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Doctor's Dissertation

The Kinetics of the Reactions Involved in the Bleaching of Eastern Spruce Groundwood with Alkaline Peroxide

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THE KINETICS OF THE REACTIONS INVOLVED IN THE BLEACHING
OF EASTERN SPURGE GROUNDWOOD WITH ALKALINE PEROXIDE

A thesis submitted by

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INTRODUCTION

Alkaline peroxide bleaching of groundwood has been favorably accepted by the pulp and paper industry because it has the advantage of producing a relatively large brightness increase at a reasonable cost, without materially decreasing the yield of pulp or adversely affecting its quality. The alkaline peroxide process is a relatively new development in the pulp bleaching field, although it has been used in textile bleaching for some time. Pulp bleaching with alkaline peroxide was considered as long ago as 1905, but successful commercial applications of the process were made only in the last 10 years. Alkaline peroxide bleaching was developed originally for improving the poor color of unbleached groundwood pulp. However, now it is considered, experimentally at least, in connection with the bleaching of all types of wood pulp.

Alkaline peroxide bleaching of groundwood pulp has been the subject of many investigations and reports with respect to its commercial application. The variables of the process have been well defined by laboratory experiments and mill operations. J. S. Reichert and co-workers (1-4) were responsible for much of the initial investigation on commercial applications of the process. Kauffmann (5), McEwen (6), and Stobo and Russell (7) also considered bleaching variables in their publications. As a result of the work of these investigators the optimum bleaching conditions for a commercial operation can be established with little difficulty. However, these investigations of process variables and commercial applications have provided little information on the fundamental chemistry of the alkaline peroxide bleaching process. The present investigation is
intended to provide a broader knowledge of the chemistry of alkaline peroxide bleaching through a study of the kinetics and mechanisms of the reactions which take place.

The historical development of alkaline peroxide bleaching, and publications which are devoted to methods of applying the process do not bear directly on the present investigation. The history of the process and a complete review of the literature on the alkaline peroxide bleaching of groundwood and other pulps have been presented by Jones (8) and by Reihart and Pete (9). The latter authors also provide a comprehensive summary of the peroxide bleaching process for groundwood, and consider the commercial status of the process. In their publications these authors have covered the literature available up to the end of 1948.

In the last two years considerable interest has developed in processes which involve impregnating a high-consistency pulp, such as wet lap, with various types of alkaline peroxide bleaching solutions. The impregnated pulp is stored or shipped while the bleaching action is taking place, a matter of one to several days. The bleached pulp can be used directly in the furnish; however, neutralization and acidification are recommended in some cases. Variations of this process are the subject of several articles and patents (10, 11, 12, 13, 14). Two patents have been granted for processes involving the application of alkaline peroxide bleach liquor on the paper machine; the bleaching is completed as the paper is made (15, 16). McEwen (17) has patented a process for the pretreatment of groundwood pulp with sulfuric acid at a pH below 3.0, followed by a standard alkaline peroxide bleach.
Richardson (18) discusses a commercial, medium-consistency (13-16%) alkaline peroxide bleaching system, in operation at the present time. He also considers some of the bleaching variables in relation to this system. McNiven (19) has patented a high-density bleaching process using 2% hydrogen peroxide and 8% sodium silicate (based on the weight of O. D. pulp). Bleaching is carried out at a consistency of 20-35% for one to four hours at 40-50°C.

Brecht, Jayne, and Schuster (20) present the results of an extensive investigation of the variables of alkaline peroxide bleaching. Groundwood bleaching with alkaline peroxide is compared with bleaching of the same pulp with sodium bisulfite and sodium hydrosulfite on the basis of convenience and economy.

Experimental conditions used in the present investigation were based on the commercial bleaching process. Therefore, it is desirable to consider those operations and variables which are involved in commercial alkaline peroxide bleaching, and the results afforded by the process. The alkaline peroxide process has been applied successfully to the bleaching of groundwood and neutral sulfite semichemical pulps, as well as for final-stage bleaching of sulfite and kraft pulps (2, 21, 22, 23). Because the peroxide bleaching process is applied most extensively to groundwood, and because groundwood pulp was used in the present investigation of peroxide bleaching, the following discussion has been limited to this pulp. Detailed and comprehensive information on the peroxide bleaching process is available in various publications (1, 5, 6, 7, 8, 24, 25).
Sodium or hydrogen peroxide furnish the active bleaching agent in peroxide bleach liquor. Sodium silicate is added to the liquor to provide part of the necessary alkali, to stabilize and buffer the peroxide solution, to act as a detergent and penetrant, and to serve as a corrosion inhibitor. Magnesium sulfate acts to inhibit the peroxide decomposition which is promoted by trace metallic catalysts. Caustic soda or sulfuric acid is used to produce the proper alkalinity in the bleach liquor; alkali is usually necessary in liquor made with hydrogen peroxide, and acid is used with sodium peroxide as the liquor base. A reducing and neutralising agent such as sulfur dioxide or sulfite cooking liquor is necessary in the final pulp treatment.

In most cases bleaching is carried out with 1 to 2% of sodium peroxide (based on the weight of the oven dry pulp). The exact amount of peroxide for a given operation is a function of the brightness requirement and economy. As the amount of peroxide is increased, relatively less brightness increase is obtained for a given increment in peroxide concentration.

Time, temperature, and stock density are more or less interrelated in their effects on bleaching results. A shorter bleaching time is required as the temperature and/or density is increased. Greater bleaching efficiency is obtained when bleaching at higher densities. Temperature has little effect on bleaching results over the usual range of 90 to 150°F. The bleaching time is dependent on the other bleaching variables; however, a prolonged bleaching period will bring about some reversion of brightness.
The initial alkalinity of the pulp slurry is an important factor in achieving maximum bleaching efficiency. The range of alkalinity over which maximum brightness can be obtained varies somewhat with other bleaching conditions. Reichert and Pete (2) give 10.0 to 10.5 as the desirable range for initial pH in the pulp slurry after adding the bleach liquor. Relatively greater alkalinity is required when bleaching at a low consistency than at a high consistency.

Wood species vary in their response to alkaline peroxide bleaching. Good results have been obtained with aspen, spruce, and balsam, among others. Woods having a high resin content do not usually respond well to peroxide bleaching. Fresh or moderately aged wood gives the best bleaching results.

The purity of the water supply is an important factor in obtaining satisfactory brightness increases from peroxide bleaching. The presence of colored materials or color-forming materials, such as iron, in the water will decrease the brightness development. Iron, copper, and manganese, often present as traces in mill water, will catalyze peroxide decomposition and thereby decrease the bleaching efficiency. Control of metallic catalysts is discussed by Reichert, Campbell, and Mills (2).

The cleanliness of the pulp and pulp system can have a considerable influence on bleaching results. The growth of bacteria in groundwood pulp often results in the formation of catalase, an enzyme which accelerates peroxide decomposition (3, 4). The effect of catalase on bleaching is minimized by bleaching freshly ground pulp and by efficient slime control.
Pretreatment with oxidizing or chlorinating agents is often used to control enzyme-catalyzed decomposition during bleaching.

There are three essential steps in all peroxide bleaching systems: (1) the groundwood pulp and alkaline peroxide liquor are thoroughly mixed in the proper proportions; (2) the treated slurry is retained for a time sufficient to produce maximum brightness increase; (3) the residual peroxide in the pulp slurry is reduced and the pH lowered to the level desired for the paper furnish. The above steps can be applied in either a continuous or a batch system. At the present time most peroxide bleaching operations are carried out at low (4-6%) or medium (9-15%) consistency. The low-consistency system is more economical to install, particularly if existing equipment is converted, but the medium-consistency system is more economical to operate. Consistencies over 25% have not been used extensively for commercial bleaching as yet, although some investigators have reported favorably on the process (26). The selection and proper operation of groundwood bleaching equipment is considered by Coleman (26), Lee (27), Reichert and Pete (2), and Ullman (28).

The usefulness of groundwood pulp is greatly enhanced by peroxide bleaching. Bleached groundwood is more desirable than unbleached groundwood because, in addition to giving the groundwood-containing sheet a better color, more groundwood can be used in the furnish, resulting in increased opacity and a better general appearance. Bleached groundwood pulp works better on the machine and gives better formation and feel than the unbleached pulp. Bleaching also improves the cleanliness and absorbency of groundwood pulp. Bleached groundwood provides the good printing charac-
teristics which are inherent in groundwood sheets, along with improved sheet appearance. Beeman, Goodwill, and Shearer (29) and Reichert and Pete (2) discuss the properties of bleached groundwood pulp in more detail.

Of the many investigations in the field of alkaline peroxide bleaching, only a limited number can be considered to shed any light on the fundamental chemistry of the bleaching process. Stobo and Russell (2) carried out an investigation on the effect of pH, time, temperature, wood species, and pulp consistency on the brightness increase obtained in bleaching. In interpreting their results these authors suggest reaction mechanisms which could be involved in the development of brightness during bleaching. Stobo and Russell found that there is a very sharp optimum initial pH value at which maximum brightness is obtained. From this fact, combined with their results for peroxide consumption and pH drop during bleaching, they infer that the reaction responsible for bleaching is an acid-forming reaction which is allowed to predominate at or below the optimum pH value, and that the course of this reaction is influenced by pH. Stobo and Russell also observed that the rate of peroxide consumption is very rapid in the initial stages of the reaction, and that the initial rate decreases and becomes first order in the latter portion of the reaction period. They consider that the first-order reaction represents spontaneous decomposition of peroxide, and, therefore, bleaching is no longer taking place during that period. However, they found that brightness continues to develop even though there is no apparent consumption of peroxide in bleaching. From this information, Stobo and Russell assume that the development of brightness occurs in two stages, the first an extremely rapid reaction, followed by a slower reaction in which brightness
is actually developed. Stebo and Russell point out that the above conclusions are only tentative.

Jones (2) studied the effect of sodium peroxide bleaching on the components of eastern spruce groundwood. He found that alkaline peroxide bleaching does not cause any large scale chemical changes in the known components of spruce groundwood. Jones determined that lignin is responsible for about 40% and hemicellulose about 60% of the total peroxide consumed during a normal groundwood bleaching operation. The peroxide consumption of other wood components is of minor importance. Qualitative optical data suggested that the major bleaching effect during alkaline peroxide bleaching results from a reaction with the lignin. Jones deduces that the lignin is attacked through a portion of the carbonyl groups and possibly the phenolic hydroxyl groups in the lignin structure. His studies indicate that lignin is composed of two or more fractions which are essentially the same in elementary composition and methoxyl content but which differ from each other with respect to their intrinsic color and chemical reactivity toward sodium peroxide. Jones suggests that the bleaching action of sodium peroxide on spruce groundwood may be the result of a chemical reaction between this reagent and the more highly colored lignin fractions. He infers that the remarkable efficiency of the bleaching reaction might be attributed to a relatively high specificity on the part of sodium peroxide toward these particular fractions.

Van den Acker, Lewis, Jones, and Buchanan (30) studied the nature of color changes in groundwood. Their results indicate that lignin is primarily responsible for the yellowish color of groundwood pulp, and for the yellowing and darkening of color produced by light.
Previous investigations have shown that control of the alkalinity of the peroxide bleaching system is of major importance in achieving maximum bleaching efficiency. One phase of peroxide bleaching which has received little attention in the literature is the behavior of sodium peroxide in solution and the variation of its solution characteristics with pH.

