 cu. ft. per min., was used to promote circulation within the oven, and to aid heat transfer to the reaction apparatus. A small thermometer within the reaction vessel gave the temperature of the linters within the vessel; this temperature was generally 2-3° less than the oven temperature.

The absorbents used in the absorption train were Anhydrone (anhydrous magnesium perchlorate), Hopcalite (a catalyst, composed of heavy metal oxides, for oxidizing carbon monoxide to carbon dioxide), and Ascarite (sodium hydrate and asbestos fiber). These absorbents were used, in both the purification and absorption trains, in the following order: Anhydrone, Ascarite, Anhydrone, Hopcalite, Ascarite, and Anhydrone. The order of gas absorption was thus water, carbon dioxide, and carbon monoxide (as carbon dioxide).

OPERATION

The warmup period of the reaction oven was about 90 minutes. During this time the absorption tubes and reaction vessel containing the dried linters were weighed; the sample size was 40-45 grams of dry cotton linters. After the reaction temperature was reached, the system was flushed with the gas to be used in the reaction for 15-20 minutes, after which the absorption train was connected and the reaction vessel (see Figure 2) containing the dried sample was inserted. Reaction time was measured from the time the sample was inserted. The gas flow was then adjusted to 125± 5 ml. dry gas (S.T.P.) per minute. After the reaction period was over, the reaction vessel and absorption tubes were removed and weighed. Evolved water was calculated from the weight increase of the three Anhydrone tubes, carbon dioxide from the weight increase of the first Ascarite-Anhydrone combination, and carbon monoxide from the weight increase of the second Ascarite-Anhydrone combination.

Since the Hopcalite catalyst requires oxygen to oxidize carbon monoxide to carbon dioxide, the absorption train had to be rearranged when runs in nitrogen were made. The flowmeter was placed after the first Ascarite-Anhydrone combination, and oxygen was bled into the absorption system immediately prior to the Hopcalite tube, so that both the exhaust nitrogen and pure oxygen flowed through the Hopcalite tube and the second Ascarite-Anhydrone combination.

Blank runs, without a sample, were made to determine the efficiency

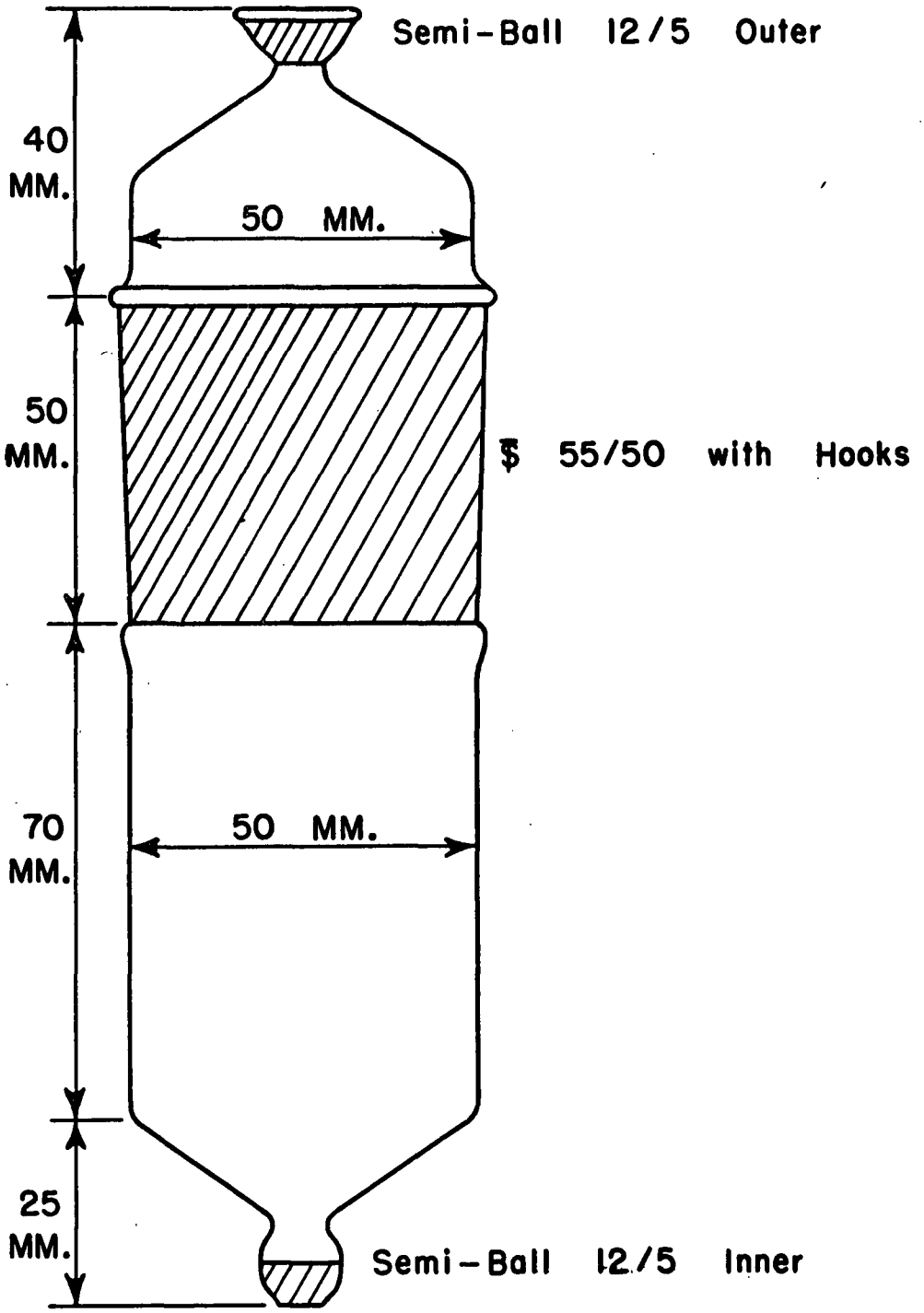


Figure 2. Reaction Vessel

of the gas purification train. The results of these runs, each of which lasted twelve hours at 170°, are shown in Table II.

TABLE II

BLANK RUNS IN THE OPEN SYSTEM

| Evolved Gas | Oxygen Blank | Nitrogen Blank |
|---|---|---|
| $H_2O$, mmoles[1] | 0.189 | 0.332 |
| $CO_2$, mmoles | 0.016 | 0.002 |
| CO, mmoles | 0.050 | 0.025 |

[1]millimoles

The values shown above are only a small percentage of the actual values determined during comparable runs. Since the blank runs were made after the purification train had been used for most of the degradation runs, the values shown are considered the maximum error. No corrections were made for the error in the analytical values given for the various degradation runs, since the error did not appear to be constant.

For two of the runs in the open system, a cold trap was inserted before the absorption train as shown in Figure 1. This trap was kept at a temperature of -10° with an ice-salt bath. The outlet from the trap led directly into the absorption train.

## PREDRYING OF RUN SAMPLES

Before linter samples were placed in the reaction apparatus, they

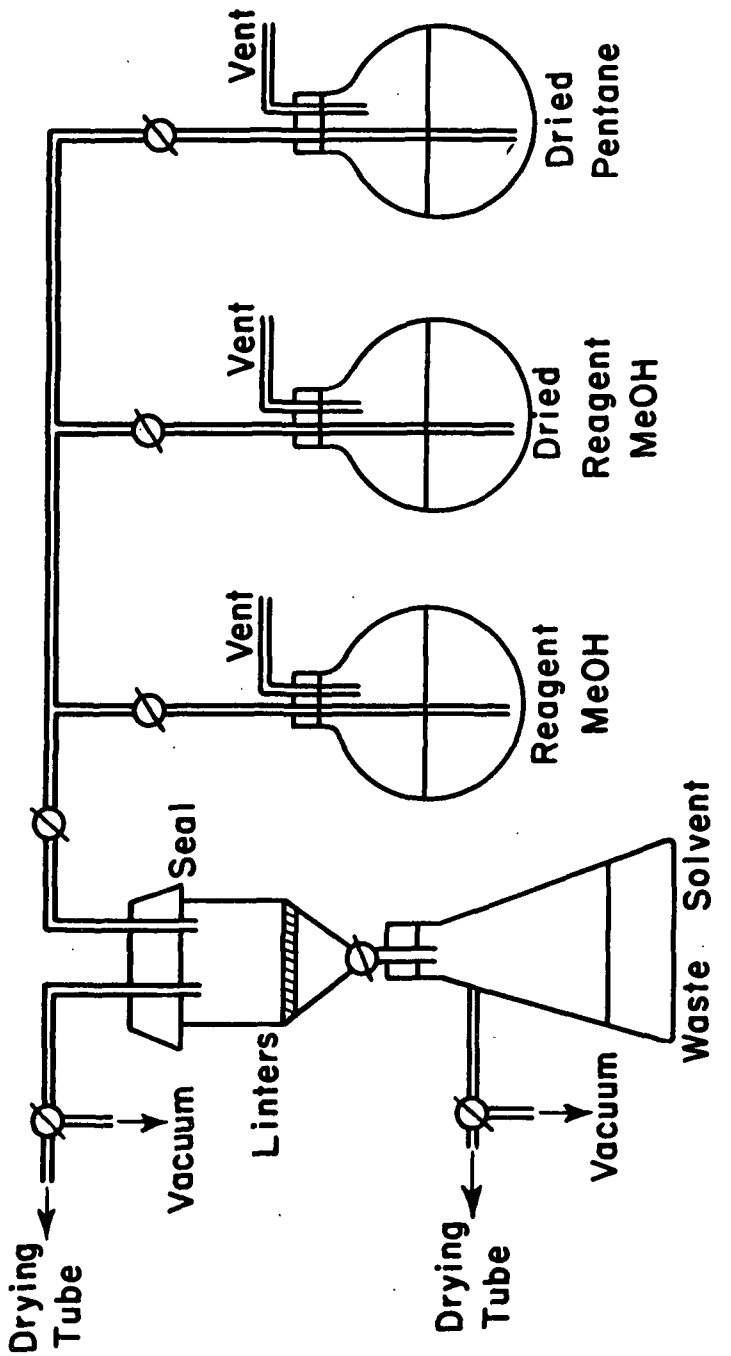


Figure 3. Solvent-Exchange Apparatus

were dried in order to remove as much water as possible from the system. The linters were first placed in the reaction vessel, then dried in a vacuum oven at 60°C. over Anhydrone for at least 24 hours. This was found to dry the linters slightly more thoroughly than oven drying at 105°C., and avoided the higher temperature of the open oven.

## SOLVENT-EXCHANGE DRYING

The apparatus for solvent-exchange drying is shown in Figure 3. The linters were soaked in distilled water overnight, then transferred to the apparatus. Then, without further exposure to the atmosphere, the linters were treated successively to 30-minute soaks in three 300-ml. portions of reagent methanol, two 300-ml. portions of dried reagent methanol, and two 300-ml. portions of dried n-pentane. The linters were then sealed from the atmosphere in the sintered funnel, removed to a dry-box, and transferred to the reaction vessel while in the dry-box. The solvent was removed from the linters by passing dried prepurified nitrogen, heated to 30°C., through the reaction vessel overnight. The nitrogen flow rate was 50 cc. (S.T.P.) per minute. Merchant (38) found a surface area of 85 to 90 square meters per gram for cellulose treated in this manner.

The methanol was dried by shaking overnight with calcium sulfate, then distilling from the calcium sulfate through a heated Widmer column. The pentane was refluxed overnight over fresh sodium wire, then distilled to another flask.

## CARBONYL CONTENT

This method is based on the reduction of carbonyl groups with sodium borohydride in a buffered solution. The borohydride solution will quantitatively reduce aldehydes, ketones, and lactones, but not carboxyl groups when the latter are in the salt form (39, 40). The following determination is a modified version of the method of Strȍle (41).

### REAGENTS

Sodium borohydride: Approximately one gram of sodium borohydride was dissolved in 0.1N sodium hydroxide to make one liter of 0.1% solution. This solution slowly lost hydrogen, but was sufficiently stable to be used over a period of several weeks.

Buffer: A 500-ml. solution of 3.753 grams glycine and 2.926 grams sodium chloride in distilled water was prepared. A 490-ml. portion of this solution was added to 500 ml. of 0.1N sodium hydroxide to obtain a pH of 11.0.

Acid: Sulfuric acid was diluted to approximately 2N with distilled water.

### PROCEDURE

The apparatus is illustrated in Figure 4a. The sample (0.5-1.5 g.) was placed in section B, along with 20 ml. of buffer solution. Five milliliters of acid were placed in section C. The vessel was stoppered,

placed in a constant-temperature bath, and allowed to stand ten minutes; stopcock $S_1$ was then closed from the atmosphere and the buret reading taken. A two-ounce bottle had been previously filled with the borohydride stock solution and stoppered with a serum cap; this was sufficient for three blanks and one pair of duplicate determinations. Ten milliliters of the borohydride solution were removed from the serum bottle by positive pressure displacement using two 20-ml. hypodermic syringes. Care was necessary to prevent loss of hydrogen during the transfer. The solution-containing syringe was weighed, and the solution injected into the reaction vessel (arm A) through a serum cap which covered the open end of stopcock $S_2$. The stopcock was then closed, and the empty syringe reweighed. The vessel was tipped to permit the borohydride solution to run into section B with the sample, and allowed to stand two hours. (The two-hour reaction period was not used when running blanks.) The acid was then tipped into the mixture to release the excess (unreacted) hydrogen from solution. The volume of hydrogen evolved was read from the gas buret.

The increase in volume read on the buret was corrected for the volume of borohydride solution added, and the volume of hydrogen evolved was then corrected to standard conditions (10 grams of borohydride solution, 25°C., one atmosphere). During summer months a water jacket was added around the gas buret, and water at 25°C. circulated through the jacket. This eliminated the need for temperature correction. The following order of determination was used: blank A, sample 1, blank B, sample 2, blank C. Each sample was compared

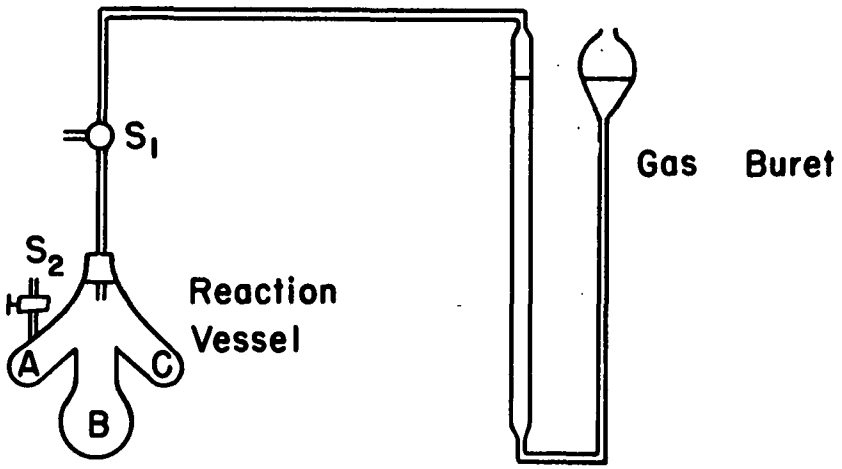


Figure 4a. Apparatus for Carbonyl Determination

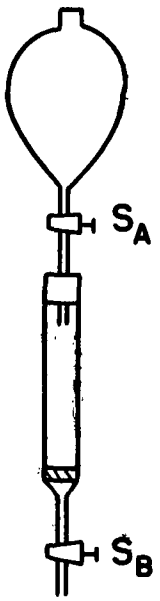


Figure 4b. Apparatus for Carboxyl Determination

with the average of the blanks on either side of it to find the volume of hydrogen consumed. One mole of hydrogen reduces one equivalent of carbonyl, and the volume of hydrogen can be converted to milliequivalents (meq.) of carbonyl per 162 grams of linters by the ideal gas laws.

This method of carbonyl determination was used for all carbonyl values given in the section on Experimental Results. The standard deviation was 1.08 meq. of carbonyl per 162 g. of linters.