Hydrogen peroxide is a weak acid and sodium peroxide is its sodium salt. As the salt of a strong base and a weak acid, sodium peroxide will hydrolyze in aqueous solution, liberating hydroxyl ions. The equilibrium existing in an alkaline hydrogen peroxide solution can be expressed by the equation:

\[ \text{H}_2\text{O}_2 + \text{OH}^- \rightleftharpoons \text{OOH}^- + \text{H}_2\text{O} \quad (1) \]

It can be seen that the primary components of the system are hydroxyl ions, undissociated hydrogen peroxide (referred to as free hydrogen peroxide in this investigation) and hydroperoxide ions. Going from right to left, Equation (1) represents the hydrolysis of sodium hydroperoxide, while from left to right it represents the neutralization of hydrogen peroxide with sodium hydroxide. It is evident that Equation (1) must hold for both an alkaline solution of hydrogen peroxide and for a solution of sodium peroxide. The equilibrium constant for Equation (1) depends upon the first dissociation constant for hydrogen peroxide, \( K_a \). This constant has been determined by Evans and Uri (31) for temperatures up to 35°C. They obtained values of the order of $10^{-12}$. 
Because hydrogen peroxide is a dibasic acid, the possibility of forming the peroxide ion must be considered. Latimer (32) states that the second dissociation constant of hydrogen peroxide is about $10^{-25}$. Therefore the amount of peroxide ion will be negligible in its effect on the equilibrium in an alkaline peroxide solution.

It is evident from Equation (1) that the concentration of hydroxyl ion in an alkaline peroxide solution of a given peroxide concentration will determine the degree of ionization of the peroxide. It is reasonable to associate the effect of hydroxyl-ion concentration on the equilibrium represented by Equation (1) with the importance of pH in the peroxide bleaching of groundwood. Some investigators have suggested that the ions formed in an alkaline peroxide solution are responsible for its bleaching action (9, 33).

The variation of the concentration of hydroperoxide ion with changes in hydrogen peroxide and hydroxyl ion can be determined from Equation (1) which is shown below, with appropriate symbols assigned to the various quantities to simplify calculations:

$$\begin{align*}
\text{(a - x)} & \quad \text{(b - z)} & \quad \text{z} \\
\text{H}_2\text{O}_2 & + & \text{OH}^- & \rightarrow & \text{OOC}^- & + & \text{H}_2\text{O} \\
\end{align*}$$

(1)

where \(a\) is the molar concentration of hydrogen peroxide in the solution, \(b\) is the concentration of hydroxyl ion and \(z\) is the concentration of hydroperoxide ion. With known values of the first dissociation constant of hydrogen peroxide and the ion product of water (34), \(K_w\), the following equation can be set up in terms of the respective concentrations of the various components:
\[
\frac{\text{OOH}^-}{(\text{H}_2\text{O}_2 - \text{OOH}^-)} \cdot \frac{\text{OH}^-}{\text{OOH}^-} = \frac{I_a}{I_w} \quad (2)
\]

which can be expressed, using the simplified terminology given above, as:

\[
\frac{x}{(a - x)} \cdot \frac{(b - x)}{(b - x)} = \frac{I_a}{I_w} \quad (2a)
\]

The ratio \( \frac{I_a}{I_w} \) is constant for a given temperature. At 35°C, the value of this ratio is 160 (accurate to two significant figures).

Bunton and Minkoff (35), with the aid of Equations (1) and (2a), established the fact that hydroperoxide ion is responsible for the alkaline peroxide oxidation of alpha and beta unsaturated ketones. The reaction is kinetically of the first order with respect to hydroperoxide-ion concentration.

The relation between hydroperoxide-ion concentration \( x \), total peroxide concentration \( a \), and hydroxyl-ion concentration \( b \), as determined by Equation (2a), is most readily demonstrated by graphical means. Figure 1 gives this relationship for conditions which are met in alkaline peroxide bleaching. Concentrations are shown as grams per liter of sodium peroxide up to 1.2 g./l. total peroxide concentration \( a \). The concentration of bleach liquor in bleaching with 2% sodium peroxide at 5% consistency is about 1 g./l. Curves given for various concentrations of hydroxyl ion \( b \) are labeled with the corresponding pH value for convenience.

An examination of the curves in Figure 1 shows that the concentration of hydroperoxide ion approaches a maximum with increasing concentration of total peroxide. The value of this maximum depends upon the alkalinity of the solution. The effect of the alkalinity on the composition of a peroxide solution is better illustrated in Figure 2, where the percentage of peroxide as hydroperoxide ion is plotted against the hydroxyl-ion concen-
\[ \text{FIGURE 1} \]

Hydroperoxide-Ion Concentration in Alkaline Hydrogen Peroxide Solution at 35° C.
FIGURE 2

Effect of pH on Peroxide Ionization at 35° C.

Total peroxide concentration, (as Na₂O₂)

Curve (a) 0.2 g./l.
Curve (b) 0.6 g./l.
Curve (c) 1.0 g./l.

(a) (b) (c)
tration expressed as a pH value. It is apparent that the hydroperoxide-ion concentration increases markedly with increasing alkalinity.

The effect of pH control at a constant level on the equilibrium represented by Equation (1) is of interest in the present investigation. It is evident that the hydroxyl-ion concentration, and therefore the pH of an alkaline peroxide solution depends upon the amount of hydroxyl ion which is not combined as hydroperoxide ion. Therefore, the pH of the solution is a measure of the quantity \((b - x)\) in Equation (2a). If the pH is maintained at a constant level regardless of the concentration of undissociated (free) hydrogen peroxide and hydroperoxide ion, the quantity \((b - x)\) is constant and Equation (2a) becomes:

\[
\frac{x}{(a - x)} = \left(\frac{b_0}{b} \right) \text{ (constant) \quad (2b)}
\]

It is evident that the ratio of hydroperoxide-ion concentration \(x\) to free hydrogen peroxide concentration \((a - x)\) is constant at a given pH level. An equation for simple calculation of the percentage of total peroxide as hydroperoxide ion at a given pH level is given on page 72. Reichert and Hull (36) have shown that a glass electrode can be used for measuring the pH of peroxide solutions.

It is a well-known fact that peroxide solutions will decompose to form molecular oxygen, and that such decomposition is accelerated by a large number of catalysts. Peirron (37) has shown that alkali metal hydroxides are among these catalysts. The effect of sodium hydroxide on peroxide decomposition was studied by Bredig and von Berman (38), both with and without other catalysts. They found that the rate of peroxide
decomposition in a sodium hydroxide solution (with or without added catalysts) does not conform to any particular kinetic order. However, the rate of decomposition depends on the sodium hydroxide concentration and passes through a maximum with increasing concentrations of sodium hydroxide. Catalytic decomposition of neutral or acid solutions of hydrogen peroxide is almost invariably of the first order. Dörfelt (39), in connection with a study of the alkaline peroxide bleaching of cotton, confirmed the results of Bredig and von Berneck. Dörfelt observed that the rate of peroxide decomposition is dependent upon the concentration of sodium hydroxide in the peroxide solution, but is not proportional to the pH. He found that the rate of decomposition increases with increasing sodium hydroxide concentration, passes through a maximum, decreases appreciably, and then increases again, but never to a greater degree than is obtained at the maximum point.

In connection with his study of cotton bleaching, Dörfelt observed that alkaline peroxide solutions are stabilised by materials extracted from the cotton during bleaching. Dillenius (40) also noted the stabilising effect of cellulosic materials on peroxide solutions.

Dörfelt appears to have been the first investigator to evaluate alkaline peroxide bleaching efficiency by bleaching in a gastight system and determining the loss of peroxide due to decomposition by measuring the amount of evolved oxygen. Simon and Drehlich (41) used a similar technique in their investigation of the alkaline peroxide bleaching of cotton. A gastight system for determining peroxide decomposition during peroxide bleaching of groundwood is employed in the present investigation.
The present investigation is intended to provide a more complete understanding of the nature of the chemical reactions involved in alkaline peroxide bleaching. A study of peroxide bleaching kinetics constitutes the primary means of attack on the problem. Information presented in the foregoing pages, especially the discussion of peroxide chemistry, forms the basis for the present investigation.
PRESENTATION OF THE PROBLEM

Previous investigations on alkaline peroxide bleaching of groundwood have been concerned primarily with the establishment of optimum conditions for the process. Therefore the effects of the various peroxide bleaching process variables have received considerable study. However, the fundamental chemistry of the process is not completely understood. The present investigation is designed to obtain information on the kinetics of the peroxide bleaching process, with the thought that such information might provide a more complete understanding of the underlying principles.

In its execution, an investigation of peroxide bleaching kinetics resolves itself into several individual but related problems:

1. Establishment of a continuous oxygen balance for the bleaching system during the reaction period so that the disposition of peroxide can be determined.

2. Measurement of the rate of the reaction, or reactions, involved in peroxide consumption, separately if possible.

3. Determination of the effect of bleaching variables on the various reaction rates.

4. Determination of the changes in pulp characteristics which are effected by bleaching, the rate of such changes, and their relationship to the reactions taking place during bleaching.
All of the problems stated above have not been considered in full detail in the present investigation. The phases of these problems which seemed most likely to provide practical as well as fundamental information on alkaline peroxide bleaching were selected for study.
EXPERIMENTAL PROCEDURES

RAW MATERIALS

GROUNDWOOD PULP

Eastern spruce groundwood pulp was selected for use in this investigation because it is one of the species which is commonly bleached by the alkaline peroxide process, and because it has been used as the raw material in previous investigations of peroxide bleaching (8, 24).

It was decided that the experimental results obtained during this investigation would be more uniform if all experimentation could be carried out with pulp obtained under identical conditions. For this reason, fresh groundwood pulp, procured as needed, could not be used because mill conditions could be expected to vary considerably over the period of the present investigation. Therefore the procedure given below was adopted to provide the necessary groundwood pulp.

The groundwood pulp was obtained through the co-operation of a local mill. One grinder was thoroughly washed and used to grind hand-selected eastern spruce wood. Groundwood slurry was removed directly from the grinder pit so as to minimize contamination from the rest of the system. The pulp slurry was taken to The Institute of Paper Chemistry and screened on a laboratory-size flat screen. The screened pulp was pressed and air dried. The entire quantity of pulp was thoroughly mixed and separated into various lots by quartering, each lot being representative of the whole. As groundwood pulp was needed, it was selected at random from a well-mixed lot. By this procedure it was deemed that the samples of groundwood used for
individual experiments would be as representative of the original pulp as possible. The airdry pulp was stored in tight containers with a humidifying solution included to maintain the moisture content of the pulp at about 10%.

HOLOCELLULOSE

The holocellulose used in this investigation was prepared by Fublit's (42), as his cock No. 9. Alcohol-benzene extracted, black sprucewood meal (6-48 mesh) was chlorite for 4.5 hours at a temperature of 75-80°C., using a total of 107% sodium chlorite based on the weight of the wood meal. The resulting holocellulose represented 74.5% of the wood and contained 1.45% of residual Klassen lignin.

ALPHA-CELLULOSE

The alpha-cellulose used in this investigation was commercial dissolving pulp, obtained as airdry sheets. This pulp, manufactured by Rayonier, Inc., is known as Rayaceta-grade dissolving pulp.

CHEMICALS USED IN BLEACHING

Hydrogen peroxide. The hydrogen peroxide used was Merck's c.p. 30% solution, known as "Superoxol."

Sodium hydroxide. C.p. sodium hydroxide was used. All dilute sodium hydroxide solutions were made from a filtered 50% stock solution, to insure that they were carbonate-free.

Sodium silicate. A 40° Bé. aqueous solution of sodium silicate was used, as supplied by Wilkens-Anderson Co.
Magnesium sulfate. Merck's reagent grade hydrated magnesium sulfate (\(\text{MgSO}_4\cdot\text{7H}_2\text{O}\)) was used.

Sodium peroxide. DuPont technical grade sodium peroxide ("Selenoxone") was used.

Sulfuric acid. DuPont c.p. grade (96%) sulfuric acid was used.

Sulfurous acid. Sulfurous acid needed for acidifying and reducing the pulp after bleaching was prepared by bubbling sulfur dioxide into distilled water.

Distilled water was used for all bleach solutions and for preparing groundwood slurries.

ANALYTICAL METHODS

BRIGHTNESS AND SPECTRAL REFLECTANCE

It was necessary to use a nonstandard procedure in forming groundwood brightness sheets, since satisfactory sheets could not be made by the TAPPI standard method. The procedure given below was developed for this investigation.

Each brightness sample taken during a bleaching run consisted of 4 grams of pulp (ovendry basis) in about 200 ml. of slurry at pH 5.0 (see page 28). The samples were already thoroughly disintegrated. The sample of groundwood slurry was diluted to one liter and dispersed. Brightness samples other than those obtained during a bleaching run were diluted to about 400 ml. and disintegrated with a malted milk mixer before being further diluted to one liter. Five hundred milliliters of the diluted slurry (2.0 grams of ovendry groundwood) were used for each sheet. This portion
was mixed on a malted milk mixer for one minute. Then the pulp suspen-
sion was vacuum filtered on a 15-cm. Buchner funnel using a coarse filter
paper (Cenco #13255), felt side up, with care being taken to keep the
funnel level and to prevent air from being sucked through the sheet. The
funnel with the formed brightness sheet was inverted over a sheet of
18.5-cm. fine filter paper (Whatman no. 1), with the felt side up, and
the brightness sheet was deposited on the fine filter paper by blowing
through the neck of the funnel. With the brightness sheet centered on
the fine filter, the coarse filter paper was peeled from the pulp pad
and replaced with a sheet of fine filter paper. The sheets were pressed
and dried in accordance with Institute Method 412.

Brightness readings were made on a General Electric reflectance
meter. The side of the sheets which had been on top in the funnel were
read. The brightness sheets were cut into six tabs each and five bright-
ess readings were made at random from among the 12 tabs from duplicate
sheets. The five-reading average was taken as the G. E. brightness of
the sample.

Spectral reflectance curves were made on the General Electric
Recording Spectrophotometer. The sample used for spectral reflectance
measurement was selected at random from the 12-tab set of brightness
samples.

GAS ANALYSIS

An analysis of the gas evolved during peroxide bleaching was
made. The procedure for this gas analysis, which is outlined below, was
taken from that described by Carr and Selheimer (43) in detail.
A gas sample was drawn from the reaction vessel into a Hempel double gas pipet, displacing water in the pipet. The gas sample was transferred to a Haldane-type gas buret. This gas buret consisted of a 100-ml. measuring tube, fully graduated to 0.2 ml., and a compensating tube, both in a water jacket equipped with an agitator. Stopcocks were arranged so that the measuring tube could be connected to either of two inlet-outlet tubes, and to a manometer. The manometer could be balanced against atmospheric pressure or the compensating tube. For gas analysis the manometer was balanced against the compensating tube. The initial volume of the sample was determined in the gas buret (about 100 ml.). The sample was then treated with a series of gas-absorbing solutions, each in a Hempel double gas pipet. Treatment was continued with each solution until a constant volume was reached, and the decrease in gas volume after each absorption was determined from a measurement of the residual gas volume. The following absorbing solutions were used in the order given: 25% sodium hydroxide for carbon dioxide; bromine water, one volume of saturated bromine water to two volumes of water, (followed by 25% sodium hydroxide to remove bromine gas) for unsaturated hydrocarbons; 13% pyrogallol in a 17% sodium hydroxide solution for oxygen; and a saturated solution of cuprous chloride in hydrochloric acid for carbon monoxide. The amount of hydrogen and saturated hydrocarbons was determined by slow combustion in a Hempel pipet of the hot platinum wire type. The gas remaining after the complete treatment was considered to be nitrogen.

The loss in volume after each treatment for absorption of a specified gas represented the amount of that gaseous component in the original sample and was calculated as a percentage of the original gas volume. The
more involved calculations for hydrogen and saturated hydrocarbons need not be considered because these gases were not present. Analyses were considered accurate to the nearest 0.1%.

CARBON DIOXIDE ANALYSIS

The samples which were analyzed for carbon dioxide content were solutions of sodium carbonate and sodium hydroxide, in some cases with groundwood in suspension. The direct method, measuring the weight of evolved carbon dioxide, was used. The procedure is based on that given by Kolthoff and Sandell (44).

Air was drawn through a train by vacuum, passing through the various units in the following order: (1) a tube containing magnesium perchlorate followed by Ascarite to remove carbon dioxide from the incoming air; (2) a one-liter Erlenmeyer flask containing the acidified sample, with a gas-dispersion tube placed below the surface of the sample as the gas inlet; (3) one straight and one U tube containing magnesium perchlorate to remove water vapor from the gas leaving the sample vessel; (4) a U tube (the weighing tube) containing two-thirds Ascarite and one-third magnesium perchlorate to absorb the carbon dioxide removed from the sample and the water formed during carbon dioxide absorption; (5) a U tube containing Ascarite and magnesium perchlorate to protect the weighing tube.

In carrying out an analysis the alkaline sample was placed in the sample vessel and diluted, if necessary, with carbon dioxide-free distilled water. The train was flushed out until a constant weight was obtained for the weighing tube. The sample was acidified with a predetermined amount of sulfuric acid to a pH below 3.0. Air was passed through the train until a
constant weight was obtained for the weighing tube. The tube was weighed on an analytical balance, with a similar tube as a tare, to the nearest 0.001 gram. The apparatus gave satisfactory results with sodium carbonate blanks.

PEROXIDE CONTENT OF SOLUTIONS AND BLEACH LIQUORS

The following method applies to all determinations of peroxide content made in this investigation. An aliquot of the peroxide solution was pipetted into an Erlemeyer flask containing 50 ml. of distilled water and 20 ml. of 10% sulfuric acid. Ten milliliters of 10% potassium iodide and three drops of 5% neutral ammonium molybdate solution were added. The liberated iodine was titrated with 0.0128 M sodium thiosulfate, using starch indicator as the end point was reached. The concentration of peroxide was calculated from the following formula:

Sodium peroxide concn., g./l. = \( \frac{39 \text{ (ml. thiosulfate/ml. aliquot)} \times M \text{ thiosulfate}}{1000} \)

When 0.0128 M thiosulfate and a 10-ml. aliquot were used, as in most of the titrations, the concentration of peroxide, as sodium peroxide, was obtained directly as 1/20 of the buret reading in milliliters.

pH OF SOLUTIONS AND SLURRIES

All pH readings were made with a Beckman Model B-2 pH meter, using a Beckman #190-75 type K glass electrode for alkaline solutions and a standard glass electrode for other solutions. The pH of a groundwood slurry was measured directly in the slurry. Coleman buffer tablets were used to standardize the pH meter for the pH range being measured.
MOISTURE DETERMINATIONS

The moisture content of air-dry groundwood pulp and holocellulose was determined according to Institute Method 423a.

METHODS FOR DETERMINATION OF PEROXIDE CONSUMPTION

Essentially two procedures were used in obtaining the data which made up the largest part of this investigation. These procedures were carried out separately, but under the same experimental conditions. One procedure was used to measure the rate and amount of total peroxide consumption and brightness increase, the other to measure the rate and amount of oxygen evolution. By combining the data obtained by the two methods it was possible to establish oxygen balances and to characterize the individual reactions for a given set of experimental conditions. These two experimental procedures and their variations are presented below. The conditions and preparations which apply to both methods are considered first.

EXPERIMENTAL CONDITIONS

The experimental conditions which were used in carrying out bleaching experiments in this investigation were selected to be comparable to conditions used in commercial low-consistency peroxide bleaching. Such conditions were used to insure that the experimental results in this investigation would depend upon the same reactions which occur in the commercial process. The following conditions were selected as standard, and apply to all experimental bleaching data unless otherwise specified. The tolerances given represent the maximum error inherent in the equipment and methods.
Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>35.0 ± 0.1°C</td>
</tr>
<tr>
<td>Consistency</td>
<td>5.0 ± 0.1%</td>
</tr>
<tr>
<td>pH as desired</td>
<td>± 0.1 unit</td>
</tr>
<tr>
<td>Peroxide as Na₂O₂</td>
<td>2.00 ± 0.02% (based on the weight of oven-dry groundwood)</td>
</tr>
</tbody>
</table>

GROUNDWOOD PREPARATION

A sufficient amount of air-dry groundwood of known moisture content was weighed out to provide the desired quantity of oven-dry material for an experiment. This groundwood was placed in a large beaker and diluted to about 2.5% consistency with distilled water. The slurry was heated to 80°C and maintained at that temperature for one hour, while being stirred continuously with an electric motor-driven stirrer having three propellers. This treatment was sufficient to inactivate any catalase that might be present in the pulp (45), to disintegrate the pulp and to return it, as nearly as possible, to a uniformly hydrated condition.

The disintegrated pulp was filtered on a Büchner funnel and the filtrate retained. The pad of pulp from the filter was weighed and the consistency calculated. An amount of wet pulp equal to 4 grams oven-dry was weighed out and used for the unbleached brightness sample. The remaining wet pulp was placed in the reaction vessel, which was already in place in the water bath.

The filtrate from the 2.5% slurry was cooled to below 35°C and saturated with air blown in through a gas-dispersion tube. When saturated, a measured amount of the filtrate was added to the pulp in the reaction vessel to give a consistency of about 6.5%. The slurry in the reaction
vessel was covered and allowed to come to the temperature of the bath (35°C). An additional 500 ml. of filtrate, in an Erlenmeyer flask, was placed in the bath to come to bath temperature. This additional filtrate was for subsequent use in the final dilution of the pulp slurry to 5% consistency.

BLEACH LIQUOR PREPARATION

Thirty per cent hydrogen peroxide was diluted with distilled water to give a solution of about 13 grams per liter, expressed as $\text{H}_2\text{O}_2$. This solution was placed in the water bath to come to bath temperature (the decomposition of such a solution is negligible). At the same time the amount of sodium hydroxide, as a 1 M carbonate-free solution, required to give the desired pH was placed in the water bath. The sodium hydroxide necessary ranged from 1.5 to 200 ml.

Just before starting an experiment, the exact peroxide content of the hydrogen peroxide solution was determined by titration (page 25). The amount of peroxide solution equivalent to 2.00% sodium peroxide (based on the weight of oven-dry groundwood) was calculated.

DETERMINATION OF TOTAL PEROXIDE CONSUMPTION

Method 1A - Both Peroxide and Alkali Added at Start of Run - pH Controlled

The groundwood pulp and bleach liquor were prepared as previously described. The amount of pulp used was 104 grams (oven-dry), with 4 grams of this amount being used for the unbleached brightness sample.
The reaction vessel used for all bleaching experiments was a bell jar of 4500-ml. capacity. The bell jar was inverted in a constant-temperature water bath controlled to $35 \pm 0.1^\circ C$. A special stirrer was designed to agitate the groundwood slurry in a positive manner at a constant rate. An augerlike spiral of light stainless steel sheet stock was soldered to a hollow stainless steel shaft. The unit was 3.5 inches long and 3 inches in diameter (one half the diameter of the bell jar) and had four turns of the spiral. This unit was slipped over an 18-inch stainless steel stirrer shaft and secured on the end of the shaft just above a standard two-inch propeller. When the shaft and stirrer unit were rotated (in a downward direction) in the rounded bottom of the inverted bell jar, a positive vertical, rotational motion was given to the 5% groundwood slurry. This stirrer agitated from 400 to 2000 ml. (the minimum and maximum quantities used in this investigation) of 5% pulp slurry thoroughly and without channeling. The stirrer was rotated by a Mixmaster-type stirring motor, which provided a constant, reproducible speed when properly adjusted.

When the various components of the bleaching system had attained the bath temperature and the necessary volumes of hydrogen peroxide and sodium hydroxide solution had been determined, the final preparations for starting the experiment were made. The amount of additional dilution liquor (filtrate from groundwood preparation) was determined and added to the 6.5% consistency slurry, and the stirrer was started. The hydrogen peroxide and sodium hydroxide were measured into graduates, which had been prewarmed in the water bath. A buret was used for less than 10 ml. of sodium hydroxide. Because of the necessity of adding the hydrogen peroxide rapidly at the start of a run (to give an accurate zero-time point),
a recalibrated graduate was used. The error in this method of measurement was found to be less than 1.0%.