Since the sodium borohydride solution was at a pH of 11.0, there existed the possibility that chain cleavage due to alkaline sensitivity would result in the formation of additional carbonyl groups during the determination. To estimate whether this effect was occurring, the sodium borohydride method was compared to the hydroxylamine hydrochloride method of Gladding and Purves (42), in which the test solution has a pH of 5. On Run IVA linters, the sodium borohydride method gave a carbonyl content of 10.22 meq. per 162 g. of linters, while the hydroxylamine hydrochloride method gave a carbonyl content of 10.90 meq. per 162 g. Since the standard deviation of the borohydride method was 1.08 meq. per 162 g., there was no significant difference in the results obtained using the two different methods of analysis. The conclusion, therefore, was that chain scission did not occur during the borohydride carbonyl determination.

## CARBOXYL CONTENT

This method involves the dynamic ion-exchange principle in which the linters are first washed with dilute acid, then treated with an aqueous cation solution. The change in cation concentration is a measure of the carboxyl groups in the cellulose. The method used was that of Sobue and Okubo (43).

### REAGENTS

Ethylenediamine tetraacetic acid (EDTA): 1.2738 g. of Hack Chemical Co. "Titra-Ver" (disodium dihydrogen ethylenediamine tetraacetic dihydrate), equivalent to 1.0003 g. EDTA, were dissolved in distilled water to make one liter. This solution was standardized against pure calcium carbonate; one milliliter of EDTA solution was equivalent to 0.1303 mg. calcium.

Buffer: 67.5 g. of ammonium chloride were dissolved in 570 ml. of 28% ammonium hydroxide and diluted to one liter with water.

Indicator: 0.5 g. Erichrome Black T and 4.5 g. hydroxylamine hydrochloride were dissolved in 100 ml. of methanol.

Acid wash: Concentrated hydrochloric acid was diluted to approximately 0.1N with distilled water.

Calcium solution: A 0.5M stock solution of calcium acetate was prepared, and stored in a refrigerator under toluene. The dilute solution used in the analysis was obtained by diluting 0.34 ml. of the stock solution to one liter with distilled water.

PROCEDURE

The apparatus is shown in Figure 4b. The weighed sample (0.5-1.0 g.) of linters was shaken in a stoppered flask with 50 ml. of 0.1N hydrochloric acid, until the sample disintegrated, then transferred to the previously weighed reaction tube and pressed into a cake with a glass rod. The cock $S_B$ was closed and the inside of the tube washed with dilute acid. The separating funnel, containing 200 ml. of dilute acid, was connected, stopcock $S_A$ opened, and stopcock $S_B$ adjusted so that the acid passed continuously at a rate of four milliliters per minute. After the acid passed through, the tube was flushed with 20 ml. of distilled water, drained, and reweighed.

Immediately after this weighing, 50 ml. of dilute calcium acetate solution were used to wash the sides of the reaction tube (stopcock $S_B$ was closed to prevent loss of this solution), and another separating funnel, containing 200 ml. of dilute calcium acetate solution, was connected. This solution was passed in the same manner as the acid solution, and the filtrate from the tube collected in a 250-ml. volumetric flask. Additional calcium acetate solution was added to the separating funnel if the filtrate did not reach the standard line on the flask.

Twenty-five milliliter aliquots of the filtrate and the original calcium acetate solution were titrated with EDTA solution after adding 2 ml. of buffer and several drops of indicator. The end point was reached when the purple color of the indicator changed to blue-green.

The carboxyl content of the linters was calculated from the change in concentration of the calcium acetate solution, making allowance for the dilution due to water retained from the flushing operation. (The amount of water retained was known from the weight increase of the reaction tube). The standard deviation of the determination was found to be 0.18 meq. carboxyl per 162 g. of linters.

## NITRATION

A method developed by Bennett and Timell (44) was found to give a high degree of nitration. The linters (0.25 g.) were cooled to -30°C., and the nitrating mixture, prepared by combining acetic anhydride and fuming nitric acid (60% acetic anhydride by volume), added with stirring to the linters at that temperature. The nitration was carried out for three hours at 0°C., then the mixture was poured into water chilled to 0°C. and washed with more water at the same temperature. The nitrated linters were stabilized with methanol. A nitrogen content of greater than 14% was easily obtained using this method.

Some of the more highly degraded linters gave nitrated products which were only partially soluble in acetone. The nitration reaction itself was no more difficult, and the degree of nitration did not decrease markedly. However, the nitrated linters appeared very brittle; upon addition of acetone they did not become gelatinous, but rather showed up as short fiber particles which did not dissolve. The linters were also relatively insoluble in ethyl acetate and ethyl lactate.

This same effect was found by Parkinson (45) for linters oxidized with nitrogen dioxide. Since esterification before nitration did not improve the solubility of the nitrate, he concluded that carboxyl groups were not responsible for the insolubility. He then tried both oxidation and reduction prior to nitration, and found that borohydride reduction of the carbonyl groups greatly diminished the solubility problem.

In an attempt to improve solubility, the heated linters were reduced with sodium borohydride prior to nitration. The reaction was carried out for 24 hours at room temperature. Unbuffered solutions of the borohydride in water (pH of 9.7) in concentrations of 0.5M and 0.05M were used; 125 ml. of solution were used per gram of degraded linters. The reduced linters were washed, dried, and then nitrated and added to acetone in the normal way. The reduction step gave a nitrated product which was definitely more soluble in acetone; in some cases, the increased solubility gave a higher, and presumably more accurate, degree of polymerization. The effect is discussed more fully in the Appendix.

## NITROGEN CONTENT

A semimicro Kjeldahl determination published by Timell and Purves (46) was used to ascertain the degree of nitration. A 15-25 milligram sample of the nitrated cellulose was dissolved in concentrated sulfuric acid and salicylic acid; sodium thiosulfate and anhydrous potassium sulfate were added and the mixture digested until the solution was colorless. A 30% sodium hydroxide solution was added, and the ammonia

which was formed was steam-distilled into boric acid containing a mixed indicator of brom cresol green and methyl red in ethanol. Standard hydrochloric acid was used to titrate back to the red color of the indicator.

## DEGREE OF POLYMERIZATION

The viscosity of the nitrated linters was determined in acetone solution. Five hours of shaking were generally sufficient for solution; in the case of highly degraded linters, however, twenty-four hours or more were required. Solutions were prepared at concentrations of 0.025, 0.050, 0.100, and 0.200 g. of nitrated linters per 100 ml. of acetone; the exact concentrations were known. Viscosities were obtained in duplicate in Cannon-Fenske viscometers, and intrinsic viscosity obtained by extrapolation to zero concentration. To convert intrinsic viscosity to D.P., the relationship $[\eta]=\underline{K}_{\underline{m}}\underline{M}^{\underline{a}}$ was used (47), where $\underline{K}_{\underline{m}}$ is $1.1 \times 10^{-4}$ and $\underline{a}$ is 0.91 (48). This relationship is applicable to unfractionated nitrocellulose having a nitrogen content of 13.74-13.89% and a molecular weight in the range 25,000-1,000,000 when dissolved in acetone. No correction for shear rate was made, since in the D.P. range under consideration this correction is not important (49).

## WAX CONTENT

The method of Conrad (50) was used. The linters (5-8 g.) were extracted with ethyl alcohol in a Soxhlet extractor, the ethanol combined with chloroform, and the mixture then washed with water to remove sugars and other nonwaxy components.

## ASH CONTENT

The linters (2.5-3.0 g.) were charred in a porcelain crucible with a burner flame, then ignited in a muffle furnace for two hours at 750°C.

## URONIC ACID CONTENT

Institute Method 25 was used for this determination; the sample weight was 2.0-2.5 g.

## ROTATION OF SUGARS

Rotation of sugar and other solutions was determined in the standard manner, using a Zeiss Winkel polarimeter and a 1.92-ml. polarimeter tube. Solutions were filtered through activated charcoal and celite to improve clarity.

## INFRARED ANALYSIS

Infrared analyses were run by Lowell Sell of the Institute Analytical Department, using a Perkin-Elmer Model 21 Recording Infrared Spectrophotometer and the potassium bromide pellet technique. Linter samples were run through a micro Wiley Mill with an 80-mesh screen in order to reduce particle size.

## X-RAY DIFFRACTION PATTERNS

Samples for use in x-ray analysis were prepared by pressing a hand-formed ball of fibers (about 0.4 g.) in a hydraulic press at 8000-12,000 pounds. The samples were trimmed to fit the sample holder,

weighed, and the bulk density calculated. The minimum caliper used was 0.040 in.

The apparatus used to obtain the patterns was a North American Philips Co., Inc., instrument with a copper target and nickel filter, set at 35 kilovolts and 20 milliamperes. The scanning angle (2θ) was 12 to 26 degrees, the scanning rate was one-quarter degree per minute, and the slit width was one-half degree. The following rate meter settings were used: scale factor=16, multiplier=1.0, and time constant=4 seconds. The chart speed was one inch per minute.

The degree of crystallinity was calculated by two methods: that of Ant-Wuorinen (51) and that of Hermans and Weidinger as interpreted by Ant-Wuorinen (51). A sample calculation, using both methods, is given in the Appendix.

## EXTRACTION OF LINTERS

All extractions were run at room temperature. The linters and extracting liquid were placed in a jar and agitated for two to five days on a rotating mixer. The linters were then filtered off, and the extracting liquid used for further analysis. No standard sample size was used.

## DETERMINATION OF ACIDS IN AQUEOUS EXTRACTS

The aqueous extract of a degraded linters sample was extracted with ether to remove formic, acetic, and any other ether-soluble acids.

Ethanol was added to the ether layer, and the ethanol-ether solution was titrated with alcoholic potassium hydroxide using phenolphthalein indicator. A blank was also run.

## ACID HYDROLYSIS

The Forest Products Laboratory method of acid hydrolysis (52) was used. Three milliliters of 72% sulfuric acid were added to 0.3 g. of linters, and the mixture held at 30°C. for one hour. The mixture was then diluted with 84 ml. of distilled water and heated for one hour in an autoclave at 15 pounds (221°F.). After cooling, the solution was stirred with freshly washed Amberlite IR-4B carbonate-form ion-exchange resin.

For several of the hydrolyses, addition of saturated barium hydroxide solution to a pH of 5 was used to remove sulfate ions.

## ENZYMATIC HYDROLYSIS

Two enzymes, one from Aspergillus niger and one from Trichoderma viride, were used as described in the following paragraphs.

### HYDROLYSIS WITH ASPERGILLUS NIGER ENZYME

A Rohm and Haas preparation from Aspergillus niger, designated by them as "Enzyme 19, Mix 9, Sugar-Free", was used in these hydrolyses. The techniques of Walseth (53) for the use of this preparation were followed.

An enzyme solution was prepared from the dry product, and filtered to remove insoluble material. For the hydrolysis, a cellulose concentration of 3% and an enzyme concentration of 3% (both expressed as grams of solids per 100 ml. of solution) were used. An acetate buffer was used to maintain the pH at 4.5, and phenylmercuric acetate antiseptic was added in a concentration of 50 parts per million. The hydrolysis mixture, in a sealed vial, was held at 47°C. for 24 hours, with occasional shaking. After the hydrolysis period, the mixture was heated for 30 minutes at 80°C. to inactivate the enzyme, and filtered.

HYDROLYSIS WITH TRICHODERMA VIRIDE ENZYME

The sample of Trichoderma viride filtrate was obtained through the courtesy of Dr. Elwyn T. Reese of the United States Army Quartermaster Corps Research Division. The enzyme preparation was labeled as follows: "Cellulase of T. viride. QM6a. 14 $C_x$/ml. Code Tv12. pH 4.7. Optimum temperature 50-55°C. Use as is. E. T. Reese, 3/20/57."

The hydrolysis was run in sealed vials, with a cellulose concentration of 1%, for 48 hours at 50°C. The mixture was then heated at 15 pounds (221°F.) in an autoclave to inactivate the enzyme.

## PAPER CHROMATOGRAPHY

Several chromatographic solvents and spray reagents were used in an attempt to characterize the compounds obtained from hydrolysis and extraction of the degraded linters. In all cases, descending paper chromatography procedures were used, using Whatman No. 1 filter paper.

The most effective solvent system was ethyl acetate:acetic acid:formic acid:water (18:3:1:4). Other solvent systems used were ethyl acetate:acetic acid:water (9:2:2), butanol:acetic acid:water (63:10:27), butanol:pyridine:water (10:3:3), isobutyric acid saturated with water, and methyl ethyl ketone saturated with water. The developers used were:

A. Methyl orange (acids)
B. 4-(4-Dimethylamino-1-naphthylazo)-3-methoxy benzene-sulfonic acid (acids).
C. Permanganate:periodate:benzidine (general)
D. Ammoniacal silver nitrate (general)
E. p-Anisidine hydrochloride (sugars)
F. o-Amino biphenyl (sugars)
G. 2,4-Dinitrophenylhydrazine (carbonyl compounds)
H. Diazotized p-nitroaniline (phenols)
I. Diazotized benzidine (phenols)
J. Ferric chloride (phenols)

Spray B, an acid-base indicator, was also known as EK 1954. The most useful sprays were B, C, F, G, H, and I.

## EXPERIMENTAL RESULTS AND DISCUSSION

The conditions of reaction and the results of analytical studies of the degradation runs are given in Tables III, IV, and V. The runs were designated by Roman numerals. Those followed by an "A" were run in oxygen, those followed by a "B" were run in nitrogen. Runs which have the same Roman numeral were run under identical conditions, with the exception of the gas which was used as the surrounding atmosphere during the run.

In the sections to follow, the degraded linters will be identified by the run from which they were obtained, e.g., "Run IVA linters" designates the degraded linters residue obtained from Run IVA.

### RUNS IN THE CLOSED SYSTEM

The results of runs made in the closed system are given in Table V. Due to leakage within the system, these runs were not very successful. A comparison of Runs IIIA and IIIB (closed system) with Runs IVA and IVB (open system), all of which were made at 170°, shows definite discrepancies. Run IIIB linters, for example, were more highly degraded than Run IVB linters. It is felt that this was due to the presence of oxygen, from an air leak, in the supposedly oxygen-free atmosphere of Run IIIB. The agreement between Runs IIIA and IVA was better, presumably because an air leak in an oxygen system would have less effect than an air leak in an inert system.

TABLE III

RESULTS OF DEGRADATION RUNS IN THE OPEN SYSTEM AT 170°C.

| Run No. | Atmos. | Time, hours | Analytical Results: Yield, %[a] | [η] | D.P. | Carboxyl,[b] meq./162 g. | Carbonyl,[c] meq/162 g. | Evolved Gases, mmoles/162 g. $CO_2$ | CO | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Orig. | | | | 17.50 | 1775 | 0.42 | 2.85 | | | |
| VIIIA | $O_2$ | 2 | 100.11 | 13.20 | 1220 | 0.92 | 4.53 | 0.96 | 0.46 | 21.90 |
| IXA | $O_2$ | 6 | 99.95 | 9.85 | 920 | 1.10 | 7.04 | 1.73 | 0.85 | 23.35 |
| XIA | $O_2$ | 12 | 99.75 | 5.94 | 540 | 1.35 | 6.64 | 5.52 | — | 32.30 |
| XIIA | $O_2$ | 18 | 98.57 | 6.07 | 540 | 1.55 | 8.10 | 7.67 | 2.65 | 120.50[d] |
| IVA | $O_2$ | 24 | 98.45 | 3.96 | 340 | 2.29 | 10.22 | 9.38 | 4.10 | 44.40 |
| IVAA | $O_2$ | 24 | 99.09 | 4.31 | 375 | 2.20 | 10.03 | 12.11 | 5.38 | 65.40 |
| XA | $O_2$ | 96 | 97.04 | 2.36 | 190 | 8.40 | 24.10 | 49.65 | 28.40 | 279.00 |
| VIIIB | $N_2$ | 2 | 99.80 | 15.50 | 1530 | 0.45 | 5.35 | 0.22 | 0.35 | 14.50 |
| IXB | $N_2$ | 6 | 99.83 | 15.35 | 1510 | 0.57 | 6.15 | 0.39 | 0.41 | 25.30 |
| XIB | $N_2$ | 12 | 99.95 | 15.32 | 1510 | 0.41 | 6.64 | 0.99 | 1.01 | 24.62 |
| XIIB | $N_2$ | 18 | 99.69 | 13.22 | 1280 | 0.44 | 7.30 | 0.18 | 0.73 | 28.76 |
| IVB | $N_2$ | 24 | 99.61 | 13.21 | 1280 | 0.42 | 7.05 | 0.22 | 1.32 | 33.20 |
| XB | $N_2$ | 96 | 99.68 | 8.34 | 770 | 0.34 | 8.73 | 1.55 | 4.36 | 31.10 |

a Per cent of ovendry degraded linters based on ovendry original linters.

b Standard deviation of carboxyl determination was 0.18 meq./162 g. of linters.

c Standard deviation of carbonyl determination was 1.08 meq./162 g. of linters.

d Includes water not removed during regular drying procedure.