To start the run, the measured amounts of hydrogen peroxide and sodium hydroxide were added to the slurry. A stopwatch was started as the two bleach liquor components were added to the slurry, marking zero time. At this point the slurry was at 5% consistency, except in cases to be mentioned below. After waiting for one minute to allow for thorough mixing (tests indicated that mixing was complete in less than 30 seconds), the stirrer was stopped and the pH measured by inserting the electrodes directly in the slurry. The pH meter was standardized just prior to each run with a buffer of appropriate pH at the temperature of the reaction. If additional sodium hydroxide was required to give the desired pH level, it was added from a buret while the slurry was being stirred. At pH levels above 11.0 it was found desirable to start the run at a consistency of 5.02% to allow for the addition of about 10 ml. of sodium hydroxide at the one-minute pH-adjustment point. This was done to prevent the attainment of a higher pH level than desired. If it was not necessary to add 10 ml. of sodium hydroxide at the one-minute point, the consistency of the slurry was adjusted to 5.0% with dilution liquor. When the desired pH was attained, in two minutes or less, the first sample was taken. As the run continued, further samples were taken at intervals approximately as follows: 5, 8, 11, 15, 20, 25, 35, 45, 60, 75, 90, 120, 150, and 180 minutes. These intervals were satisfactory for following the course of the reaction, which was essentially complete in 180 minutes in almost all cases.

Samples were taken as follows:
At the desired time intervals, an 80-ml. cup was filled with groundwood slurry. This size sample gave 4 grams of oven-dry groundwood, enough for two brightness sheets. The sample was shaken from the cup into an 8-inch square of muslin. The liquor was squeezed through the cloth into an evaporating dish. The pulp remaining in the cloth was removed, placed in a 250-ml. beaker containing a solution of sulfurous acid of predetermined concentration. The sulfurous acid reduces the residual peroxide and neutralizes the alkali. Two 10-ml. samples were immediately pipetted from the filtrate and run into the sulfuric acid solution for the residual peroxide determination. The method for residual peroxide determination is given on page 25. Then the pulp sample was stirred in the beaker with a malted milk mixer. The entire procedure, from the point at which the sample was filtered, took less than 30 seconds. The time at which the sample was filtered was taken as the time value for each sample. Special experiments showed that the peroxide concentration of the liquor which was squeezed from the pulp was the same as that remaining in the pulp.

When time permitted, the acidified pulp samples, already roughly adjusted to pH 5.0 with the aid of indicator paper, were adjusted to pH 5.0 ± 0.2 using the pH meter. Either sodium hydroxide or sulfurous acid was used in making the adjustment. Brightness sheets were made about three hours after the final pH adjustment. The sheet-making procedure is given on page 21.

During the period of the run, the pH of the slurry was checked frequently, and sodium hydroxide solution was added in small increments to maintain the pH within 0.1 pH unit of the desired value. In most cases it
was possible to keep the pH within 0.05 unit of the desired value. The amount of alkali addition per sample interval was recorded.

It is evident that the removal of pulp from the system, and the addition of sodium hydroxide solution during the reaction period must have changed the consistency of the slurry, especially near the end of the reaction period. This dilution effect would tend to decrease the residual peroxide concentration, thus, the value for peroxide consumption would be superficially high. The magnitude of this error was calculated for the experiment in which the most sodium hydroxide solution was added during the reaction period. It was found that the error due to dilution of the liquor was negligible in relation to the accuracy of the titration for residual peroxide content.

Method 1B - Preliminary Addition of Alkali Followed by Addition of Hydrogen Peroxide - pH Controlled

This method of carrying out an experiment for the determination of total peroxide consumption and brightness development is a variation of Method 1A. The procedure was the same as that used in Method 1A up to the point of final preparation for starting the run. In Method 1B the groundwood slurry in the reaction vessel at the temperature of the bath was adjusted to the pH of the experiment by adding sodium hydroxide to the slurry, and, at the same time, to a consistency of about 5.5% by adding dilution liquor (filtrate from groundwood preparation). The pH of the slurry was controlled at the desired level by adding small increments of sodium hydroxide. The alkali consumption of the pulp leveled off after about 30 minutes of treatment, but the pH was controlled at the desired level for three to four hours before adding hydrogen peroxide, to insure thorough
impregnation of the pulp with sodium hydroxide.

At the end of the pH preadjustment period the consistency was adjusted, and hydrogen peroxide was added in accordance with Method 1A. Initial addition of sodium hydroxide was not necessary. The remainder of the experimental procedure was the same as described for Method 1A.

**Method 1C – Both Peroxide and Alkali Added at Start of Run – pH Uncontrolled**

The procedure for determining total peroxide consumption and brightness development during experiments made without controlling the pH was essentially the same as Method 1A, page 28. Method 1A is carried through to the point of adjusting the pH to the desired value at one minute after the start of the run. At this time the pH was adjusted to the value of initial pH for the experiment by adding additional sodium hydroxide solution if necessary. The run was continued as with Method 1A except that no more alkali was added to the slurry. The pH of the slurry was determined at frequent intervals and the values recorded.

**Method 1D – Bleaching with High Initial Hydroperoxide-Ion Concentration**

The procedure used for bleaching with a liquor containing a high initial concentration was essentially the same as Method 1B. All variations in procedure are considered in the following discussion. The pH of the pulp slurry was preadjusted to 10.0, and maintained at that level for two hours. An alkaline solution of hydrogen peroxide was substituted for the hydrogen peroxide solution used in Method 1B. This alkaline solution was 1 M with respect to sodium hydroxide and contained about 25 g./l. of peroxide as \( \text{H}_2\text{O}_2 \). Method 1B was followed with respect to calculating, measuring, and
adding the proper amount of this alkaline peroxide solution to the pulp slurry. Because of the sodium hydroxide content of the peroxide solution, its addition resulted in an increase in the pH of the pulp slurry above the preadjusted value of 10.0. The pH of the slurry was determined at one minute after the start of the experiment, and was controlled at this determined pH level (11.6) for the remainder of the reaction period. Method 1B was followed in all other respects.

DETERMINATION OF PEROXIDE CONSUMPTION BY DECOMPOSITION

Method 2A - Both Peroxide and Alkali Added at Start of Run - pH Controlled

The experimental conditions and procedure for Method 2A are comparable to those used for determining total peroxide consumption by Method 1A.

The procedures used for groundwood and bleach liquor preparation were the same as those previously described on pages 27 and 28. Fifty grams of ovendry groundwood pulp were used in the determination of peroxide consumption by decomposition. This amount was sufficient because no samples were removed from the system during a run. An initial brightness sample was taken from the pulp prepared for each run. The 50-gram (ovendry) sample of prepared groundwood was placed in the inverted bell jar used for Method 1A. The pulp was brought to about 6.5% consistency by the addition of dilution liquor.

As the next step in preparing for an experiment, a cover was sealed on the open end of the bell jar. This cover consisted of a circular piece of plate glass of the same diameter as the bottom of the bell jar.
The cover was bored with three holes to accommodate (1) a mercury seal for the stirrer, (2) the connections between the glass electrodes and the pH meter, and (3) the gas-outlet and solution-inlet tubes. The purpose of sealing the system was to permit measurement of the volume of oxygen formed by peroxide decomposition during bleaching. The use of stopcock grease to seal the cover to the bell jar was found to be satisfactory.

The inverted bell jar with the cover sealed on and the stirrer in place (centered through a mercury seal fitted into the cover) was clamped into the water bath. The pulp and equipment were given time to attain the temperature of the bath.

To standardize the pH meter for the conditions of the experiment, the electrodes were entirely closed in a glass container with the proper Coleman buffer solution in the bottom. The container was placed in the water bath controlled at 35°C. When the electrodes and buffer came to the bath temperature, the meter was standardized at the proper value for the buffer. The electrodes were removed from the container and inserted in the reaction vessel through one of the holes in the cover. The electrode leads were sealed into a rubber stopper which was placed in the electrode entry hole. The connection permitted the electrodes to be moved in and out of the pulp slurry in the reaction vessel without disturbing the gastight seal.

The bleach liquor components were prepared as previously described on page 28, and allowed to come to bath temperature. The necessary amount of additional dilution liquor was added to the pulp slurry after determination of the amounts of hydrogen peroxide and sodium hydroxide needed for the experiment.
As with Method 1A, when all the materials were at the bath temperature, the run was started by adding the measured amounts of hydrogen peroxide and sodium hydroxide to the pulp slurry with the stirrer in operation. A stop watch was started at the time of peroxide addition. The peroxide and alkali were added through the third hole in the reaction vessel cover. This hole was then sealed with a two-hole rubber stopper. One of the holes in the rubber stopper contained a gas-outlet tube which was connected to the gas buret described on page 23. A 10-ml. buret filled with sodium hydroxide solution was immediately inserted in the other hole of the stopper. The time lapse from the addition of peroxide to the slurry until the system was sealed gastight and connected to the gas buret was less than 20 seconds. At this point the consistency of the pulp was 5.0%.

In one minute the stirrer was stopped, the glass electrodes were lowered into the pulp slurry, and the pH was determined. The pH was adjusted, after removing the electrodes and starting the stirrer, by adding any necessary sodium hydroxide from the buret inserted through the rubber stopper.

The volume increase of the sealed system, due to oxygen evolution, was measured as follows:

As mentioned above, the Haldane-type gas buret was connected directly to the reaction vessel. As oxygen was evolved from the reaction mixture, the pressure in the reaction vessel increased. This pressure increase displaced the level in a manometer connected to the gas buret—reaction vessel system. The liquid level in the gas buret was then lowered
to return the manometer to equilibrium. The manometer was balanced against atmospheric pressure. The increase in the volume of the sealed system was read directly from the change in the liquid level in the gas buret. The first measurement of the volume of gas evolved was made in about two minutes, after the pH of the slurry had been properly adjusted. Subsequent volume-increase readings were made on the same time schedule used for sampling in Method 1A. All volume measurements were made with the stirrer in operation and the glass electrodes out of the slurry. Atmospheric pressure data and the temperature of the evolved gas were determined and recorded to be used in calculating the volume increase of the system in terms of standard temperature and pressure. The rate and amount of oxygen evolution were also calculated in terms of weight of sodium peroxide consumed in decomposition.

The need for additional alkali was determined by frequent measurement of the pH. The pH was controlled to ± 0.1 unit during the 180-minute reaction period by the addition of sodium hydroxide solution from the sealed-in buret. The volume increase of the system at any time point was corrected for the volume of alkali added up to that point.

At the completion of the 180-minute reaction period a pulp sample was taken by the method described in Method 1A, and the residual peroxide concentration was determined. Brightness sheets were made from this 180-minute sample. Final brightness and residual peroxide concentration served as checks to ascertain whether the run for the determination of the rate and amount of decomposition properly paralleled the run for the determination of total peroxide consumption made under the same conditions.
The accuracy of the equipment and procedure was tested by decomposing a known quantity of hydrogen peroxide under the experimental conditions used in carrying out bleaching reactions. For a series of four experiments at different pH levels the maximum error in the amount of oxygen evolved, as compared to the amount of peroxide decomposed, was 4.4%, with an average error of 2.3%.

Method 2B - Preliminary Addition of Alkali Followed by Addition of Hydrogen Peroxide - pH Controlled

Method 2B for the determination of peroxide decomposition in experiments made with a preadjusted pH compares with Method 1B for total peroxide consumption under the same conditions.

The experimental procedure used in the present method was the same as in Method 2A, except that sodium hydroxide was added to the groundwood slurry at a time prior to the addition of hydrogen peroxide. The pH of the slurry was maintained at the pH level for the experiment (as with Method 1B) for about three hours before the peroxide was added to start the bleaching reaction.

Method 2C - Both Peroxide and Alkali Added at Start of Run - pH Uncontrolled

Methods 2C and 1C represent the same experimental conditions, but differ in the type of data obtained during the reaction.

The procedure used in determining peroxide decomposition by Method 2C was essentially the same as used in Method 2A. After the initial adjustment of pH during the first two minutes of the reaction period, no further alkali was added to the system. The pH of the slurry was measured and recorded at frequent intervals.
Method 2D - Decomposition During Bleaching with Commercial-Type Liquor

The procedure used in determining the rate and amount of decomposition from a commercial-type liquor is the same as that used for Method 2C, as given above, except that the bleach liquor contained sodium silicate and magnesium sulfate. The grades of chemicals used in making up the liquor are listed on pages 20 and 21.

In making up the bleach liquor the chemicals were added to 900 ml. of distilled water in the order given: (1) magnesium sulfate, 0.70 g.; (2) 40° Be. sodium silicate, 52.6 g.; (3) sodium peroxide, 20.0 g.; (4) 95% sulfuric acid, 16.0 g. The solution was stirred during the addition of chemicals, and each chemical was dissolved before the addition of the following one. This bleach liquor was then diluted to one liter in a volumetric flask. This bleach liquor is similar in composition to those used in commercial groundwood bleaching operations.

The experiment was carried out in accordance with Method 2C, with the above bleach liquor taking the place of the hydrogen peroxide and sodium hydroxide solutions. One minute after the start of the run, the pH of the slurry was adjusted to 11.0 with sodium hydroxide solution. No further additions of alkali were made. The pH was measured and recorded at frequent intervals.

Method 2E - Decomposition of Alkaline Peroxide Solutions

Blank experiments on the decomposition of alkaline peroxide bleach liquor without the presence of groundwood were carried out according to Method 2C. This procedure was followed in all details, except that ground-
wood was not included in the system. The volume of distilled water, hydrogen peroxide solution, and sodium hydroxide solution in the system was 950 ml. during the experiment. The pH was not controlled during the experiment. Both the rate and amount of oxygen evolution during the reaction period were determined as a function of time. The runs were stopped at 120 minutes instead of 180 minutes because the decomposition of alkaline peroxide solution was more rapid when groundwood was not present.

MISCELLANEOUS PROCEDURES

PREPARATION OF GROUNDWOOD EXTRACTS FOR STABILIZATION TESTS

As the first step in this procedure, airdry groundwood pulp was diluted, heated and filtered as described on page 27. The experimental conditions used were 3.0% consistency, 35°C, 2.00% peroxide as H₂O₂, pH as desired. A 500-ml. sample of slurry was used for each extract. The experiments were carried out in jars, with occasional stirring by hand. Hydrogen peroxide and sodium hydroxide were used as bleaching chemicals. Groundwood filtrate was used for dilution.

Two samples were run for each pH level. Consistency, temperature, and pH level were duplicated in the two samples. However, peroxide was included in the liquor for only one of the samples. The pH level was maintained in both samples (by adding sodium hydroxide) until the exhaustion of the liquor in the sample which contained peroxide. At the end of the bleaching period each sample was vacuum filtered on a Büchner funnel. The filtrate was rerun through the groundwood pad to remove colloidal material. The filtrates were used in testing peroxide stability in the presence of groundwood extracts.
A distilled water extract of groundwood was also obtained by diluting and heating airdry groundwood pulp as described on page 27. The low-consistency slurry was vacuum filtered on a Buchner funnel, and the filtrate was rerun through the groundwood pad. This refiltered extract was also used in testing peroxide stability.

PEROXIDE STABILIZATION TESTS

Two similar procedures were used in determining the stability of alkaline peroxide solutions in the presence of various groundwood extracts. The following method was used with the extracts that were obtained from bleached and alkali-treated groundwood.

A 50-ml. sample of the extract being tested was pipetted into a beaker. This extract was already at the pH desired for the test. For blank determinations, a sodium hydroxide solution of the desired pH was used in place of the extract. A pipet was used to add 10 ml. of hydrogen peroxide solution to the extract. The concentration of the hydrogen peroxide solution was adjusted to give an initial peroxide concentration of 1 g./l. as Na₂O₂ in 60 ml. of solution. The sample was titrated for residual peroxide concentration after about one hour of reaction and again after about 10 hours of reaction. The procedure given on page 25 was used for this titration, with a 5-ml. aliquot. The reaction time was noted at the time of each sampling for the residual peroxide determination. The residual peroxide and reaction-time data were used to calculate decomposition rates for the various samples.
The following method was used with the distilled water extract of groundwood. A 50-ml. sample of the extract was adjusted to the pH desired for the test. Ten milliliters of a hydrogen peroxide solution were added to give a concentration of about 1 g./l. of peroxide (as Na₂O₂) for the entire sample. The pH was readjusted to the desired value for the test, and the initial peroxide concentration of the sample was determined immediately. As with the previous method, the residual peroxide concentration was determined at two time intervals, after one hour and after six hours. The time between peroxide concentration determinations was recorded. The residual peroxide and reaction-time data were used to calculate decomposition rates for the samples.

Both of the above procedures were carried out at room temperature, about 28°C. The pH was not controlled during stabilization tests.

PREPARATION OF PULP SAMPLES FOR CARBON DIOXIDE TESTS

Airdry groundwood pulp was diluted, heated, and filtered, as described on page 27. Four 500-ml. samples of groundwood slurry at a consistency of 1% were made from the prepared groundwood. Filtrate from the groundwood preparation was used for dilution. One of the samples was not given any further treatment. The other three samples were treated individually as follows: One sample was adjusted to pH 11.5 with sodium hydroxide solution; a second sample was adjusted to pH 11.5 and gaseous oxygen was passed through the pulp suspension for 0.5 hour; the third sample was adjusted to pH 11.5, and sufficient hydrogen peroxide was added to give a concentration of 1.0 g./l. of peroxide (as Na₂O₂). The four
samples were maintained at 25°C for 12 hours. At the end of this period the pH of each of the samples was determined. The entire 500 ml. of pulp slurry was used in the determination of carbon dioxide content according to the method given on page 24.

LOSS IN HOLOCELLULOSE DURING BLEACHING

A quantitative determination of holocellulose loss during bleaching was carried out with holocellulose and pre-reacted holocellulose. These materials are discussed on pages 192 and 200. The procedure used was similar to Method 1A (exceptions are discussed below), with the holocellulosic materials substituted for groundwood. The initial oven-dry weight of holocellulosic material was accurately determined. The sample size was 300 ml. of 5% slurry. The reaction was carried out in a vessel of suitable size, with the samples stirred intermittently by hand. The pH of the samples was controlled at the desired level (11.0) for the 180-minute reaction period, by measuring the pH and adding sodium hydroxide solution as needed. No samples were taken during the reaction period. At the end of the reaction period the pH of each sample was adjusted to 5.0 with sulfuric acid. The acidified samples were vacuum filtered on a Buchner funnel and washed acid-free with distilled water. Then the samples were washed with acetone and air dried. The air-dry pulp was transferred to weighing bottles and dried to constant weight in a vacuum oven at 60°C. All operations were carried out quantitatively. The loss in weight of holocellulose and pre-reacted holocellulose due to treatment with alkaline peroxide was determined from the weight of the oven-dry samples.
EXPERIMENTAL DATA

THE EVOLUTION OF OXYGEN DURING THE REACTION OF ALKALINE PEROXIDE WITH GROUNDWOOD

A factor of primary importance in a study of the nature of the reaction between alkaline peroxide and groundwood is the amount of peroxide decomposition to oxygen which occurs simultaneously with the bleaching reaction.

The decomposition of aqueous hydrogen peroxide is promoted by a wide variety of catalysts, both chemical and physical in nature. Among the chemical catalysts are alkali metal hydroxides, including sodium hydroxide (37). As mentioned previously, Dörfelt (39) has shown that the rate of hydrogen peroxide decomposition is closely related to the concentration of sodium hydroxide catalyst. Therefore it can be expected that aqueous solutions of sodium peroxide and alkaline hydrogen peroxide, as used in groundwood bleaching, will be subject to catalytic decomposition.

Other investigators (2, 32) have demonstrated that peroxide bleach liquors will decompose, and that this decomposition can be minimized by adding stabilizers to the bleach liquor.

Before beginning the present investigation it was decided that bleaching would be carried out with a liquor composed of c.p. hydrogen peroxide and carbonate-free, c.p. sodium hydroxide, referred to as c.p. liquor in this investigation. The use of such a bleach liquor provides the simplest possible system for a study of the kinetics of the reaction between alkaline peroxide and groundwood. It was assumed that the amount of decompo-
sition of the unstabilised bleach liquor used in the present investigation would be larger than that occurring with stabilised commercial bleach liquors. However, appreciable decomposition was not considered a disadvantage in the present experimental work because the amount of decomposition was quantitatively determined.

The purpose in carrying out the initial series of experiments, to be discussed below, was to evaluate the importance of peroxide decomposition in the presence of groundwood, using various bleach liquors. As explained in the experimental procedure, the groundwood used in all experimentation was treated so as to destroy any catalase that might be present, thus eliminating peroxide decomposition by enzyme action.

OXYGEN EVOLUTION FROM RUNS NOT pH CONTROLLED

With Chemically Pure Liqueur

Two runs were made with c.p. liquor, one at an initial pH of 10.5 and the other at an initial pH of 11.5. The runs were carried out using Method 2C (page 38). The amount of oxygen evolved during the course of these experiments is shown graphically in Figure 3, where milliliters of oxygen evolved, calculated to standard temperature and pressure (0°C, 760 mm.), are plotted against time in minutes. Curves (a) and (b) represent data taken at pH 10.5 and 11.5, respectively.

The amount of peroxide added to the groundwood slurry at the start of each run was one gram expressed as weight of sodium peroxide. *

*Throughout this dissertation all weights or concentrations of peroxide are calculated as sodium peroxide unless otherwise specified.
FIGURE 3
Oxygen Evolution from Runs not at a Controlled pH

(a) Initial pH 10.5
(b) Initial pH 11.5
(c) Initial pH 11.0, with commercial-type liquor

FIGURE 4
Oxygen Evolution from Runs at a Controlled pH (pH 11.0)

(a) With c.p. liquor
(b) Magnesium sulfate added
(c) Sodium silicate added
This quantity of peroxide is capable of liberating 144 ml. of oxygen at S.T.P. upon complete decomposition.

Calculations of the percentage of peroxide decomposed to oxygen show that (from Figure 3) the 78 ml. of gas evolved at an initial pH of 10.5 represent 54% of the available peroxide, and the 74 ml. of gas evolved at an initial pH of 11.5 represent 51% of the available peroxide. The residual peroxide at the end of each run was negligible. The amount of peroxide consumed in reaction with groundwood is the difference between the amount of peroxide consumed in all reactions (calculated by subtracting final peroxide concentration from initial peroxide concentration) and the amount of peroxide decomposing to oxygen (measured volumetrically). The above data indicate that less than one half of the available peroxide was utilized in bleaching under the conditions of the experiment. For the purposes of this discussion, the quantity of peroxide which reacts with groundwood will be considered as having been consumed in bleaching. A brightness increase of 3.6 points was obtained at pH 10.5, and 5.7 points at pH 11.5, corresponding to about one half of the brightness increase of 8 to 10 points usually obtained in commercial peroxide bleaching of groundwood with the same initial peroxide concentration used in these experiments.

With Commercial-Type Liquor

One run was made at an initial pH of 11.0 using a commercial-type liquor containing sodium peroxide ("Soloxone"), sodium silicate, sulfuric acid, and magnesium sulfate and prepared as specified by Jones (2). This liquor was added to the groundwood slurry, the initial pH was adjusted to
11.0, and the amount of gas evolution was determined according to Method 2D (page 39). This procedure gave a measurement of the amount of oxygen evolved during the bleaching period which can be compared quantitatively with those values discussed in the foregoing section.