TABLE IV

THE EFFECT OF TEMPERATURE AND SOLVENT-EXCHANGE DRYING ON DEGRADATION

Runs in Oxygen in the Open System

| Run No. | Time, hours | Temp., °C. | Yield, % | $[\eta]$ | D.P. | Carboxyl, meq./162 g. | Carbonyl, meq./162 g. | Evolved Gases, mmoles/162 g. $CO_2$ | CO | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Orig. | | | | 17.50 | 1775 | 0.42 | 2.85 | | | |
| XXXIA | 12 | 170 | 99.75 | 5.94 | 540 | 1.35 | 6.64 | 5.52 | 1.66[a] | 32.30 |
| VA | 12 | 185 | 98.60 | 2.35 | 185 | 3.00 | 17.03 | 18.49 | 8.66 | 117.20 |
| VIIA | 12 | 200 | 96.74 | 1.97 | 160 | 7.42 | 21.90 | 19.06 | 9.47 | 99.25 |
| IVA | 24 | 170 | 98.45 | 3.96 | 340 | 2.29 | 10.22 | 9.38 | 4.10 | 44.40 |
| IVAA | 24 | 170 | 99.09 | 4.31 | 375 | 2.20 | 10.03 | 12.11 | 5.38 | 65.40 |
| VIA[b] | 24 | 170 | — | 2.35 | 185 | 4.41 | 15.80 | 18.47 | 12.88 | 338.00[c] |

a. Estimated from Fig. 9.

b Solvent-exchanged linters.

c Includes evolved solvent.

TABLE V

RESULTS OF DEGRADATION RUNS IN THE CLOSED SYSTEM

| Run No. | Atmos. | Time, hours | Temp., °C. | $[\eta]$ | D.P. | Carboxyl, meq./162 g. | Carbonyl, meq./162 g. |
|---|---|---|---|---|---|---|---|
| Orig. | | | | 17.50 | 1775 | 0.42 | 2.85 |
| I | $O_2$ | 10 | 143 | - - | — | 0.86 | — |
| IIA | $O_2$ | 12 | 150 | 12.29 | 1200 | 0.37 | 5.62 |
| IIB | $N_2$ | 12 | 150 | 12.42 | 1200 | 0.92 | 3.24 |
| IIIA | $O_2$ | 24 | 170 | 4.69 | 400 | 1.20 | 10.67 |
| IIIB | $N_2$ | 24 | 170 | 7.70 | 750 | 0.71 | 9.77 |

The runs in the closed system did serve to show that degradation at temperatures of 150°C. and less was too mild to be easily measured after a relatively short reaction period, i.e., several hours.

## RUNS IN THE OPEN SYSTEM

### THE EFFECT OF SOLVENT-EXCHANGE DRYING

The linters used in Run VIA were dried by solvent exchange before insertion in the reaction apparatus, using a solvent sequence of water, methanol, dried methanol, and dried n-pentane. Merchant (38) found that cellulose dried in this manner had a surface area (as measured by nitrogen adsorption) of 85-90 square meters per gram, while cellulose dried directly from water had a surface area of 0.5-1.0 square meters per gram. A comparison of Run VIA (solvent-exchange-dried) with Runs IVA and IVAA (both water-dried), all of which were run under the same reaction conditions, is given in Table IV.

The linters which had been dried by solvent exchange were degraded much more than those which had been dried from water. The much higher value for evolved water was probably inaccurate, because retention of solvent definitely occurs (38) and the measured weight gain of the Anhydrone tubes was due primarily to evolved solvent. The increased degradation of the solvent-dried sample was probably due to greater accessibility of the cellulose to the reactant. The effect of this increased accessibility was comparable to a 15° increase in reaction temperature or a 24-hour increase in reaction time

(compare Run VIA data with Figures 5, 7, and 8). Thus, even though one would expect that accessibility would have but little influence in a reaction between molecular oxygen and fibrous cellulose, the data from Table IV indicate that accessibility may be a factor in the reaction. The retained solvent may also have had some effect, although the methanol, which could have been oxidized to formic acid, presumably was completely removed by the n-pentane.

THE EFFECT OF TEMPERATURE

Only a limited number of runs is available to illustrate the effect of temperature on the extent of degradation. The analytical results for these runs are shown in Table IV.

Runs XIA, VA, and VIIA were made in an oxygen atmosphere for twelve hours. As the temperature of the reaction increased, the extent of degradation increased, although not smoothly. The greatest change occurred between 170 and 185°; only the carboxyl content showed a comparable increase between 185 and 200°. It thus appears that the extent of oxidative degradation is not a linear function of temperature over the range 170-200°C., but the data are not sufficient to permit an explanation of the changes in rates. Agster (5), Clark (3), and Farquhar et al. (2) suggested that pyrolysis becomes more important than oxidation in this temperature range, which would tend to explain the results in Table IV. Haas (6), however, postulated that oxidation is the primary reaction above 200°, which is an apparent contradiction of the data obtained here.

THE EFFECT OF TIME

Most of the runs were devoted to investigating the changes which took place as heating progressed at a given temperature. A temperature of 170°C. was selected because oxidative effects at this temperature were pronounced enough to be measured, and because pyrolytic effects were less pronounced than at a temperature near 200°.

At the temperature of 170°, six runs were made in both oxygen and nitrogen; the reaction times used were 2, 6, 12, 18, 24, and 96 hours. Duplicate runs were made in oxygen for 24 hours in order to estimate the reproducibility of the runs. The degree to which reproducibility was attained can be seen by a comparison of Runs IVA and IVAA in Table III. The carboxyl and carbonyl contents for these two runs agreed well within the standard deviations of the analytical methods, and the viscometric D.P.'s were very close in value. The values for evolved gases were somewhat lower for Run IVA. The primary reason for this was assumed to be insufficient packing of the absorption tubes, since channeling was observed. This condition was corrected in Run IVAA and all subsequent runs (i.e., those numbered higher than IV).

The analytical results for all runs made at 170° in the open system are given in Table III, and shown graphically and discussed in the following pages.

The Effect of Heating Time on D.P.

As shown in Figure 5, the D.P. of the cotton linters decreased when heated, regardless of whether the heating took place in an oxygen or a nitrogen atmosphere. Since the D.P. was determined using nitrate viscosity, the chain length decrease was a true decrease, rather than a result of a secondary reaction as might be the case in an alkaline cellulose solution. The decrease in chain length was quite rapid in oxygen during the first twenty hours; the rate then gradually diminished until a leveling-off D.P. of about 200 was reached after forty hours. This effect was suggested by the incomplete data of Staudinger and Jurisch (10). The D.P. dropped less rapidly in nitrogen; it reached 800 after 96 hours, but there was no evidence of a leveling-off D.P. at that point.

McBurney has stated (54) that the change in intrinsic fluidity is the best measure of chain breakage. The validity of this statement was established in a derivation which involved several basic assumptions: 1) the rate of chain breakage was independent of link position, and proportional only to the concentration of unbroken links, 2) the ratio of broken to unbroken links was low, and 3) the viscosity average molecular weight was approximately equal to the weight average molecular weight. Using these assumptions, McBurney showed that both the number of broken links and the change in intrinsic fluidity were proportional to the time of degradation.

The data used in Figure 5 were recalculated, and are shown in

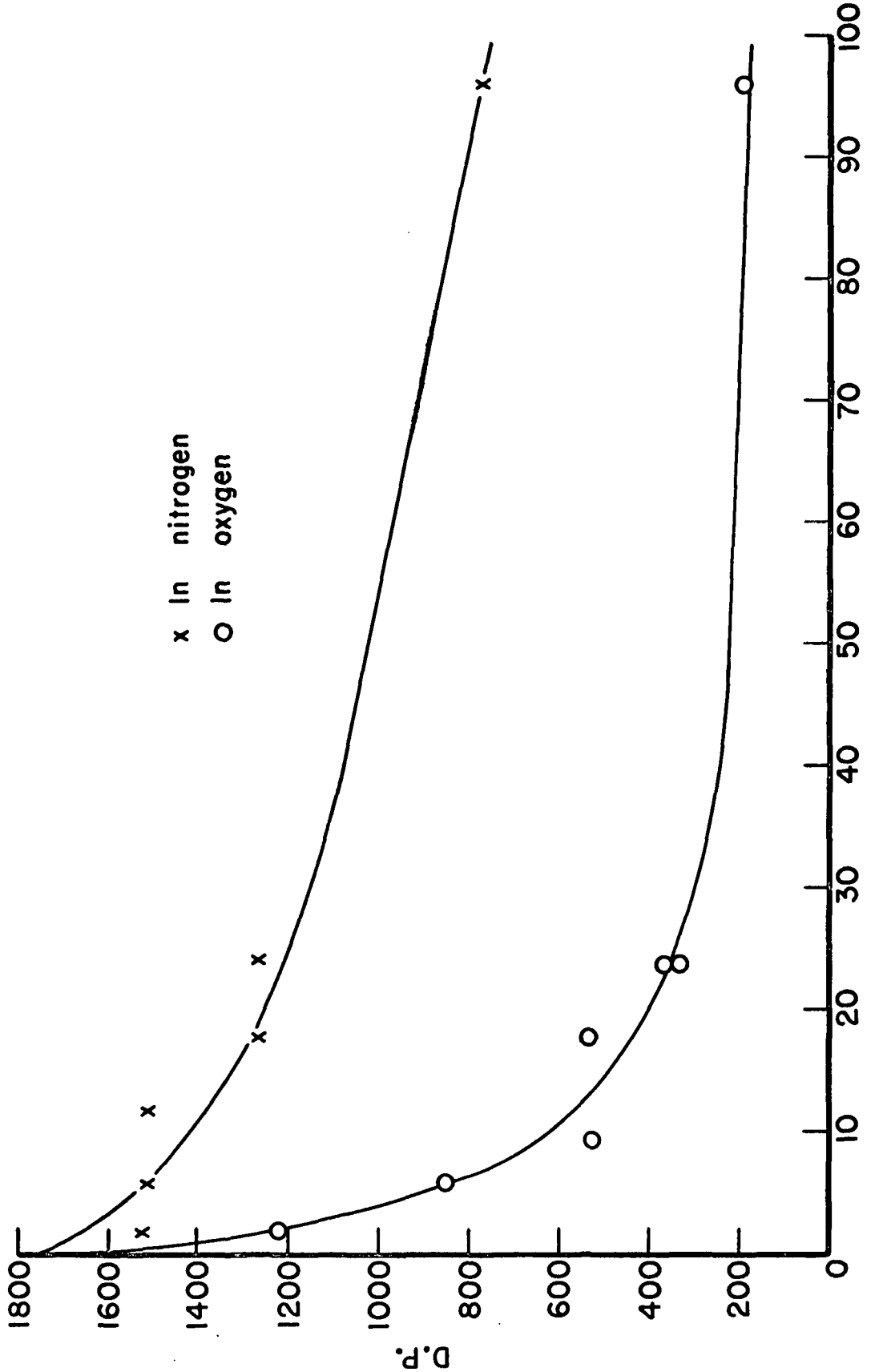


Figure 5. Effect of Reaction Time at 170° on D.P.

Figure 6, in terms of intrinsic fluidity vs. time. From this figure, it appears that the rate of chain breakage in nitrogen is a simple zero-order reaction with respect to time, since the fluidity change was linear with time. The rate of chain breakage in oxygen was linear up to about thirty hours, but then decreased. The available data show only the general shape of the curve after 24 hours. However, it would seem likely that the rate in oxygen approaches the rate shown for the degradation in nitrogen. Orr and co-workers (7) did not find this decrease in rate after 50 hours at 162°C.

It is apparent that, under the reaction conditions used, heating in oxygen does not lower the D.P. of the cotton linters below approximately 200. In Run VIIA (200°, 12 hours), which appeared to give a highly degraded residue, the D.P. of the degraded linters was likewise only slightly below 200. Several authors have determined the length of cellulose crystallites by subjecting the cellulose to severe hydrolysis followed by ultrasonic dispersion. Nickerson and Habrle (55) found the crystallite length of cotton linters to be approximately 1200 Å, corresponding to 240 D.P., while Rånby and Ribi (56) suggested a leveling-off D.P. of 100 after very severe hydrolytic degradation. Thus, the leveling-off D.P. reached after prolonged heating in oxygen at 170° appears to be rather closely related to the size of the cotton linter crystallites. This would imply that the oxygen attack on fibrous dry cellulose takes place primarily and preferentially in the amorphous regions.

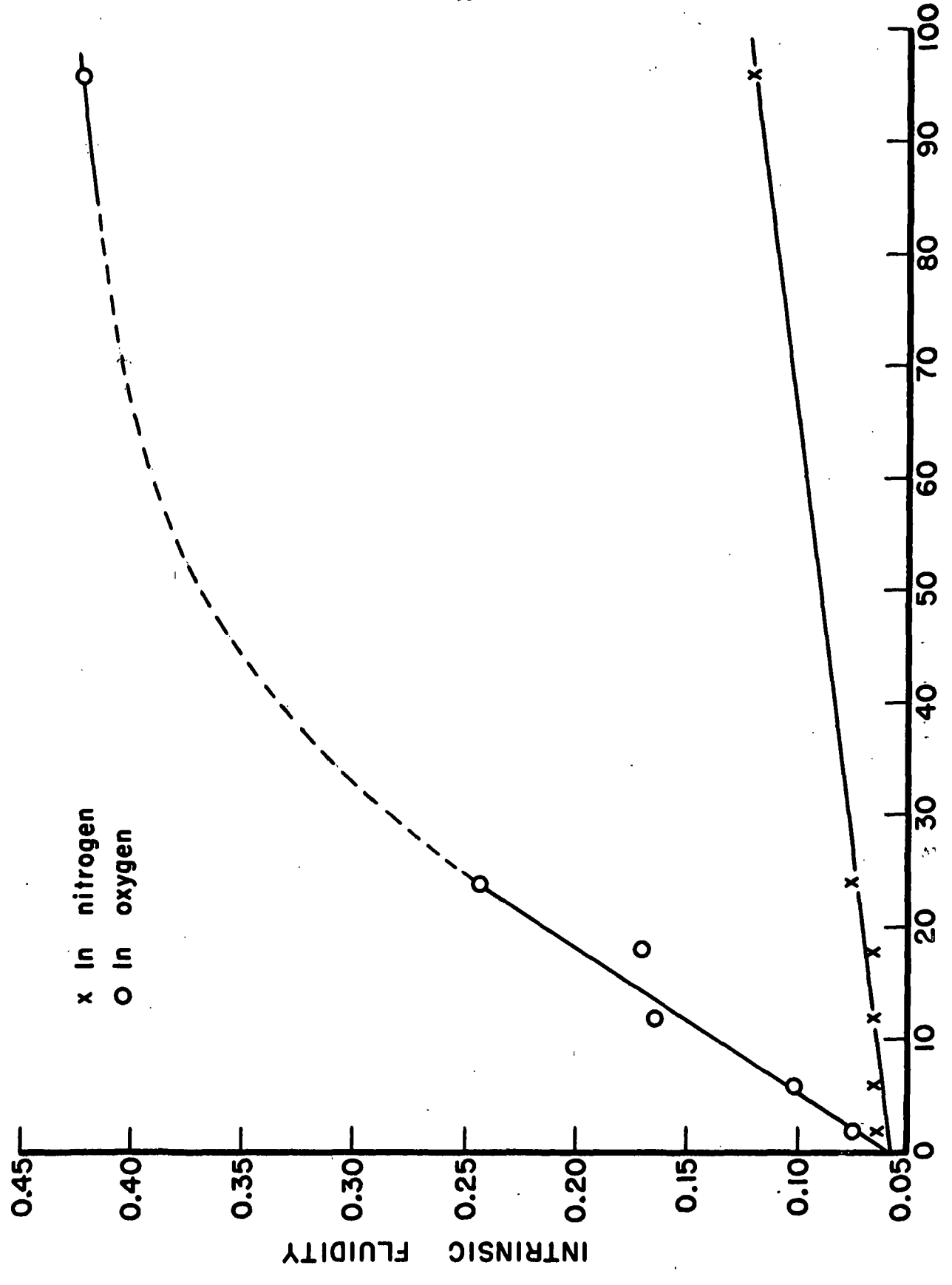


Figure 6. Effect of Reaction Time at 170° on Intrinsic Fluidity

Davidson (57) and Nevell (58) have studied the effect of specific oxidants[1] (periodate and nitrogen dioxide) and a nonspecific oxidant[1] (chromic acid) on the x-ray diffraction pattern of cellulose. With the nonspecific oxidant, no change was observed in the x-ray diagram, and the result was similar to that of acid hydrolysis. For the specific oxidants, however, a gradual change in the x-ray diagram was noted, which was described as an increase in the diffuse nature of the characteristic cellulose bands. They concluded that the specific reagents were attacking throughout the cellulose, but that the non-specific reagent was limited in its attack to the amorphous region. Moreover, the nonspecific oxidant continued to react in the amorphous region with the primary products of oxidation, giving rise to a heterogeneous series of compounds. The nature of these secondary reaction products would thus be dependent upon the conditions of reaction. McBurney (35) also pointed out that, at comparable degrees of oxidation, cellulose oxidized by specific oxidants retained its fibrous structure, while cellulose oxidized by nonspecific oxidants became a friable powder.