The amount of oxygen evolved during the run is plotted in Figure 3, Curve (c), for comparison with the data presented in the previous section.

In this case, a calculation of the percentage of peroxide decomposed to oxygen shows that the 21 ml. of gas evolved represents 14.3% of the available peroxide. The residual peroxide at the end of this run was 0.29 g./l. Therefore, of the 0.73 gram of peroxide which reacted during the bleaching period, 0.14 gram, or 19.2%, was decomposed to oxygen.

With more peroxide being consumed in the bleaching reaction than in these experiments discussed in the preceding section, the brightness increase was correspondingly greater. A brightness increase of 8.9 points was obtained.

To determine the amount of decomposition in the original bleach liquor over the three-hour period of the bleaching reaction, a blank was prepared by diluting concentrated bleach liquor to the starting concentration for the run discussed above. The blank was maintained at the reaction temperature of 35°C. At the end of the three-hour period the blank showed no decomposition.

From the above data it is evident that the peroxide is decomposed and oxygen is evolved during the reaction between alkaline peroxide and
groundwood even though a stabilized bleach liquor is used. In addition, the fact that the blank did not decompose indicates that groundwood itself will catalyze peroxide decomposition.

**OXYGEN EVOLUTION FROM RUNS AT A CONTROLLED pH**

Peroxide bleaching with the pH uncontrolled introduces a variable, the hydroxyl-ion concentration, which would unduly complicate a study of the kinetics of groundwood-peroxide reactions. The decrease in hydroxyl-ion concentration which normally accompanies an uncontrolled reaction between alkaline peroxide and groundwood is appreciable in both magnitude and effect; therefore most of the kinetic data obtained in the present investigation are at some controlled pH. As will be demonstrated in a later section, both peroxide decomposition and the bleaching reaction are affected by changes in pH. Data on oxygen evolution at a controlled pH are presented in this section to establish a background for further data and discussion on the kinetics of groundwood-peroxide reactions, as well as to indicate the effect of controlling pH on the course of the decomposition reaction.

**With Chemically Pure Liquor**

The data from a run made at pH 11.0 are given graphically in Figure 4, Curve (a). These data were obtained using Method 2A (page 34) and are quantitatively comparable to the data given in the preceding section on runs made without pH control.

As shown in Figure 4, 52 ml. of oxygen were formed by peroxide decomposition, representing 38.4% of the 0.94 gram of peroxide which reacted during the period of the run. The 0.56 gram of peroxide which was used in
bleaching produced a brightness increase of 4.8 points.

**With Chemically Pure Liquor and Added Stabilizers**

Sodium silicate and magnesium sulfate are included in commercial bleach liquors because, among other reasons, they perform the important function of minimizing peroxide decomposition. The value of these bleach liquor components has been well established (2, 2), but it was considered a matter of interest to obtain data on their stabilizing effect under the experimental conditions used in this investigation. An extensive investigation of this point was not deemed necessary; therefore experiments were conducted at only one pH level.

**Sodium Silicate**

In carrying out a run with sodium silicate added as a stabilizer, Method 2A (page 34) was used, modified as follows: Just prior to adding the peroxide solution to the groundwood slurry, 3.5 grams of 40° Be. sodium silicate, equal to 7% of the weight of oven-dry groundwood, were mixed with the slurry in the reaction vessel. Then the peroxide was added, the system sealed, and the oxygen evolution measured as usual. The run was controlled at pH 11.0.

The oxygen-evolution data for this run are presented graphically as Curve (c) in Figure 4. Except for the presence of sodium silicate, all experimental conditions are the same as those used in obtaining the data for Curve (a), Figure 4. It is evident from a comparison of these two curves that the addition of sodium silicate greatly decreased the quantity of oxygen formed. The 7 ml. of oxygen formed during this run represent only
9.9% of the 0.71 gram of peroxide reacting during the experiment. A brightness increase of 9.0 points was produced by the 0.66 gram of peroxide consumed in the bleaching reaction.

Magnesium Sulfate

Method 2A (page 34) was used to obtain data on oxygen evolution from c.p. liquor stabilized with magnesium sulfate. As suggested by Jones (2), 0.0035% of Epsom salt (MgSO₄ • 7H₂O), based on the concentration of sodium peroxide, was taken as the optimum concentration of stabilizer. The Epsom salt was mixed into the groundwood slurry prior to starting the run.

The oxygen evolution data for this run are shown graphically as Curve (b), Figure 4. Comparison of the three curves in Figure 4 indicates that Epsom salts have a stabilizing effect on peroxide decomposition, but this effect is not as marked as that obtained by adding sodium silicate.

The amount of peroxide reacting during the run was 0.98 gram, of which 0.27 gram, or 27.6%, decomposed to form oxygen. A brightness increase of 6.6 points was obtained from the 0.71 gram of peroxide used in the bleaching reaction.

ANALYSIS OF THE GAS EVOLVED DURING THE REACTION OF ALKALINE PEROXIDE WITH GROUNDWOOD

In the preceding presentation of data on the evolution of oxygen during peroxide bleaching of groundwood, it was assumed that oxygen was the only gas evolved. The formation of other gases during the reaction is not beyond the realm of possibility. Therefore, it was deemed necessary to carry
out a complete gas analysis on the gas evolved during bleaching.

Carbon dioxide is the gas most likely to be formed from oxidation of the organic materials present in the reaction mixture. However, the bleach liquor is alkaline (contains sodium hydroxide), and thus any carbon dioxide formed would be converted to sodium carbonate and would not appear as a gas. There is also the possibility of forming carbon monoxide, hydrocarbon gases, both saturated and unsaturated, and hydrogen.

The procedure used in analyzing the gas evolved during the bleaching reaction was designed to detect unsaturated hydrocarbons (ethylene, acetylene, etc.), oxygen, carbon monoxide, hydrogen, and saturated hydrocarbons (methane, ethane, etc.) in quantities over 0.2 ml. The complete analysis procedure is given on page 22.

It was considered desirable to have as large an amount of evolved gases as possible in the sample used for gas analysis. Therefore, duplicate gas-evolution runs made at pH 11.0 with 4.0% peroxide (based on the weight of oven-dry groundwood) were selected for gas analysis. Since these runs were made with twice the amount of peroxide used in most of the experimental work, a larger amount of gas was obtained. Sampling was done before adding peroxide and sodium hydroxide to the system, and also after the run was completed. In this way, two samples were obtained which could be compared as to the presence of any new gas formed during the run, as well as any change in the quantity of gases initially present in the reaction vessel.
To remove gas samples from the reaction vessel without contamination, a water-filled sampling tube connected to a water-filled Hempel gas pipet was inserted into the sealed reaction vessel. The sample was drawn into the pipet, the water was displaced, and the pipet was sealed when it contained about 100 ml. of gas. Analysis of each gas sample was carried out according to the procedure on page 22.

The results of the gas analysis showed that the sample taken before the start of each run contained measurable amounts of carbon dioxide and oxygen, in addition to nitrogen, i.e., the normal components of air. The sample taken at the completion of the run contained slightly less carbon dioxide and more oxygen, but no new components could be detected. It can be concluded that only oxygen is formed during the course of the reaction between peroxide and groundwood.

An oxygen balance can be calculated from the quantitative data obtained by gas analysis. The calculations below are based on percentages. Gas pressure and temperature are not involved since all volumes given are at equal pressure (atmospheric at the time of the experiment) and temperature (35°C.). The reaction vessel has a free gas volume of 3500 ml. The initial concentration of oxygen was analysed as 20.7%. The total oxygen present in the system was, therefore, 20.7% of 3500 ml., or 724 ml. During the course of the reaction, 180 ml. of gas were evolved. However, the carbon dioxide content of the gas decreased by 0.11%, equivalent to 4 ml. of gas. Therefore the total oxygen increase was 184 ml. Thus the system should contain, at the time of the final sampling, a total of 724 plus 184 or 908 ml. of oxygen in 3680 ml. of gas, and the analysis should show 24.6%
oxygen. The analytically determined concentration of oxygen was 24.1%, or a total of 890 ml. of oxygen in 3680 ml. of gas. To summarize: The gas analysis indicates that there are 18 ml. less oxygen present at the end of the run than the amount of experimentally determined, evolved oxygen. Based on the total evolved oxygen (180 ml.), this is an error of 10%. A 10% error is reasonable when it is considered that only the oxygen which reaches the free volume of the reaction vessel was included in the final gas analysis sample. A considerable quantity of adsorbed and dissolved air was present in the groundwood slurry because the slurry was saturated with air at the temperature of the experiment, before the start of the run. If a portion of this adsorbed and dissolved air was displaced by oxygen during the run, and it may be so assumed, the concentration of oxygen in the free volume above the slurry would be lower than such concentration when calculated from the gas volume increase of the system.

It should be mentioned here that the alkaline liquor from the completed bleach was analyzed for the presence of sodium carbonate. This analysis was carried out by filtering the groundwood slurry, acidifying a portion of the filtrate, and gravimetrically determining the amount of evolved carbon dioxide. Carbon dioxide was found in appreciable quantity. The formation of sodium carbonate during the reaction between alkaline peroxide and groundwood will be discussed in detail in a subsequent section of this work.

The data presented in this section establish certain facts which are necessary to the study of the kinetics of the reaction between alkaline
peroxide and groundwood, as discussed in a following section. Of primary importance is the fact that oxygen, and only oxygen, is evolved simultaneously with the reaction between peroxide and groundwood under the experimental conditions described. It can also be concluded that oxygen is evolved in appreciable quantities regardless of the type of bleach liquor used. Stabilizers added to the liquor decreased the amount of oxygen evolved, but not to the point of insignificance. Controlling the pH does not diminish the effectiveness of the stabilizers used. Commercial-type bleach liquor, even though stable when not in contact with groundwood, will form oxygen in the course of bleaching.

The data also indicate that pH control during bleaching will decrease the amount of oxygen evolution.

Some data on the relationship of brightness to the amount of peroxide used in the bleaching reaction have been included in this section to demonstrate the fact that bleaching was accomplished in all experiments. Further data on brightness and color change during bleaching will be discussed in a following section.

More complete data on the nature of the peroxide decomposition reaction will be presented in later sections of this work.
THE EFFECT OF GROUNDWOOD ON PEROXIDE DECOMPOSITION

It was pointed out in the previous section that apparently stable alkaline peroxide solutions would decompose in the presence of groundwood. Any catalytic effect that groundwood might have on the decomposition of peroxide would be of importance in understanding the kinetics of the bleaching system. Therefore several experiments were designed to investigate the effect of groundwood on peroxide decomposition. The results of these experiments are presented in this section.

It is possible for groundwood to catalyze peroxide decomposition in two ways: because of its finely divided physical state, and because of materials dissolved from the groundwood during the course of the bleaching reaction. Such decomposition as is due to the heterogeneous nature of the groundwood-peroxide system can be expected to remain a constant factor in the present investigation, since the same type and concentration of groundwood was maintained throughout the kinetic studies undertaken. Therefore experiments on the effect of groundwood on peroxide decomposition were confined to materials solubilized from groundwood and producing homogeneous catalysis.

EXTRACTS MADE AT VARIOUS pH LEVELS

An investigation of the effect of pH on the catalytic action of groundwood extract, and of the catalytic action of groundwood extracts obtained at various pH levels was undertaken. Another point of interest was whether the action of peroxide during bleaching would have any effect on the catalytic nature of the materials extracted from groundwood.
For the initial experiment in studying the effect of groundwood extracts on peroxide decomposition, a series of extracts was obtained under varying conditions, similar to those encountered in peroxide bleaching. The procedure used is given on page 39.