Since a leveling-off D.P. was attained after about forty hours at 170°, and since the Run XA linters resembled a friable powder, the comparison with the behavior of the specific oxidants mentioned in the above paragraph was further studied by means of x-ray diffraction

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[1] A specific oxidant for cellulose is one which attacks the anhydroglucose unit only at specific hydroxyl groups, while a nonspecific oxidant is one which attacks the anhydroglucose unit at any point.

curves, the data for which are discussed in a later section. In summary, essentially no change in crystallinity was found when samples of original, Run XA, and Run XB linters were compared at equal bulk density. Thus, the data suggest that the attack in oxygen takes place preferentially in the amorphous region, while the wide range of reaction products obtained (to be discussed in later sections) suggest that oxygen is a nonspecific oxidant.

The continuous drop in D. P. which occurred when cotton linters were heated in nitrogen was probably due mainly to pyrolytic effects; Clark (3) has also shown degradation to occur in the absence of oxygen. Some oxidative degradation may have occurred, however, due to the presence of oxygen retained on the starting material or to the slight oxygen contamination of the nitrogen which was used. Although the amount of moisture present was low, some very localized hydrolysis may also have taken place.

## The Effect of Heating Time on the Formation of Carboxyl and Carbonyl Groups

The formation of carbonyl and carboxyl groups during heating in oxygen and nitrogen is shown in Figures 7 and 8. There was essentially no formation of carboxyl groups when the linters were heated in nitrogen. In oxygen, on the other hand, the formation of carboxyl groups was almost linear with time, with some indication of a rate increase after about fifty hours. After 96 hours of heating in oxygen at 170°, there was approximately one carboxyl group for every one hundred anhydroglucose units.

The rate of carbonyl group formation was somewhat different than that of carboxyl formation. In oxygen, the rate appeared to be almost linear, with no evidence of a rate increase after fifty hours. There was, in fact, some indication that the rate decreased somewhat after about fifteen hours. After 96 hours, the amount of carbonyl formed in oxygen-heated linters was one carbonyl group for every forty anhydroglucose units.

There was also definite evidence of the formation of carbonyl groups when the heating was done in nitrogen. The formation appeared to take place primarily during the first 25 hours, after which the rate became essentially zero. This is contrary to Clark's work, since he found (3) that the copper number continued to increase when manila paper (0.05% moisture) was heated in sealed vials in a nitrogen atmosphere. However, the increase noted by Clark may have been the result of hydrolysis due to the presence of acidic noncellulosic materials. As shown in Figure 8, the amount of carbonyl groups determined in both the linters heated in oxygen and those heated in nitrogen was greater than would be anticipated from the amount of reducing end groups calculated from the D.P. This difference was also noted for the original linters; in this case the discrepancy between actual and calculated carbonyl (about 2.5 meq. per 162 g.) was probably due to carbonyl groups introduced during the bleaching stage of the linter purification, but might have been due to the constant used to calculate the D.P. Regardless of this original discrepancy, however, carbonyl groups definitely were produced during the heating of linters in nitrogen. Since most of this carbonyl content was formed in the first few hours, it may have been due to oxidation or hydrolysis from oxygen or water retained on the linters.

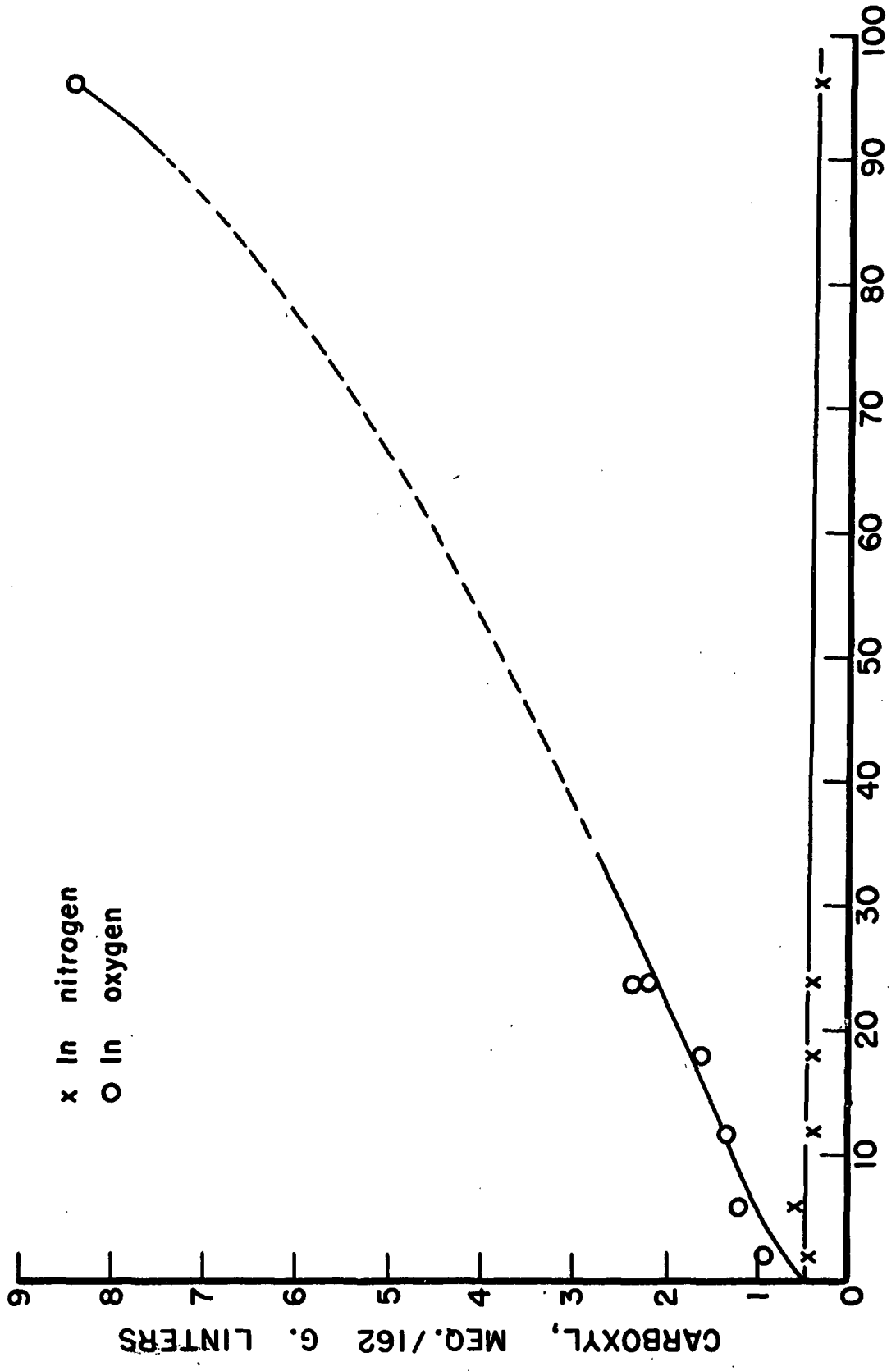


Figure 7. Formation of Carboxyl Groups During Heating at 170°C.

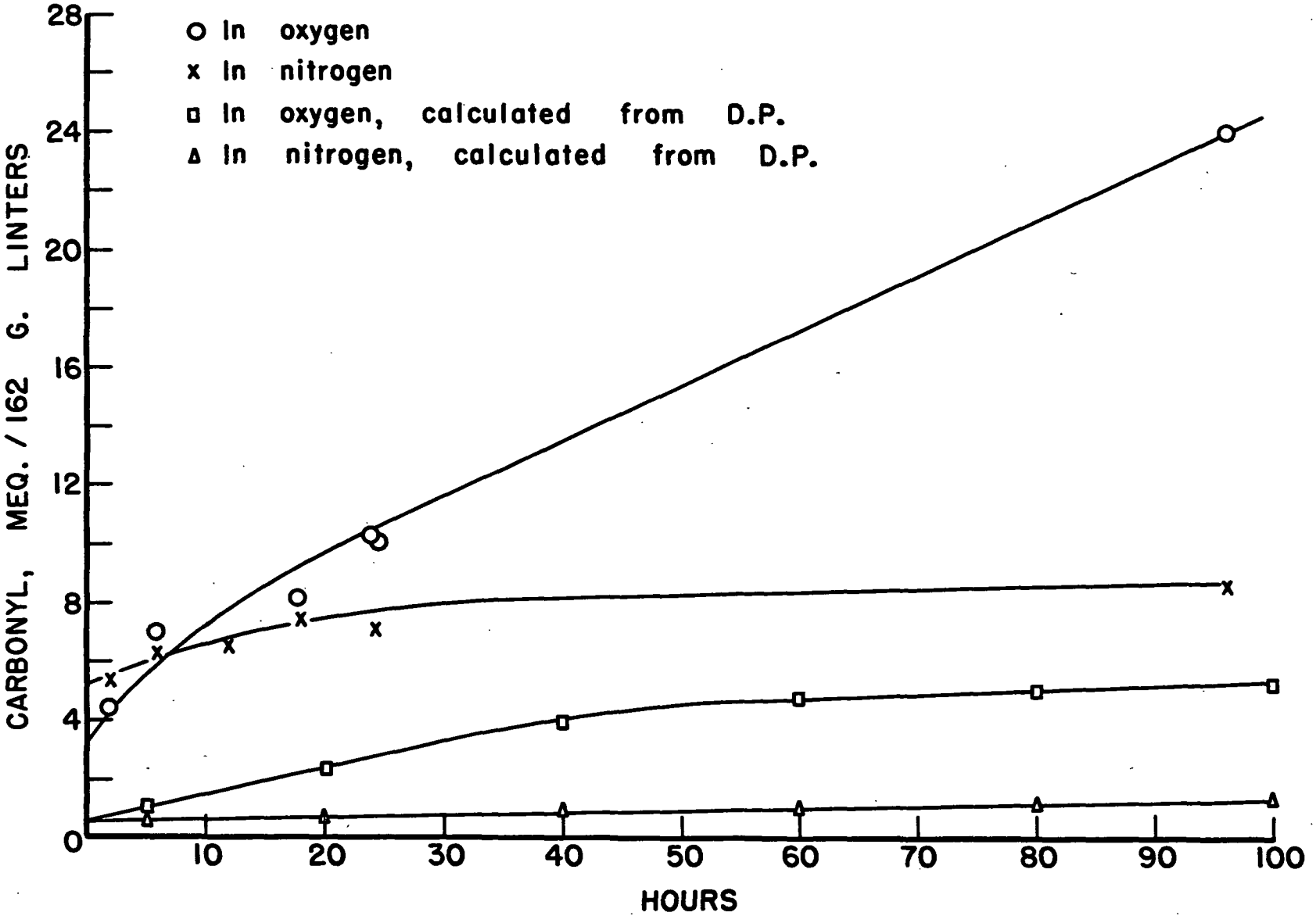


Figure 8. Formation of Carbonyl Groups During Heating at 170°C.

The Effect of Heating Time on the Evolution of Gases

The evolution of carbon monoxide and carbon dioxide from the linters during heating is shown in Figure 9. During heating in oxygen, the carbon dioxide and carbon monoxide evolution followed a pattern similar to that shown in the formation of carboxyl groups. At any given time, the amount of carbon monoxide evolved was about half the amount of carbon dioxide evolved.

It is felt that the carbon monoxide and carbon dioxide came from different sources, i.e., that carbon dioxide was not an oxidation product of carbon monoxide. This is substantiated by the work of Kondrat'ev, who showed (60) that oxygen and carbon monoxide are able to coexist at 650 to 700°C. with only a very small amount of reaction. As shown by Hurd (13), both carbon dioxide and carbon monoxide can be formed by thermal decomposition of various reactive groups and compounds. It is therefore suggested that the carbon dioxide and carbon monoxide isolated from the reaction in oxygen are the products primarily of the decomposition of carboxyl and carbonyl groups, respectively. During 96 hours of heating in oxygen, one mole of carbon dioxide was evolved for every 20 moles of anhydroglucose, and one mole of carbon monoxide was evolved for every 36 moles of anhydroglucose.

In the inert atmosphere very little carbon dioxide and carbon monoxide were formed. This was especially true of carbon dioxide. This, combined with the finding that no carboxyl groups were formed during heating in nitrogen, is a further indication that the carbon dioxide was a product of the decomposition of carboxyl groups. At 170° in an inert atmosphere Clark (3) found no evidence of evolved gases until heating had progressed for 17 hours. The present data show no sign of this "dormant period."

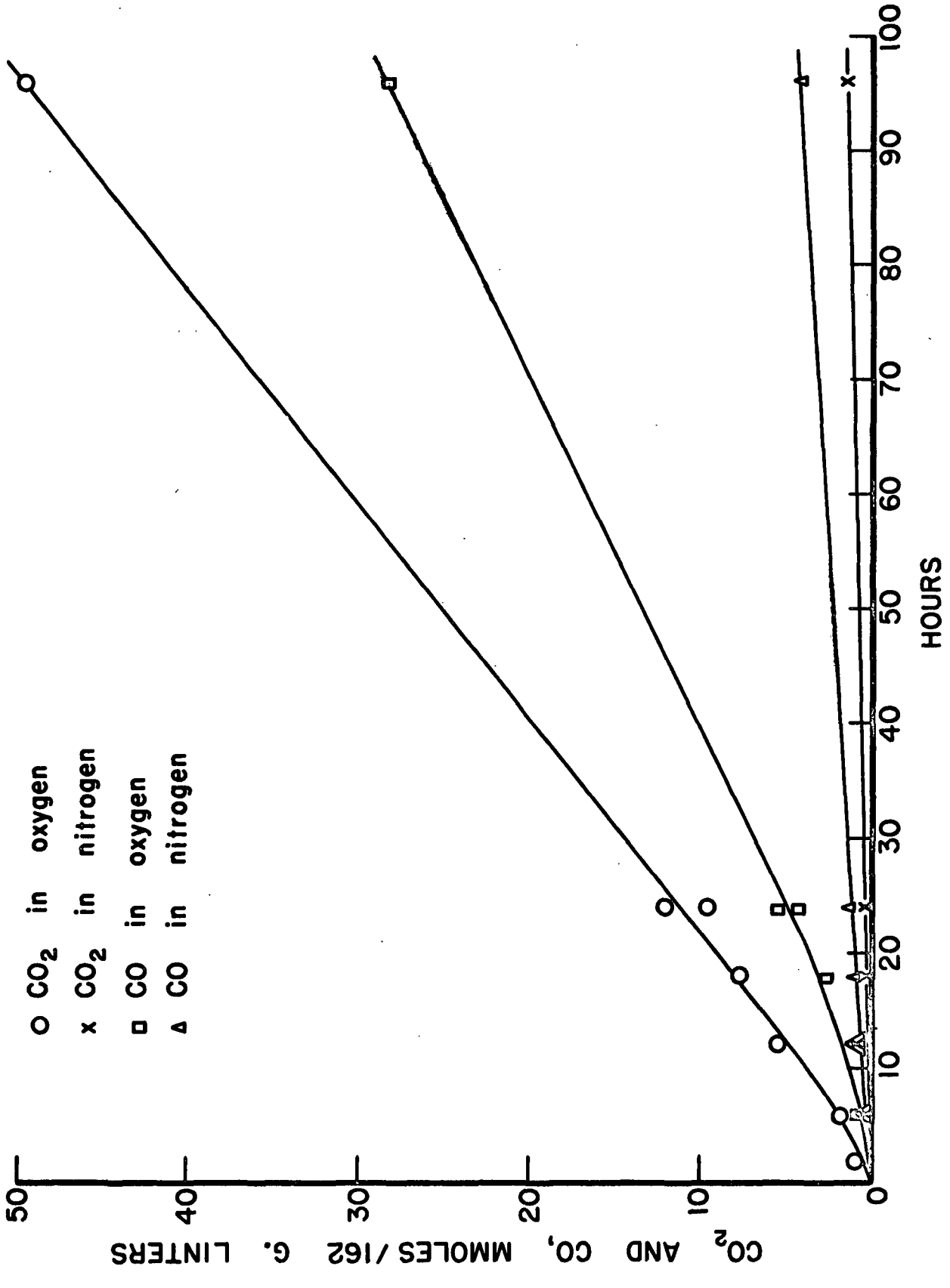


Figure 9. Evolution of Carbon Dioxide and Carbon Monoxide During Heating at 170°C.

The amount of water evolved from the linters during heating in oxygen and nitrogen is shown in Figure 10. The values are subject to some uncertainty, since the samples of linters were not necessarily dried to exactly the same moisture content. The value for Run XIIA, for example, was two and one-half times greater than anticipated from the curve in Figure 10. It was later determined that the amount of water removed from this sample during predrying was not as great as was removed from most of the others. In addition, volatile "tars" which were given off during the degradation were retained in the Anhydrone tubes, and were thus weighed as water. In Runs XA and XB this error was largely prevented by the use of the cold trap.

In a nitrogen atmosphere, most of the water was evolved in the first ten hours, indicating that the water evolved was composed almost entirely of sorbed moisture. Although Murphy (21) stated that the water of adsorption was indistinguishable from the water of composition, he found that when paper was heated at 160° a very definite decrease in the rate of water evolution occurred after 24 hours. At a higher temperature, it would be anticipated that this rate decrease would occur at an earlier point in the heating cycle.

The rate of water evolution in oxygen appeared to increase with time. This is in accord with the work of Murphy, since he found that exposing paper to oxygen at moderate temperatures temporarily increased the rate of gas evolution when the paper was subsequently heated in a vacuum at a higher temperature. It is suggested that the water which was

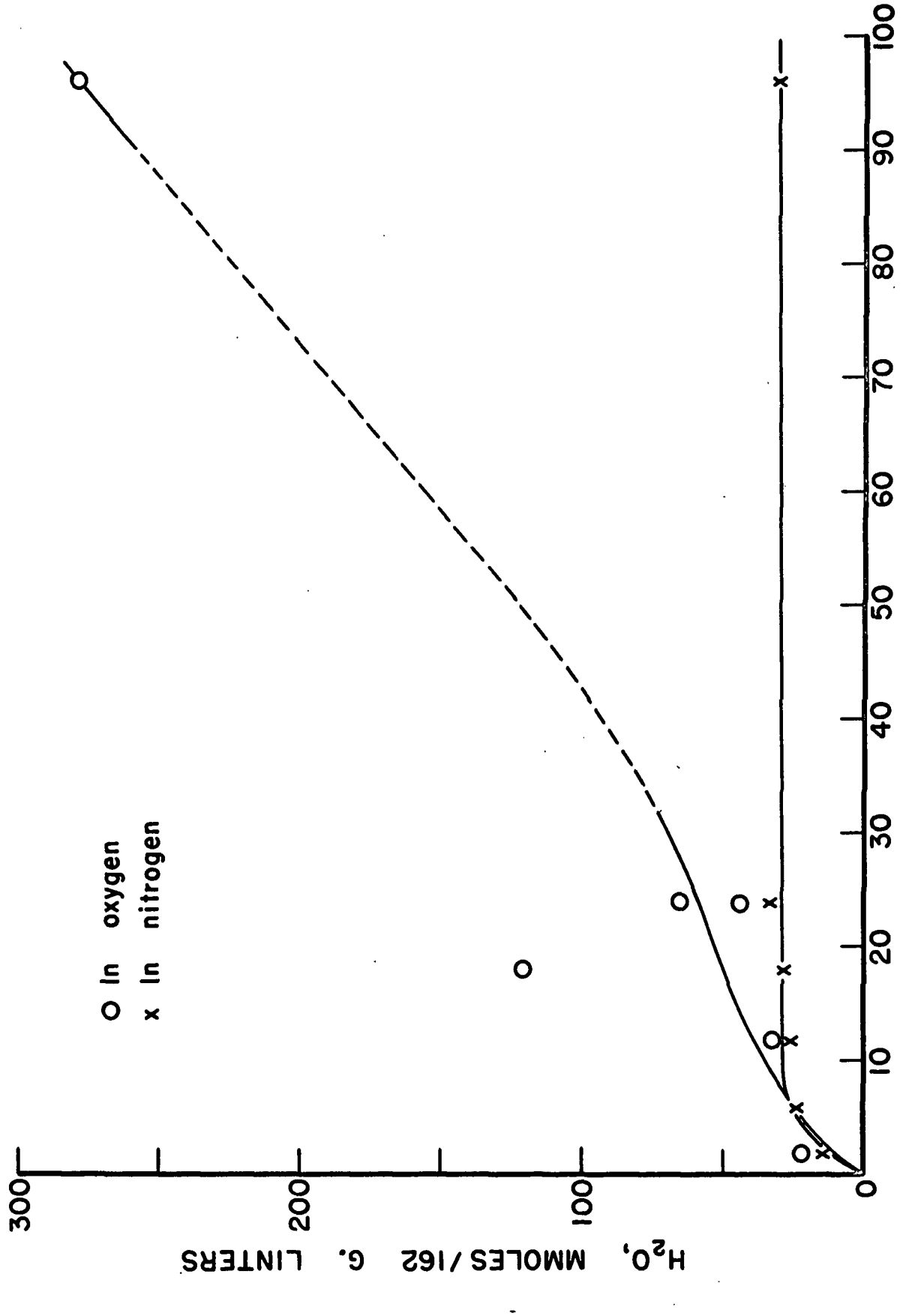


Figure 10. Evolution of Water During Heating at 170°C.

evolved during heating in oxygen was a result of at least three effects: the removal of sorbed water (in the first ten hours), the formation of anhydro rings, and the oxidation of hydroxyl groups. If it is assumed that one molecule of water is released for every carboxyl and carbonyl group formed and for every molecule of carbon dioxide and carbon monoxide evolved, approximately forty per cent of the water evolved during degradation in oxygen can be accounted for as a by-product of the oxidation of hydroxyl groups.

The Relation Between Evolved Gases and Reactive Groups and the D.P. of the Residue

An interesting relationship is shown when the carboxyl and carbonyl contents, or the amounts of evolved gases, are plotted against the D.P. values obtained at the corresponding time in the degradation. The curves are given in Figures 11, 12, and 13. Since these curves were drawn using points taken from the curves in Figures 5 and 7-10, no experimental points are shown.

All three figures show the same effect: in oxygen the group (or gas) at first increased slowly with decreasing D.P., over the D.P. range 1775-400. Below a D.P. of 400, the rate of formation increased rapidly, so that at a D.P. near 200 there was a large increase in the amount of the reactive group or gas, with no corresponding decrease in the chain length. This pattern is in accord with the picture of oxygen as a non-specific oxidant, and appeared to be the result of two types of reaction. The primary oxidation resulted in some formation of carbonyl and carboxyl

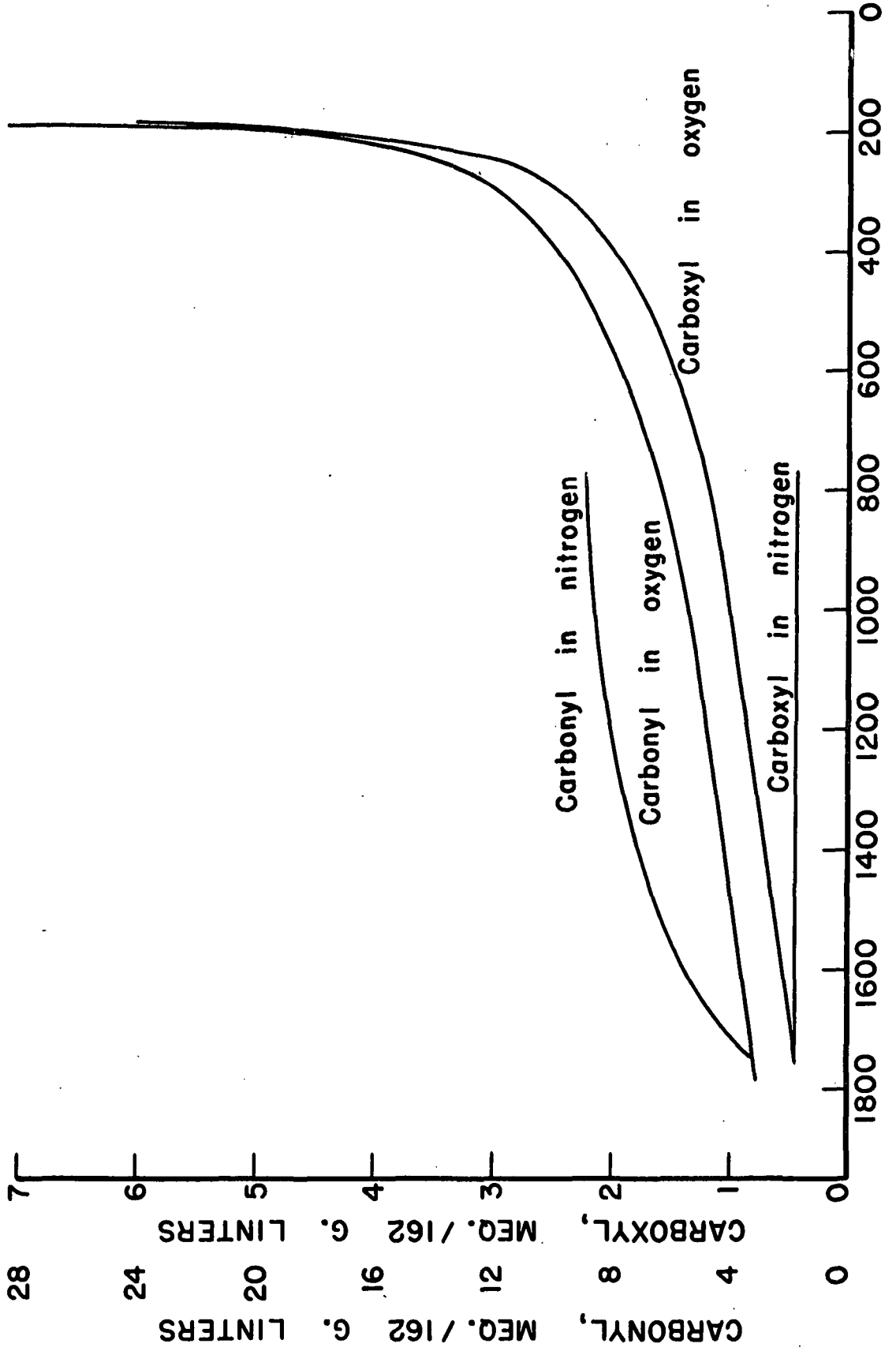


Figure 11. Carbonyl & Carboxyl Content at Various D.P. Levels.

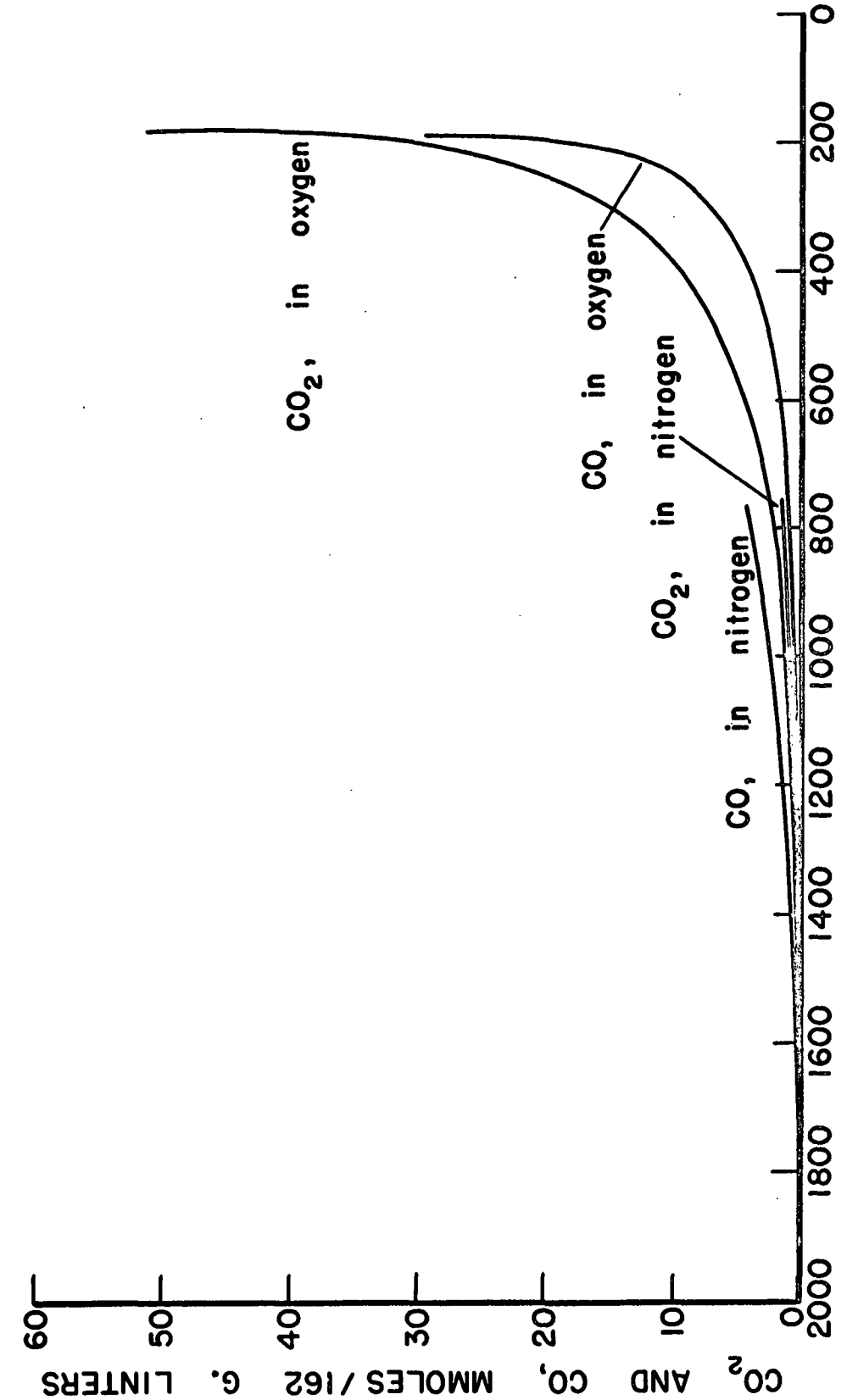


Figure 12. Evolution of Carbon Dioxide and Carbon Monoxide at Various D.P. Levels