Groundwood extracts were obtained at three pH levels, 10.5, 11.5, and 12.5. At each pH level the groundwood was subjected to two treatments. For the first sample the groundwood was bleached, with pH controlled and constant, using 2% peroxide. The bleaching was carried to exhaustion. For the second sample the peroxide was omitted, that is, the sample was treated with sodium hydroxide and maintained at a constant pH for the same period of time as the corresponding bleached sample. Each of the six samples was filtered at the end of the reaction time, and the filtrate was rerun through the groundwood pad to remove as much colloidal material as possible. In addition, a distilled water extract was obtained from groundwood heated to 80°C. and stirred for one hour (the treatment given groundwood before use in any reaction in the present investigation).

The six extracts were used according to the procedure given on page 40 to test their effect on the decomposition of alkaline peroxide solutions. Each extract was tested at two pH levels, the one at which it had been prepared, and at pH 11.0. The distilled water extract was tested at pH 11.0. In addition, blanks were run for pH 10.5, 11.0, 11.5, and 12.5. First-order reaction-rate constants were calculated from the change of peroxide concentration in each of the samples over a known period of time. The formula

\[ k \text{ (rate constant)} = (2.303/\text{time, min.}) \cdot \log(\text{initial concentration/final concentration}) \]
was used to calculate the constants, which are expressed in reciprocal minutes. Although this decomposition reaction is not precisely of the first order, the first-order constant provides a good estimate of the rate of decomposition.

The results of the decomposition tests are given in two tables below. Table I shows those samples which were tested at the same pH as that of the extract preparation. The first column in Table I indicates the pH at which the peroxide decomposition test was carried out. The second column describes the sample of groundwood extract which was being tested; for example, the first sample listed is the extract which was obtained from a bleach carried out at pH 10.5, while the second listing in the column is the corresponding extract made at pH 10.5 with no peroxide present. The third column in Table I gives the rate constant obtained in each test.

**TABLE I**

**THE EFFECT OF GROUNDWOOD EXTRACTS ON PEROXIDE DECOMPOSITION AT THE pH OF EXTRACTION**

<table>
<thead>
<tr>
<th>pH of Test</th>
<th>Sample</th>
<th>Rate Constant x 10^4, min^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5</td>
<td>Extract, bleached, pH 10.5</td>
<td>2.6</td>
</tr>
<tr>
<td>10.5</td>
<td>Extract, unbleached, pH 10.5</td>
<td>2.7</td>
</tr>
<tr>
<td>10.5</td>
<td>Blank, pH 10.5</td>
<td>0.7</td>
</tr>
<tr>
<td>11.5</td>
<td>Extract, bleached, pH 11.5</td>
<td>5.4</td>
</tr>
<tr>
<td>11.5</td>
<td>Extract, unbleached, pH 11.5</td>
<td>1.7</td>
</tr>
<tr>
<td>11.5</td>
<td>Blank, pH 11.5</td>
<td>292</td>
</tr>
<tr>
<td>12.5</td>
<td>Extract, bleached, pH 12.5</td>
<td>2.4</td>
</tr>
<tr>
<td>12.5</td>
<td>Extract, unbleached, pH 12.5</td>
<td>1.4</td>
</tr>
<tr>
<td>12.5</td>
<td>Blank, pH 12.5</td>
<td>70</td>
</tr>
</tbody>
</table>
It is apparent from the results given in Table I that groundwood extract is a stabilizer for peroxide decomposition rather than a positive catalyst. The rate of decomposition for the sample containing groundwood extract was approximately the same, regardless of the pH at which the extract had been obtained. At pH 10.5 the rate of decomposition of the blank was very small, and the extract exerted a slight catalytic effect on the decomposition. At pH 11.5 and 12.5 the decomposition of the blank was rapid and the samples containing groundwood extract decomposed comparatively slowly.

The data in Table I indicate that, although the rate of decomposition of the blanks varied greatly with a change in pH, the rate of decomposition of samples containing extracts varied only slightly. Data on the effect of the groundwood extracts on peroxide decomposition at pH 11.0 are given in Table II. To obtain these data the extracts made at different pH levels were adjusted to pH 11.0 with sodium hydroxide or sulfuric acid and tested for their effect on rate of decomposition as before.

The data in Table II indicate that there is no appreciable difference between groundwood extracts made at different pH levels. All extracts had a stabilizing effect, causing decomposition to take place much more slowly in samples containing extract than in the blank. The distilled water extract appears to be somewhat the best stabilizer.

It is interesting to note that the rate of decomposition of the blanks passes through a maximum. As mentioned previously, Dorfert (39) also
TABLE II

THE EFFECT OF GROUNDWOOD EXTRACTS ON PEROXIDE DECOMPOSITION
AT pH 11.0

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate Constant x 10^4, min^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extract, bleached, pH 10.5</td>
<td>3.8</td>
</tr>
<tr>
<td>Extract, unbleached, pH 10.5</td>
<td>4.1</td>
</tr>
<tr>
<td>Extract, bleached, pH 11.5</td>
<td>5.4</td>
</tr>
<tr>
<td>Extract, unbleached, pH 11.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Extract, bleached, pH 12.5</td>
<td>7.0</td>
</tr>
<tr>
<td>Extract, unbleached, pH 12.5</td>
<td>5.1</td>
</tr>
<tr>
<td>Extract, distilled water</td>
<td>0.7</td>
</tr>
<tr>
<td>Blank, pH 11.0</td>
<td>427</td>
</tr>
</tbody>
</table>

observed this phenomenon when experimenting on the catalytic effect of sodium hydroxide on hydrogen peroxide decomposition.

DISTILLED WATER EXTRACT

A further series of tests on the effect of distilled water extract on the decomposition of peroxide was carried out to provide more information on the stabilizing power of groundwood extract and also on the catalysis of peroxide by sodium hydroxide. For this experiment groundwood extract was prepared according to the procedure given on page 41. The rate-of-decomposition tests were carried out by a procedure given on page 42, which is a slight modification of the procedure used in the preceding section.

A series of 12 samples was used, consisting of a blank and an extract-containing sample at 0.5-pH unit intervals from pH 10.0 to 12.5.
The data on change in concentration of peroxide for a specified time interval was used, as before, to calculate the first-order reaction-rate constant. These data are given in Table III below.

**TABLE III**

<table>
<thead>
<tr>
<th>pH of Test</th>
<th>Reaction-Rate Constant x $10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without Extract, min$^{-1}$</td>
</tr>
<tr>
<td>10.0</td>
<td>4.4</td>
</tr>
<tr>
<td>10.5</td>
<td>13.6</td>
</tr>
<tr>
<td>11.0</td>
<td>16.5</td>
</tr>
<tr>
<td>11.5</td>
<td>248</td>
</tr>
<tr>
<td>12.0</td>
<td>201</td>
</tr>
<tr>
<td>12.5</td>
<td>39.6</td>
</tr>
</tbody>
</table>

The first column in Table III gives the pH at which the rate of decomposition was determined. The second and third columns in the table give the calculated rate constants, with and without the addition of groundwood extract to the sample.

An examination of the data in Table III shows the maximum through which the peroxide decomposition rate passes with increasing pH. The stabilizing effect of groundwood extract is very apparent. Decomposition was decreased by extract addition at all pH levels.

The data presented in the two preceding sections show conclusively that materials which can be extracted from groundwood treatment with alkali by boiling and by the peroxide bleaching process itself will stabilise the decomposition of alkaline peroxide. Although pH greatly affects the rate of decomposition of unstabilised peroxide, there appears to be a tendency
for the decomposition rate to remain constant in the presence of ground-
wood extract, regardless of the pH level.

GROUNDWOOD PULP

Although no experiments were made to determine specifically the
effect of groundwood pulp on peroxide decomposition, some data on this
effect are available from other experiments.

A series of determinations of alkaline peroxide decomposition
rate were made in the apparatus used to carry out bleaching experiments.
These determinations were made under conditions comparable to the actual
bleaching experiments, according to Method 2E on page 39. The rate of
decomposition was determined from oxygen evolution. The first-order
reaction-rate constants were calculated and used as a measure of the de-
composition rate.

It will be demonstrated in the following section that a rate
constant can be obtained for the decomposition of peroxide during a bleach-
ing experiment, that is, in the presence of groundwood pulp. This rate
constant is a true first-order constant. The two sets of first-order rate
constants, with and without the presence of groundwood, are presented in
Table IV. The bleaching experiments which provided data for calculating
the following rate constants were made with unstabilized c.p. liquor.

The data in Table IV indicate that groundwood pulp, as well as
groundwood extract, will slow the rate of decomposition of alkaline per-
oxide. As in the experiments with groundwood extract, the decomposition
rate of peroxide in the presence of groundwood pulp is approximately constant
TABLE IV
RATE OF OXYGEN EVOLUTION FROM ALKALINE PEROXIDE

<table>
<thead>
<tr>
<th>pH of Experiment</th>
<th>First-Order Reaction-Rate Constant Without Groundwood, min.(^{-1})</th>
<th>First-Order Reaction-Rate Constant With Groundwood, min.(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5</td>
<td>0.017</td>
<td>0.009</td>
</tr>
<tr>
<td>10.8</td>
<td>0.029</td>
<td>--</td>
</tr>
<tr>
<td>11.0</td>
<td>--</td>
<td>0.011</td>
</tr>
<tr>
<td>11.5</td>
<td>0.050</td>
<td>0.010</td>
</tr>
<tr>
<td>12.0</td>
<td>0.080</td>
<td>0.011</td>
</tr>
<tr>
<td>12.4</td>
<td>--</td>
<td>0.003</td>
</tr>
<tr>
<td>12.5</td>
<td>0.093</td>
<td>--</td>
</tr>
</tbody>
</table>

over the pH range covered.

It was demonstrated in a previous portion of this work that groundwood would promote the decomposition of stabilized, commercial-type bleach liquors. Therefore it must be concluded that groundwood pulp will promote or stabilize the decomposition of alkaline peroxide, the nature of the effect depending on the stability of the original peroxide solution.

THE KINETICS OF THE REACTION BETWEEN ALKALINE PEROXIDE AND GROUNDWOOD

The major interest in the present work is to establish, as completely as possible, the kinetic relationships between the various components of the groundwood-peroxide system. The data in this section are presented toward that end.
Two methods are in general use for following the course of
the reaction between peroxide bleach liquor and groundwood. These methods
are: (1) change in pulp brightness with time and (2) decrease of peroxide
concentration with time. The first method is not sufficiently refined to
permit its use in the present investigation of reaction kinetics in any
but a qualitative sense. The second method makes no allowance for peroxide
which might be decomposed to oxygen during the course of the reaction, but
measures the amount of peroxide utilized in all reactions during the
bleaching period. As was demonstrated in a previous section, it is possible
to measure the rate of oxygen evolution during peroxide bleaching, using
the methods and equipment developed for this investigation. With the in-
formation experimentally available on the rate of decomposition of bleach
liquor during the bleaching period it is possible to calculate the amount
of peroxide which actually reacts with groundwood components and the rate
of this groundwood-peroxide reaction.

Other factors besides that of chemical reaction rate often enter
into the kinetics of a heterogeneous reaction such as that between peroxide
and groundwood. However, previous investigators (Z, 9) have shown that
the rate of peroxide consumption by groundwood more than doubles with a
temperature increase of 10°C. This behavior is characteristic of homo-
genous chemical reactions and not of heterogeneous reactions. Therefore
it was assumed that kinetic data from the groundwood-peroxide system could
be analyzed by well-established reaction-rate equations, rather than by the
more empirical methods necessary for establishing reaction rates in a
heterogeneous system. This assumption proved to be correct.
EXPERIMENTS WITH THE pH UNCONTROLLED*

As the initial experimentation related to the kinetics of groundwood-peroxide reactions, two sets of rate data were obtained without controlling pH during the reaction. These runs were undertaken to test the experimental methods and to provide a comparison of uncontrolled pH runs with those to be made at a controlled pH. Each set of data consisted of one run made according to Method 2C, page 38, and one run according to Method 1C, page 33. These two runs establish separately the rate of oxygen evolution and the rate of peroxide consumption for a groundwood bleach under duplicate conditions. By combining the two types of rate data, the course of the reaction between groundwood and peroxide can be determined.