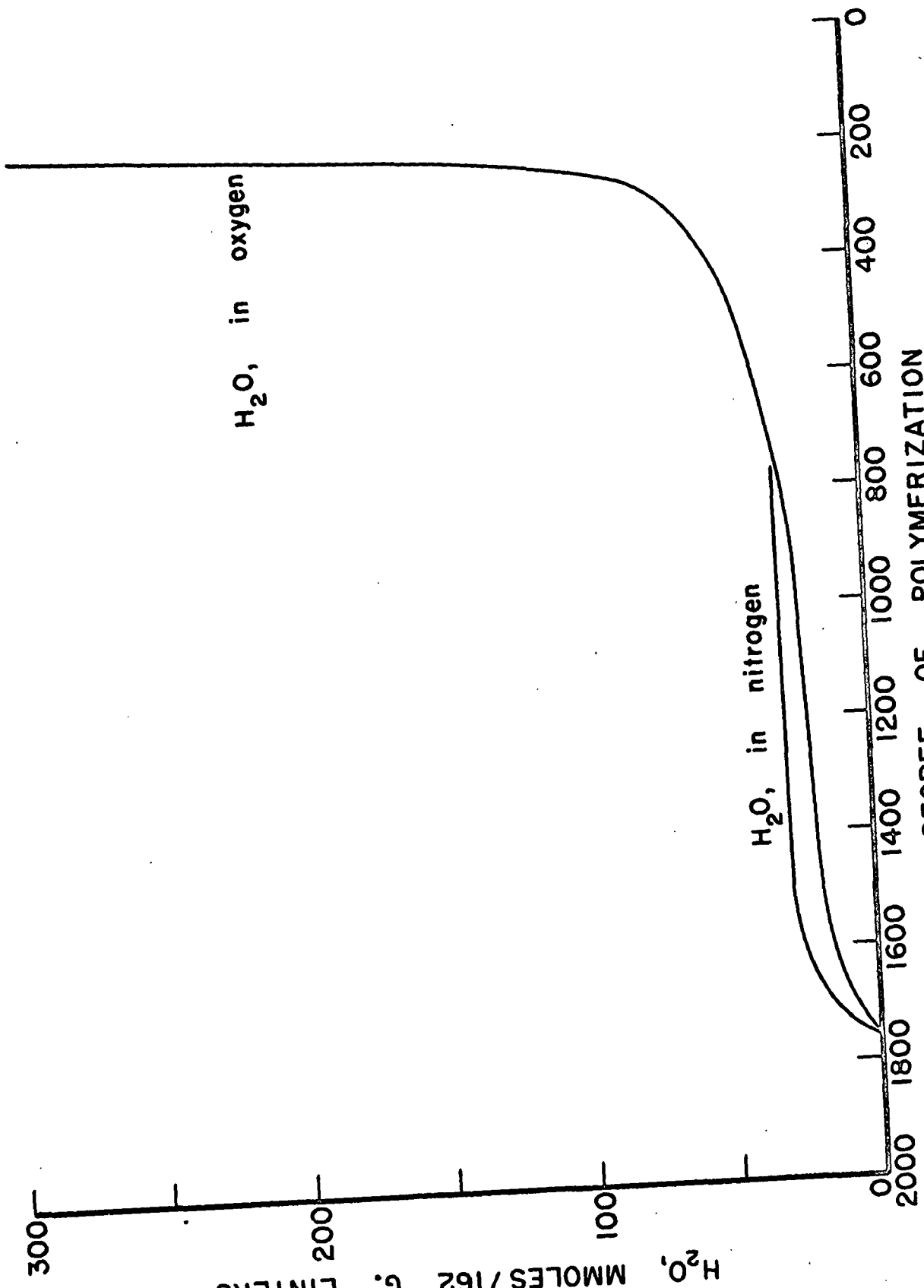


Figure 13. Evolution of Water at Various D.P. Levels.

groups and evolution of gases, as well as some chain splitting. As the D.P. was reduced to a value corresponding to the size of the crystallites, a secondary oxidation of the primary products ensued. Since this attack would be concentrated on the fragments in the amorphous region, which in cotton linters constitutes only about 10-20% of the total material (61), a relatively severe attack on the amorphous region, including chain cleavage, would result in only a very gradual decrease in the average D.P. of the total sample. This suggested reaction path is in accord with the theory of Waller, Bass, and Roseveare (1), who suggested that the primary reaction was oxidation, followed by decomposition of the oxidized cellulose.

No comparable pattern could be shown when linters were heated in nitrogen; the D.P. range where severe secondary reactions were postulated was not reached in this atmosphere. Moreover, no change in rate would be expected at any D.P. level, since the reaction path suggested above depends upon the presence of oxygen.

## SUMMARY

Dry cotton linters were heated in both a closed circulating system and an open steady-flow system, in atmospheres of nitrogen and oxygen, for periods of time up to 96 hours over a temperature range of 143 to 200°C. As the time or temperature was increased, the carbonyl and carboxyl contents increased, the D.P. decreased, and the amounts of evolved carbon dioxide, carbon monoxide, and water increased. In all cases, the degradation was much greater in an oxygen atmosphere than in a nitrogen atmosphere.

The majority of runs were made at 170° in the open system, for reaction times ranging from 2 to 96 hours. In an oxygen atmosphere, the carbonyl and carboxyl content and the amounts of evolved gases increased at rates relatively constant with time, but the D.P. decreased rapidly in the first 24 hours, then leveled off at a value slightly less than 200. The D.P. dropped more slowly in nitrogen; it reached about 800 after 96 hours, but there was no evidence of leveling off at that point. No change in crystallinity, as measured by x-ray diffraction, was found to occur upon heating in oxygen or nitrogen.

The results indicate that the attack was concentrated in the amorphous region. Secondary oxidation reactions involving fragments of the amorphous region would then account for the increasing formation of carbonyl and carboxyl groups and evolution of carbon dioxide, carbon monoxide, and water with only a very slight decrease in the chain length during the later stages of the degradation.

## HYDROLYSIS AND EXTRACTION OF THE DEGRADED LINTERS

### ACID HYDROLYSIS OF DEGRADED LINTERS

The Forest Products Laboratory method for acid hydrolysis was used to degrade several samples of heated linters. Most of the hydrolyzates were used for chromatographic analyses; the results of this work will be discussed in a later section. One quantitative hydrolysis was made using samples of the original and Run XA linters. No significant difference was found between the specific rotations of these hydrolyzates.

ENZYMATIC HYDROLYSIS OF DEGRADED LINTERS

A cellulase obtained from Trichoderma viride was used to hydrolyze original linters, Run VIIA linters, Run VIIA linters which had been reduced with sodium borohydride, and Run XA linters. The conditions of hydrolysis are given in the section on Methods. The extent of hydrolysis, as measured by weight loss, was 37.6% for original linters, 4.8% for Run VIIA linters, 6.5% for reduced Run VIIA linters, and 7.7% for Run XA linters. Aspergillus niger cellulase was also used to hydrolyze the original linters and Run VIIA linters; the extent of hydrolysis was 7.0 and 0.0%, respectively. This definitely increased resistance to hydrolysis was in line with the work of Farquhar and co-workers (2), but was much greater than found by these authors. The reduced susceptibility to hydrolysis of the heated linters was due probably to two effects. Jermyn (62) suggested that enzyme attack on cellulose can take place only at β-1,4 linkages between unsubstituted glucose residues, while Siu and co-workers (63) found that nitrogen dioxide-oxidized cellulose became increasingly resistant to cellulase attack as the degree of substitution increased, and was completely resistant at a degree of substitution of one. Also, as previously mentioned, heating has been found to reduce the hygroscopicity of cellulose (12). Thus, the increased resistance of the degraded linters was probably due to the presence of carbonyl and carboxyl groups in the cellulose, as well as a lower swelling and, thus, availability of the cellulose.

AQUEOUS EXTRACTION OF THE DEGRADED LINTERS

Several qualitative extractions were run on various degraded linters samples to obtain material for chromatographic analysis. In addition, quantitative aqueous extractions were made on Run XA and Run XB linters. The results of the quantitative extractions are shown in Table VI.

TABLE VI

QUANTITATIVE AQUEOUS EXTRACTION OF DEGRADED LINTERS

| | Run XA | Run XB |
|---|---|---|
| Weight loss of linters, %[a] | 3.50 | 0.13 |
| Material insol. in 50% EtOH, % | 0.27 | 0.04 |
| Material insol. in 10 ml. $H_2O$, % | 0.07 | 0.00 |
| Material sol. in 10 ml. $H_2O$, % | 3.16 | 0.09 |
| Portion sol. in EtOH, % | (0.09) | (0.04) |
| Total wt. of extr'd material, % | 3.50 | 0.13 |
| pH of aqueous extract | 3.1 | 4.5 |

[a] All percentages based on dry weight of degraded linters.

The degraded linters were extracted by placing a ten-gram sample, with enough water to make a 3% slurry, in a sealed jar, and agitating with a laboratory tumbler. After five days the linters were filtered off through a coarse fritted glass funnel, and washed with 150 ml. of water. The filtrate was then concentrated (using a rotary vacuum concentrator) from 480 ml. to 50 ml., and added to 50 ml. of absolute ethanol. A flocculent precipitate was observed, which was separated by centrifuging.

This precipitate is shown in Table VI as "material insoluble in 50% ethanol." The clear solution was then concentrated to approximately 10 ml.; the flocculent precipitate which formed was removed by centrifuging, and is shown in the table as "material insoluble in 10 ml. of water." The clear solution known as "material soluble in 10 ml. of water," was dried in a vacuum desiccator over Anhydrone and weighed. Ten milliliters of absolute ethanol were added with stirring, the mixture centrifuged, and the clear solution, shown as "portion soluble in ethanol" in Table VI, was dried at 60°C. and weighed.

The differences between heating in oxygen and heating in nitrogen are quite pronounced, as shown in Table VI. The oxygen-heated linters contained almost thirty times more water-extractable material than did the nitrogen-heated linters. A difference was also shown in the pH of the aqueous extracts. The pH of the triple-distilled water which was used was 6.6; the pH of the aqueous extract of the original linters was 6.6, of the Run XA linters was 3.1, and of the Run XB linters was 4.5. Both Lloyd (64) and Clark (3) found that an aqueous extract of heated cellulose was slightly acid. Clark found, however, that the presence of oxygen had practically no effect on the pH of the extract. This is contrary to the effect shown in the above data.

The Run XA and Run XB aqueous extracts were extracted with ether, and the ether solutions titrated with alcoholic potassium hydroxide to determine the amount of ether-soluble acid present (e.g., acetic and formic acids). No ether-soluble acids were detected in the Run XB extract, but 1.26 meq. of acid per 162 g. of linters was detected in the Run XA extract.

All fractions obtained from the aqueous extracts were tested chromatographically for carbonyl compounds, acids, sugars, and phenols. It was found that, for both Run XA and Run XB extracts, the material insoluble in 50% ethanol and the material insoluble in 10 ml. of water contained none of these compounds. It was therefore concluded that these materials consisted of oligosaccharides which were water soluble, and probably had a D. P. of less than nine.

Both the water-soluble and ethanol-soluble portions of the Run XA extract contained sugars, acids, carbonyl compounds, and phenols. The ethanol-soluble portion of the Run XB extract contained traces of these compounds, but the water-soluble portion did not. The chromatographic investigations of these materials are discussed more fully in the sections to follow.

## CHROMATOGRAPHIC INVESTIGATIONS

Various fractions of the degraded linters were investigated chromatographically in order to gain an insight into the nature of the compounds formed during degradation. Four general types of fractions were investigated: materials which distilled over from the heated linters (distillates), aqueous extracts, hydrolyzates (both acid and enzymatic), and miscellaneous extracts. The fractions were obtained from the runs which were the most severely degraded, since greater amounts of material could be obtained from these runs.

DISTILLATES

During most of the degradation runs, the exhaust gas flowed directly into the first Anhydrone tube. The Anhydrone generally became blackened during the course of the run with materials which had distilled off from the heated linters. This distillate could not be separated from the Anhydrone, and thus both were chromatographed together. The presence of the magnesium perchlorate caused some salt interference. The tarry material from Runs IVA, VA, and VIA gave a spot which corresponded to a known levoglucosan spot in two different solvents. Although Heuser (16) stated that levoglucosan decomposes during heating at atmospheric pressure, it is possible that levoglucosan in contact with a strong drying agent would not decompose. However, since levoglucosan has a melting point of 180°C., little would be expected to be carried off with the exhaust gas stream. The above data were therefore regarded merely as presumptive evidence for the presence of levoglucosan.

In Runs XA and XB a cold trap maintained at -10°C. was placed in the exit gas line before the absorption train. In each case a small amount of a brown liquid, which had a tarry or smoky odor, was collected. Run XA gave 0.09% and Run XB gave 0.0015% (based on the weight of the original linters) of this material. The distillate from Run XA had a specific rotation of -24.5° in ethanol.

The distillate from Run XA contained a large number of components which could be separated chromatographically, using an ethyl acetate: acetic acid:formic acid:water solvent. The distillate from Run XB also

contained a rather large number of compounds. The number of spots shown with various types of sprays for the Run XA and XB distillates are shown in Table VII.

TABLE VII

CHROMATOGRAPHIC INVESTIGATION OF DISTILLATES

| Spray[a] | $R_f$ Number of Spots[b] | |
|---|---|---|
| | Run XA Distillate | Run XB Distillate |
| EK 1954 (acids) | .12, .60, .70 | .12, .59 |
| DB (phenols) | .64, .71, .79, .85 | .72 |
| 2,4-D (carbonyl) | .14, .57, .70, .76 .82, .87, .93 | .57, .70, .77 |
| ABP (sugars) | .12, .55, .82, .95 | .77 |

[a] EK 1954: 4-(4-Dimethylamine-1-naphthylazo)-3-methoxy benzenesulfonic acid; DB: Diazotized benzidine; 2,4-D: 2,4-Dinitrophenylhydrazine; ABP: o-Aminobiphenyl.

[b] The $R_f$ Number is the ratio of the distance of the spot from the origin and the distance of the solvent front from the origin.

The data in Table VII show that the XA distillate contained more compounds than the XB distillate. A study of the $R_f$ values indicates that similar compounds existed in both distillates. In addition, spots having the same $R_f$ number were located using different sprays. This is probably the result of two superimposed compounds, but may indicate a polyfunctional compound.

AQUEOUS EXTRACTS

Chromatographic investigation of the aqueous extracts of original

and degraded linters gave results which were in general similar to those obtained when the distillates were investigated. However, since more material was available from the aqueous extracts, they were investigated more fully. The most intensive study was made on the aqueous extracts of original, Run XA, and Run XB linters. The investigation of these extracts is summarized in Table VIII.

TABLE VIII

CHROMATOGRAPHIC INVESTIGATION OF AQUEOUS EXTRACTS

| Spray[a] | $R_f$ Number[b] Original | Run XA | Run XB |
|---|---|---|---|
| EK 1954 (acids) | no spots | .16, .57, .70, .81 | no spots |
| DB (phenols) | no spots | .54, .65, .75, .88 | .69 |
| 2,4-D (carbonyl) | no spots | .39, .52, .65, .81 .90, .96 | .65 |
| ABP (sugars) | .12 | .12, .17, .39, .63 | no spots |

[a] For full name of sprays, see Footnote 1, Table VII.

[b] In ethyl acetate:acetic acid:formic acid:water solvent.

As in the case of the distillates, it appears that similar compounds may have been present in more than one extract. The Run XA extract gave spots with two or more sprays in the same $R_f$ position; whether this was a result of one polyfunctional compound or two different compounds in the same position was uncertain. The Run XA linter extract gave by far the largest number of spots with any given spray. Since the amount of extractable material in the Run XA linters was much

greater than in the Run XB or original linters, it is possible that these latter extracts contained more compounds, but in amounts too small to show on a chromatogram. Nevertheless, a definite difference existed.

Several known compounds were chromatographed with the Run XA extract in an attempt to make tentative identification of some of the unknown spots. Known compounds which did not correspond to any of the unknown spots were furfural, levoglucosan, D-erythrose, erythronic acid, and xylose. Known compounds which gave spots corresponding to unknown spots were glucose ($R_f$ 0.12), hydroxymethyl furfural ($R_f$ 0.81), gluconic acid ($R_f$ 0.163), and glucuronic acid ($R_f$ 0.154). Since the presence of glucose in the aqueous extract was not unexpected, no attempt was made to prove its presence.

In order to test further for the gluconic and glucuronic acids, the acids were separated from the extract through the formation of the insoluble barium salts. This separation proved to be quite complete. The barium salts were then converted back to the free acids, and the anilides formed. The unknown anilides were then chromatographed against known acid anilides using a method developed by Green (65). No spots were obtained from the unknown material, presumably because the amount of material available was too small.

The Run XA aqueous extract was found to have a spot corresponding to hydroxymethyl furfural in different solvents. Since Heuser (17) mentions this compound as a product of the distillation of cellulose, further proof of its presence was sought. The unknown spot was eluted from the sheet, and an ultraviolet spectrum run on the eluate. The

spectrum did not resemble that of hydroxymethyl furfural; instead, it had a shape similar to a lignin or similar phenolic spectrum. It could not be determined whether the unknown contained both hydroxymethyl furfural and a phenolic material, or consisted only of a phenolic compound.

Several attempts were made to prepare 2,4-dinitrophenylhydrazine derivatives from eluates of several of the larger spots isolated from the Run XA extract. Although an insoluble product was obtained in several cases, not enough of the material was available for identification. Two of the eluates ($R_f$ 0.12 and 0.62 with 2,4-D spray) gave positive aldehyde tests with Schiff's reagent.

HYDROLYZATES

Both enzymatic and acid hydrolyzates of original and degraded linters were chromatographed to determine if any differences could be attributed to degradation.

Acid hydrolyzates which had been neutralized with ion-exchange resin were found to streak rather badly. This streaking was diminished by using barium hydroxide to neutralize the sulfuric acid. When these solutions were chromatographed and tested with sugar sprays, no definite differences were found between the hydrolyzates of original and degraded linters. Both contained primarily glucose, with small amounts of cellobiose and also spots in positions closely corresponding to those of xylose and arabinose. Since Saeman and co-workers (52) found that pure glucose gave faint spots corresponding to xylose and mannose when

subjected to the hydrolysis procedure, no significance could be given to the nonglucose spots which were found.

The solutions obtained from hydrolysis with the Aspergillus niger enzyme were found to contain several nonglucose spots. However, the enzyme preparation alone caused considerable interference, and since the nonglucose spots were obtained from both degraded and original linters no further work was done with these hydrolyzates.

The hydrolyzates obtained with the Trichoderma viride cellulase were not subject to chromatographic interference from the enzyme preparation. They were found to contain primarily glucose, with some evidence of another spot slightly lower than glucose on the sheet. This position corresponded to that of a known mannose. However, since there was some indication that this spot was also obtained from a T. viride hydrolyzate from original linters, it could not be considered a degradation product.

MISCELLANEOUS EXTRACTS

Run XA linters and original linters were also extracted with ethanol and with 0.1N sodium hydroxide. The ethanol extracts of both original and Run XA linters were free of any compounds which would react with sugar, carbonyl, and oxidizing chromatographic developers. Since a portion of the aqueous extract of Run XA linters was soluble in ethanol, and did contain sugars, carbonyl compounds, acids, and phenols, it appeared that these compounds, although soluble in alcohol, were not extractable with alcohol.

The sodium hydroxide extractions were performed on linters which had been previously extracted with ethanol and water. The original linters extract was found to contain two faint sugar spots, while the Run XA extract contained four strong sugar spots and four carbonyl compounds. Some interference may have occurred from the ion-exchange resin with which the extracts were neutralized. Of the sugar spots, only one, glucose, could be matched with a known compound, although another spot was located at an $R_f$ value very close to that of D-threose. The carbonyl compounds were located in positions having $R_f$ values close to those of compounds found in both the distillate and aqueous extract.

SUMMARY OF CHROMATOGRAPHIC ANALYSIS

Several fractions of the degraded linters and the original linters were examined chromatographically. The fractions of the degraded linters which contained the most compounds were the distillates and the aqueous extract. Acid and enzymatic hydrolyzates and the alcohol extract contained only a very few compounds. The distillate and aqueous extract from linters which had been degraded in oxygen contained appreciably more compounds than corresponding fractions from original linters and linters which had been degraded in nitrogen.

The compounds found in the fractions from the oxygen-degraded linters were of four general types: 1) those which reacted with sugar sprays, 2) those which formed 2,4-dinitrophenylhydrazones, 3) those which reacted with phenolic sprays, and 4) those which were acid to an acid-base indicator spray. Compounds which were shown to be definitely not present

in measurable amounts were D-erythrose, D-erythronic acid, furfural, and xylose. Several compounds were tentatively identified by chromatographic means as being present in one or more fractions. These were glucose, gluconic acid, glucuronic acid, hydroxymethyl furfural, and levoglucosan. Of these compounds, only glucose was present in a quantity considered sufficient for identification purposes.

The chromatographic examinations showed a large number of different types of compounds to be formed as a result of the oxidative degradation. This indicated that oxygen acts as a nonspecific oxidant for cellulose, since a specific oxidant would be expected to produce only one, or a very few, products from the anhydroglucose units in the cellulose.

## OPTICAL ANALYSIS

### INFRARED ANALYSIS

Infrared absorption spectra curves were run on samples of original, Run IVAA, and Run VIIA linters, using the potassium bromide pellet technique. The original linters sample gave a spectrum similar to those found by several investigators for native cellulose (66,67). The Run IVAA and Run VIIA linters gave a spectrum similar to the original linter spectrum, except for a strong absorption band at 5.75-5.80 microns. An absorption band in this area has been attributed to the C=O stretching vibration (67,68). The absorption peak was therefore considered a result of the presence of carbonyl or carboxyl groups.

No absorption spectra were determined for linters which had been

degraded in nitrogen. However, Friedel and Queiser (26) found no differences between the spectrum of cellulose heated in nitrogen at 190° and the spectrum of unheated cellulose.

## X-RAY ANALYSIS

X-ray diffraction curves were obtained for original, Run XA, and Run XB linters. The linters were pressed into solid pads to a common bulk density, then scanned over an angle (2θ) range of 12 to 26 degrees. The degree of crystallinity was determined by the method of Ant-Wuorinen (51) and the method of Hermans and Weidinger (as interpreted by Ant-Wuorinen) (51). The results are given in Table IX.

TABLE IX

DEGREE OF CRYSTALLINITY BY X-RAY DIFFRACTION

| Sample | Density, g./cc. | Measure of Crystallinity[a] $DC_h$ | CrI |
|---|---|---|---|
| Original | 1.115 | 0.88 | 0.83 |
| Run XA | 1.151 | 0.88 | 0.81 |
| Run XB | 1.080 | 0.88 | 0.82 |

[a] $DC_h$: Hermans and Weidinger; CrI: Ant-Wuorinen

Since some minor modifications in the published methods were made, as discussed in the Appendix, no significance should be attached to the magnitude of the values obtained for crystallinity. However, there appeared to be no significant change occurring in the crystallinity as measured by either of the two techniques. It was concluded that heat

degradation had little, if any, effect upon the degree of crystallinity as measured by x-ray diffraction.

SAMPLE COLOR

As heating progressed, in both oxygen and nitrogen, the white cotton linters gradually became discolored. The sample degraded most severely in oxygen (Run XA) discolored the most; the color could best be described as resembling a golden unbleached sulfate pulp, or similar to the color of a new chamois skin. The comparable sample degraded in nitrogen (Run XB) was a very light pale, slightly yellowish gray.

## SUMMARY

Dried cotton linters were heated in a specially designed apparatus at a temperature of 170°C. for periods of time ranging from 2 to 96 hours. Other degradation runs were made at 143-200° for 10-12 hours. Throughout the course of the runs dry oxygen or nitrogen was passed through the linters sample at a flow rate of 125 ml. per minute. The evolved water, carbon monoxide, and carbon dioxide were absorbed and measured, and the degraded linters were analyzed for carbonyl and carboxyl content and degree of polymerization. In addition, various fractions of the degraded linters were examined chromatographically. The observations which were made concerning the heat degradation of cellulose under the specified conditions are summarized in the following paragraphs.

In confirmation of previous work (2,4,7-10), the D.P. of the cellulose was found to decrease with increasing time and temperature in both oxygen and nitrogen. In addition, however, it was found that the D.P.-time curve for linters heated in oxygen at 170° leveled off at a D.P. value of slightly less than 200 after approximately forty hours. This effect has not been mentioned by previous investigators, although the incomplete data of Staudinger and Jurisch (10) suggest it. The D.P. dropped less rapidly in nitrogen; it reached 800 after 96 hours, but there was no evidence of a leveling-off D.P. at that point. The change of intrinsic fluidity was linear with time (0-96 hours) for linters heated in nitrogen at 170°. For linters heated in oxygen at 170° the change of intrinsic fluidity was linear with time for the first 30 hours, after

which the rate of change decreased, possibly approaching the rate for linters in nitrogen.

The carbonyl content of linters heated in both oxygen and nitrogen increased with time and temperature; the increase was greater for linters heated in oxygen. These effects have been shown by previous investigators (1-4) using approximately the same heating conditions. It was also found that the carbonyl content became constant after the linters had been heated in nitrogen for about 24 hours at 170°.

The carboxyl content of linters heated in oxygen increased with both time and temperature. The change in carboxyl content for linters heated at 170° in oxygen was approximately linear with time, but showed some indication of an increased rate after fifty hours. No increase in carboxyl content was found when linters were heated in nitrogen. The change of carboxyl content with time has not been determined under these or similar conditions by previous investigators.

The evolution of water, carbon dioxide, and carbon monoxide from the linters heated in oxygen at 170° began before two hours of heating time; the amount of each gas evolved was approximately linear with time. The molar ratio water:carbon dioxide:carbon monoxide was very roughly 10:2:1 after about thirty hours. This is the same ratio found by Murphy (21) for paper heated in a vacuum at 160°, but does not agree with the data of Clark (3). Very little carbon monoxide, and essentially no carbon dioxide, was evolved from linters heated in nitrogen. The evolution of water from linters heated in nitrogen at 170° was initially rapid, but

ceased after about ten hours. Forty per cent of the water evolved from linters heated in oxygen could be accounted for as a by-product of oxidation reactions.

Although the D.P. of linters heated in oxygen at 170° reached a leveling-off value of slightly less than 200, no decrease in the rate of oxidation reaction occurred. As a result, when carbonyl and carboxyl contents, as well as evolved carbon dioxide, carbon monoxide, and water, were plotted against the corresponding D.P. for linters heated in oxygen, each value was found to increase slowly with decreasing D.P. until a D.P. level of about 400 was reached. Thereafter, the increase became more rapid, until at a D.P. level of 190 the curves became almost vertical.

No significant change in crystallinity could be detected by two methods of evaluating x-ray diffraction patterns obtained for original linters and linters degraded 96 hours at 170° in oxygen and nitrogen. This led to the conclusion that the oxidation reactions were concentrated in the amorphous regions. The infrared absorption spectrum of linters degraded in oxygen was the same as that of the original linters, with the exception of an absorption band at 5.75-5.80 microns which was attributed to the presence of carbonyl and carboxyl groups. Friedel and Queiser (26) found no change in the spectrum for cellulose heated at 190°C. in nitrogen. No other investigators have applied x-ray or infrared spectroscopy to the heat degradation of cellulose.

Undegraded linters and oxygen-degraded linters were hydrolyzed with acid quantitatively. No significant differences between the hydrolyzates

were found by comparing the specific rotations or chromatographic analyses for sugars. Similar types of linters were hydrolyzed enzymatically using Aspergillus niger and Trichoderma viride cellulases. The extent of hydrolysis was much less for the degraded linters than for the original linters; the difference was much greater than that found by Farquhar et al. (2) using Aspergillus niger cellulase. The enzymatic hydrolyzates were compared chromatographically, but no definite differences could be found.

Far more material could be extracted with water at room temperature from linters heated in nitrogen under the same conditions. The oxygen-degraded linters lost 3.50% by weight, while the nitrogen-degraded linters lost only 0.13% by weight. In both cases the extracts contained some material which was insoluble in 50% ethanol and was assumed to be made up of oligosaccharides. The aqueous extract of oxygen-degraded linters was found to contain 1.26 meq. of ether-soluble acid per 162 g. of linters, while the extract from nitrogen-degraded linters contained none. The pH of the aqueous extract of linters heated in oxygen for 96 hours at 170° was 3.1, that of linters heated similarly in nitrogen was 4.5. The acidity of the aqueous extract has also been observed by other investigators (3,64).

Several fractions of the degraded linters were examined chromatographically. These examinations have not been made in previous investigations of the heat degradation of cellulose. Chromatographic analysis of the aqueous extract from linters heated 96 hours at 170° in oxygen showed several compounds which reacted with chromatographic developers for

acids, phenols, carbonyl compounds, and sugars. In contrast, an extract of linters heated under the same conditions in nitrogen showed no compounds which reacted with sugar or acid sprays, and only one spot each was developed by carbonyl and phenol sprays, respectively. The original linters extract showed one spot which reacted with a sugar spray, and no evidence of acids, phenols, or carbonyl-containing compounds.

A tarry material which distilled off from the reaction chamber during heating was collected and examined chromatographically. The material collected from a sample heated 96 hours in oxygen at 170° had a specific rotation of -25° in ethanol. This material was found to contain 3, 4, 7, and 4 compounds which reacted, respectively, with acid, phenol, carbonyl, and sugar chromatographic sprays. Similar material from linters heated in nitrogen contained 2, 1, 3, and 1 compounds which reacted with the same order of sprays. In many cases, the spots found were similar to those found in the aqueous extracts.

None of the compounds isolated on the chromatograms were definitely identified. Chromatographic examination showed that D-erythrose, xylose, furfural, and D-erythronic acid were not present. Glucose, gluconic acid, glucuronic acid, hydroxymethyl furfural, and levoglucosan were tentatively identified by chromatographic methods. Furfural, hydroxymethyl furfural, and levoglucosan have been found in the distillates from pyrolyzed cellulose by previous investigators (13,17).

Both the linters heated in oxygen and the linters heated in nitrogen became discolored gradually with time. Those heated in oxygen approached

a light golden brown color, similar to that of a new chamois skin. Linters heated in nitrogen did not become as dark, and approached a very light, yellowish tinted, gray. Linters heated for long periods or at high temperatures in oxygen became very friable and powdery. Those heated in nitrogen under similar conditions retained their fibrous characteristics.

# CONCLUSIONS

1. Oxidation is the primary mechanism of degradation when dry cellulose fiber is heated in a dry oxygen atmosphere at 170° and atmospheric pressure. In these reactions, oxygen acts as a nonspecific oxidant.
2. The oxidations are concentrated in the amorphous regions of the cellulose throughout the course of the degradation.
3. As the degradation proceeds, the cellulose in the amorphous regions is degraded to small chain fragments and gradually converted to a wide range of compounds.
4. During the degradation of dry cellulose fiber in a dry inert atmosphere at 170° and atmospheric pressure, the changes in the measured properties were found to be quite small. It thus cannot be determined whether the degradation under these conditions was due to oxidation, hydrolysis, or pyrolysis.

# SUGGESTIONS FOR FUTURE WORK

## DETERMINATION OF OXYGEN CONSUMPTION

The original intent in this work was to determine the consumption of oxygen as the degradation reactions progressed. However, because the closed reaction system did not function properly, this measurement could not be made. A comparison of the oxygen consumption with the measurements made during the present work would permit an oxygen balance for the degradation, while the rate of oxygen consumption would permit additional insights into the mechanism of degradation.

## INVESTIGATION OF REACTION PRODUCTS

During the course of this thesis it was determined that some of the anhydroglucose units within the cellulose were converted into a wide range of compounds, including acids, aldehydes, sugars, and phenols. At least 3.5% of the cellulose was converted into water-soluble compounds after 96 hours in oxygen at 170°. Positive identification of these compounds would provide an indication of the actual oxidation reactions, especially if some of these compounds could be obtained in relatively high yields. An investigation of this type would require a large sample size, and efficient extraction and purification techniques.

A similar study could also be made using model compounds, such as cellobiose or cellotriose, instead of cellulose. An investigation of this type might be expected to offer less difficulty in the separation of reaction products during the early stages of degradation, and thus primary reaction products might be more easily obtained.

# STUDY OF THE HEAT DEGRADATION OF PARTIALLY ACETYLATED CELLULOSE

Several investigators (30,31) have found partially acetylated cellulose fiber to be much more resistant than cellulose fiber to heat degradation. A comparative study of the heat degradation of the two materials, especially a study which included the determination of oxygen consumption, would undoubtedly make a contribution to an understanding of the degradation reactions.

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# APPENDIX

## CALCULATION OF CRYSTALLINITY FROM X-RAY DIFFRACTION CURVES

The method for obtaining the diffraction curves is described elsewhere in this report. A sample curve (for the original cotton linters) is shown in Figure 14. Two methods were used to evaluate crystallinity: that of Ant-Wuorinen (51) and that of Hermans and Weidinger as interpreted by Ant-Wuorinen (51). The necessary measurements and the construction lines required to obtain them are shown in Figure 14.

Ant-Wuorinen determined a value which he described as the "crystallinity index", CrI. The ratio of the height of the peak at 22.5° above the minimum at 18.4° (CrH') to the maximum scale reading is CrH. The distance, in radians, between the minimum at 18.4° and the "almost vertical left side of the peak at 22.5°" (51) is the amorphous width, AmW. Since the left side of the peak was not vertical in the curves which were obtained for this work, the linear portion was extended to intersect the intensity value of the 18.4° minimum. Although this changed the magnitude of AmW somewhat, it was easier to determine, and should have had no effect on comparative values. Then, the amorphous ratio=AmR=AmW/CrH, and the crystalline index=CrI=1-AmR.

Hermans and Weidinger used both height and area measurements. The height measurement method was used in this work. A tangent was drawn between the minimums at 12 and 26°. The height of the tangent above the zero intensity line at the 18.4° minimum was called the amorphous height,

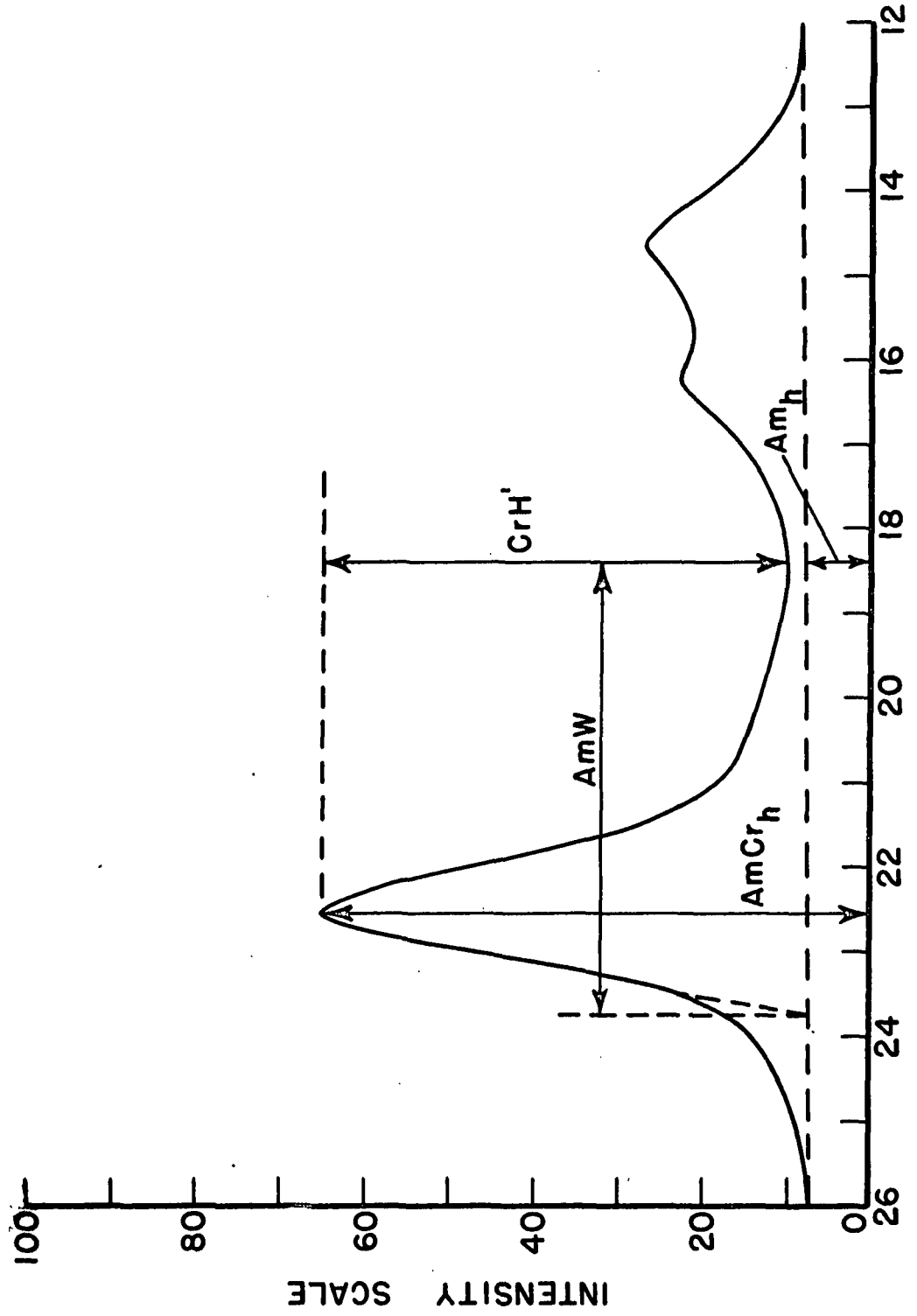


Figure 14. X-ray Diffraction Curve

$Am_h$. The height of the 22.5° peak above the zero line was termed the sum of the amorphous and crystalline heights, $AmCr_h$. Then, $DAm_h = Am_h/AmCr_h$, and the "degree of crystallinity" $DC_h = 1 - DAm_h$.

No corrections were made for miscellaneous effects, such as air scattering, in either of the calculations.

## THE CLOSED SYSTEM

The reaction apparatus designated as the closed system was used for only a small number of degradation runs, since it could not be made to function properly. The design principle was similar to the apparatus used by Evans and McBurney (28) in their study of the oxidation of cellulose acetate.

### DESCRIPTION

The reaction apparatus for closed system degradation runs is shown in Figure 15. Except for the Brewer automatic pipet, which served as a circulating pump, the apparatus was enclosed within a double-walled, insulated, Transite oven. Again with the exception of the pump, the entire system was constructed of glass; all joints were semi-ball to prevent excessive strain during the heating period. Silicone tubing, furnished by Dow Corning, was used to connect the system to the pump and the leveling bulb to the gas manometer. Dow Corning Silicone Fluid 200 was used in the balancing manometer, and tri-m-tolyl phosphate in the gas manometer. The absorption train was similar to that used in the open system (Figure 1), but was enclosed within the reaction oven.

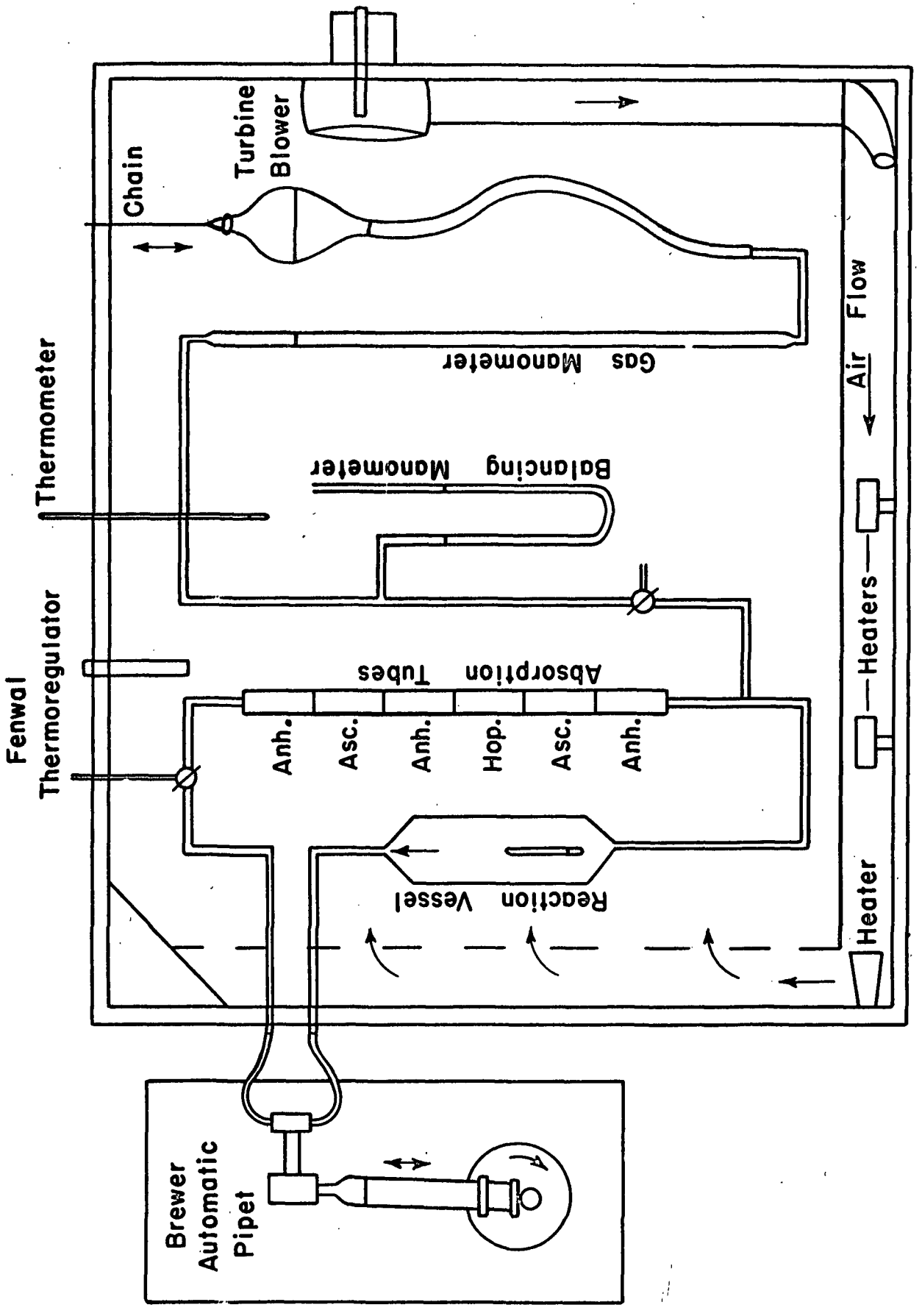


Figure 15. Closed Reaction System

The two 750-watt fin heaters and the 600-watt cone heater were capable of bringing the cabinet temperature above 200°C., and the Fenwal regulator was capable of maintaining the cabinet temperature to within ± 2°C. A turbine blower, with a capacity of 50 cubic feet per minute, was used to maintain a constant temperature throughout the cabinet and to aid heat transfer to the reaction apparatus. A small thermometer within the reaction vessel gave the temperature of the linters inside the vessel; this was generally 6-7° less than the oven temperature.

The circulating pump was set to deliver about 10 ml. per stroke, at a rate of 60 strokes per minute. This circulating rate was sufficient to change the atmosphere within the system approximately once every 50 seconds.

OPERATION

The warmup time of the system was about 90 minutes. Near the end of the warmup time, the reaction system was flushed with the gas to be used in the run. When the operating temperature was reached, the reaction vessel was inserted (the gap having been filled during the warmup period with a glass tube) and the flushing continued for several minutes. The gas flow was then shut off, the pump attached, the stopcock to the manometer system shut off, and the pumping started. At intervals thereafter, the pump was shut off, the manometer stopcock opened, and readings taken to determine the oxygen consumption. To measure the volume of the system, the leveling bulb was adjusted until the liquid in the sidearms of the balancing manometer was level; the reading on the gas manometer was then taken.

The temperature in the reaction vessel was also taken at this time. The manometer stopcock was then closed, and the pumping continued.

Several difficulties were encountered with the closed system. The absorption train did not function correctly at the temperatures used (143-170°C.), and the volume of the gas in the system increased continuously during the circulation, even when no cellulose was present in the reaction vessel, presumably due to a hidden leak in the circulating pump which could not be eliminated.

## THE EFFECT OF PRENITRATION REDUCTION ON THE SOLUBILITY AND VISCOSITY OF NITRATED LINTERS

As described in the section on Experimental Methods, some of the more highly degraded linters gave nitrated products which were only partially soluble in acetone. Reduction of the carbonyl groups, using an unbuffered sodium borohydride solution, before nitration gave a nitrated product which was far more soluble. The effect of this reduction on the solubility of several samples is shown in Table X.

The shrinkage during reduction was measured by weighing the linter sample before and after reduction. The acetone solubility was determined by shaking the acetone solution on a laboratory shaker, then centrifuging the solution and determining the per cent solids in the clear top layer by evaporation of the solvent. The top layer was also used to determine viscosity.

TABLE X

THE EFFECT OF REDUCTION ON NITRATE SOLUBILITY AND VISCOSITY

| Run | $NaBH_4$ Conc., M | Shrinkage During Redn., % | Acetone Sol'y of Nitr. Lint., % | N, % | D.P. |
|---|---|---|---|---|---|
| VA | 0.00 | - - | 74.0 | 13.65 | 185 |
| VA | 0.05 | 2.8 | 98.0 | 13.92 | 190 |
| VA | 0.50 | 2.7 | 98.6 | 13.81 | 185 |
| VIA | 0.00 | - - | 59.0 | 13.36 | 185 |
| VIA | 0.05 | 3.1 | 89.8 | 13.73 | 185 |
| VIA | 0.50 | 3.1 | 93.2 | 13.83 | 195 |
| VIIA | 0.00 | - - | 53.8 | 13.30 | 75 |
| VIIA | 0.05 | 3.6 | 86.3 | 13.58 | 160 |
| VIIA | 0.50 | 3.9 | 92.8 | 13.60 | 160 |

Reduction increased the solubility to above 90% even for the most severely degraded material, and also slightly increased the degree of nitration. Except for Run VIIA, however, no increase in D.P. was realized. This effect suggests that the insoluble material in the nitrated Run VA and Run VIA linters was of a similar D.P., but higher carbonyl content, than the soluble material. It is also possible that the lack of change in D.P. was a result of a cancellation of effects, i.e., increased solubility of long chain molecules vs. cutting of chains due to alkaline sensitivity. However, as shown in the discussion of the carbonyl determination, no apparent alkaline cleavage occurs even at a pH of 11.0. Therefore, a cancellation of effects does not seem to be a likely explanation.

The shrinkage during reduction was due probably to alkaline solubility

of very short chain lengths. As shown by Runs VA and VIA, the loss of this material had no apparent effect upon the average D.P. Shrinkage was constant regardless of the concentration of borohydride. This is due to the self-buffering action of sodium borohydride; when added to water it decomposes to form sodium hydroxide until a pH of 9.7 is reached. The decomposition then slows down to an almost negligible rate.

Davidson (54) suggested one explanation for the effect of the carbonyl content on nitrate solubility. He stated that the insolubility was definitely not due to insufficient nitration, and postulated that there may be bonds formed between carbonyl groups or a carbonyl group and a nitrate group in adjacent chains. This would prevent chain separation and solubility. From data collected by Parkinson (45) it does not seem likely that the pH of the reducing solution or the rewetting of the degraded material during reduction would be responsible for the increased solubility.