The data are given graphically in Figures 5 and 6, which represent data taken at (initial) pH 10.5 and 11.5, respectively. The curves in Figures 5 and 6 are plotted in a manner which is generally accepted for kinetic data. Concentration of peroxide in the system is given along the ordinate of the graphs and time of reaction along the abscissa. The curves labeled (T), for total peroxide, are plotted from experimental data on the change in peroxide concentration with time as produced by all reactions of peroxide during the bleaching period. Thus a point on one of the (T) curves represents the peroxide remaining in the system at a given time. These data were obtained using Method 1C, page 33.

*These experiments, and all others discussed in this work, were made with c.p. liquor unless otherwise specified.
The curves labeled (D), for decomposed peroxide, represent the amount of peroxide which decomposed to oxygen during the bleaching period, as measured volumetrically by Method 2C, page 38. The points plotted for Curve (D) were calculated from the volume of oxygen evolved up to the time represented by each point. The oxygen volume was reduced to S.T.P. and the weight in grams of sodium peroxide necessary to produce this volume of oxygen was calculated. The calculated weight of sodium peroxide was subtracted from the weight of peroxide added to the system initially (1.00 gram), and the resulting residual peroxide value was expressed in grams per liter of liquor and plotted on the graph. Therefore each point on Curve (D) represents an experimentally determined value. It should be emphasized that the actual residual peroxide value at any time during the bleaching period can be obtained from Curve (T), and that such a value from Curve (T) includes the amount of decomposition as represented by a point on Curve (D) at the selected time lapse.

The difference between Curves (T) and (D) represents the amount of peroxide which reacts with all or part of the groundwood in the system, and which is responsible for the bleaching action obtained. The curves labeled (B), for effective peroxide, were plotted from values obtained by subtracting Curve (D) from Curve (T). This calculation was performed graphically by measuring the distance between Curves (T) and (D) at frequent time intervals. The resulting values were plotted as decreases in peroxide concentration from the initial concentration of 1.052 g./l. Curves (D) and (E) do not represent a true value for the residual peroxide concentration at any time point as might appear to be the case from an examination of Figures 5 and 6. The amount of peroxide consumed by de-
composition and by the reaction between peroxide and groundwood has been represented by indicating the decrease in peroxide concentration which is due to each of the respective reactions rather than by plotting the peroxide consumption in each case. It was considered that the contribution of each of the reactions to the total peroxide consumption could be most clearly seen by plotting the peroxide consumption of each of the reactions as a decrease from the initial peroxide concentration, and in addition including total peroxide consumption data on the same graph. This procedure was used for Figures 5 and 6. For this reason the ordinate in Figures 5 and 6 has been labeled "Apparent residual peroxide" although the true residual peroxide value at any time during each experiment can be obtained from the curve labeled (T). The relationship between the three curves at any time point can be expressed as:

\[(1.052 - T) = (1.052 - D) + (1.052 - E)\] (all in grams per liter)

Graphs which are similar to Figure 5 and 6 will be found frequently in following sections of this work. In all such graphs, the calculations and nomenclature are the same as explained above.

One other feature of the curves that are shown in Figure 5 requires clarification. The data taken for oxygen evolution during the reaction between peroxide and groundwood indicate that such evolution ceases at some point during the reaction period. Additional information on this point, to be presented on page 179 et seq., shows that some of the oxygen which is evolved is subsequently reabsorbed in the reaction mixture. The implications of this fact with respect to the calculations carried out in analyzing the kinetics of the various reactions are discussed on pages 89
to 92 of this section. Because the amount of oxygen evolution cannot
be measured over the entire reaction period, the final value obtained
for peroxide consumed in the decomposition reaction is carried to the
end of the reaction period as a dotted line extending Curve (D) in
Figure 5. Curve (E) is also extended with a dotted line because it
depends in part on the values represented by Curve (D). The situation
discussed above occurs with most of the data to be considered in the
present section. In such cases the above procedure is used to represent
the course of the reactions after the apparent cessation of oxygen
evolution.

It is evident from an examination of Figures 5 and 6 that oxygen
evolution accounted for more peroxide consumption than reactions with
groundwood, under the experimental conditions used. It is also apparent
that more peroxide reacted with groundwood in the run made at an initial
pH of 11.5 than in the run made at an initial pH of 10.5. The rate of
brightness increase for these runs will be discussed in detail in a later
section of this work; however it should be noted that a greater final
brightness was obtained at pH 11.5 than at pH 10.5.

From an analysis of these data it was determined that no one of
the component curves could be fitted into any simple kinetic equation.

The variation of pH with time for these runs is also of interest.
The data from the two runs under consideration are plotted in Figure 7.
Curves (a) and (b) represent the values from runs made at initial pH 10.5
and 11.5, respectively. The two curves indicate that the pH drop is gradual,
with the rate decreasing in a regular manner with time. The c.p. liquor used
FIGURE 7
pH Variations During Bleaching

Curve (a) Initial pH, 10.5
Curve (b) Initial pH, 11.5
in these experiments does not produce a buffering effect as does the liquor used commercially.

It was mentioned previously that the pH of an alkaline peroxide solution has a pronounced effect on the ionization of peroxide; therefore, from the pH change shown in Figure 7, it can be concluded that the ionic composition of the liquor used in the two bleaches under discussion changed appreciably during the bleaching period.

EXPERIMENTS WITH CONTROLLED pH

It was pointed out in the discussion of the chemistry of alkaline peroxide solutions (page 9) that the equilibrium concentrations of free hydrogen peroxide and of hydroperoxide ion in aqueous solution are appreciably affected by changes in the hydroxyl-ion concentration. Since it is suspected that hydroperoxide-ion is the active bleaching agent in an alkaline peroxide solution, it is essential that the concentration of this ion be known if its action is to be accurately determined. By controlling the pH at a constant level, the equilibrium of the peroxide is also controlled, and the concentration of hydroperoxide ion can be calculated. Thus, bleaching at a constant pH eliminates an important variable from the groundwood-peroxide system during the reaction period and provides a more simple system for kinetic analysis. In addition, the effect of pH on the system can be more accurately evaluated by bleaching at various controlled pH levels rather than by allowing a pH change during the reaction period.

The data plotted in Figure 1 (page 12) indicate that the equilibrium between free hydrogen peroxide and hydroperoxide ion (at any constant sodium
hydroxide concentration) will shift as the total peroxide concentration
is decreased. It was stated (page 11) that equilibrium concentrations
of the various components of the system could be calculated from the
equation:

$\frac{[\text{SOOH}^-]}{([\text{H}_2\text{O}_2] - [\text{SOOH}^-])} \left( [\text{OH}^-] - 2[\text{SOOH}^-] \right) = K_a/K_w \tag{2}$

In this equation the term $([\text{OH}^-] - 2[\text{SOOH}^-])$ represents the total free hydroxyl
ion in the system at any time. When a constant pH level is maintained, the
hydroxyl-ion concentration cannot change and the term $([\text{OH}^-] - 2[\text{SOOH}^-])$
becomes a constant. Therefore, it is evident that the ratio between the
concentration of free hydrogen peroxide and the concentration of hydro-
peroxide ion, which would normally decrease as the total peroxide in the
system decreases, will remain constant if a given pH level is maintained.
This effect has been discussed in detail on page 14.

Equation (2) can be simplified to permit easy calculation of the
ratio of hydroperoxide ion to the total peroxide in an alkaline peroxide
solution at any pH. For example, the equation

$$\text{Hydroperoxide, } \% = \frac{160 ([\text{OH}^-] - 2[\text{SOOH}^-])}{1 + 160 ([\text{OH}^-] - 2[\text{SOOH}^-])} \times 100 \tag{2a}$$

can be used to calculate the percentage of the total peroxide which is
combined as hydroperoxide ion at 35°C. The quantity $([\text{OH}^-] - 2[\text{SOOH}^-])$ is
the hydroxyl-ion concentration as determined by measurement of pH. As a
matter of interest, the percentage (to the nearest 0.1%) of total peroxide
which is combined as hydroperoxide ion has been calculated for the pH range
used in the following experiments and tabulated in Table V. The values in
Table V apply to a solution of pure hydrogen peroxide and sodium hydroxide at 35°C.

**TABLE V**

PERCENTAGE OF PEROXIDE COMBINED AS HYDROPEROXIDE ION

<table>
<thead>
<tr>
<th>pH</th>
<th>Hydperoxide Ion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0</td>
<td>0.2</td>
</tr>
<tr>
<td>9.5</td>
<td>0.5</td>
</tr>
<tr>
<td>10.0</td>
<td>1.6</td>
</tr>
<tr>
<td>10.5</td>
<td>4.8</td>
</tr>
<tr>
<td>11.0</td>
<td>13.8</td>
</tr>
<tr>
<td>11.5</td>
<td>33.6</td>
</tr>
<tr>
<td>12.0</td>
<td>61.5</td>
</tr>
<tr>
<td>12.5</td>
<td>83.5</td>
</tr>
<tr>
<td>13.0</td>
<td>94.1</td>
</tr>
</tbody>
</table>

**Runs Initiated with Separate and Simultaneous Addition of Hydrogen Peroxide and Sodium Hydroxide**

The first series of bleaches made at a controlled pH level consisted of seven sets of data taken at intervals over the pH range 9.0 to 12.5. This range was selected because it includes the pH values encountered in commercial bleaching as well as values above and below the commercial bleaching range. The pH range which was selected also presents a large variation in concentration of hydroperoxide ion, as shown in Table V.

The data at each pH level include a run for the measurement of the rate of oxygen evolution, made according to Method IA, page 28; and a
run for the measurement of total peroxide decomposition, made according to Method 2A, page 34. Hydrogen peroxide and sodium hydroxide were added to the groundwood separately and simultaneously at the start of each run. This method is similar to the process followed commercially in that the bleach liquor is added to groundwood which is neutral or slightly acid before starting the bleach; however, it differs from the commercial process in that the peroxide and alkali are added separately. Commercial bleach liquor, which is a concentrated alkaline peroxide solution, has a high concentration of hydroperoxide ions for a short period until equilibrium is reached. In the method used for this work the initial concentration of hydroperoxide ion increases from zero to the equilibrium value in the same short period. It was necessary to use separate additions of the peroxide and alkali in the present investigation because of the difficulty of controlling the concentration of an unstabilized alkaline peroxide solution within the limits necessary to permit attainment of initial conditions rapidly and accurately.

The data obtained in the series of experiments under consideration are presented graphically in Figures 8 through 14. These original data have been modified by the method of calculation previously described (page 67) to obtain the form best suited to graphical presentation. The curves on Figures 8 to 14 are labeled as stated in the previous section: (T) for total peroxide consumed, (D) for peroxide decomposed to oxygen, and (E) for peroxide reacting with groundwood.

It should be noted that the data for the entire 180-minute bleaching period are shown in Figures 8 and 9. In figures 10 to 14 only
the data for the first 90 minutes of the bleaching period are plotted, since the reactions are practically complete in that time.

From a qualitative comparison of the data for all pH levels it is quite evident that a change in pH has a marked effect on both the decomposition reaction and the reaction with groundwood. A brightness increase was obtained in all cases, the amount of which varied with the pH level. The relation of brightness increase to the peroxide consumed in reaction with groundwood will be discussed in a later section of this work.

At pH 9.0 both reactions are very slow, with the decomposition reaction predominating. Eighty-two per cent of the total peroxide consumed went to decomposition over the 180-minute reaction period. At the next higher pH level, 10.0, the total reaction rate was almost doubled, and the amount of peroxide decomposed over the 180-minute reaction period was 65% of the total peroxide consumed. It is interesting to note that the rate of consumption of the total peroxide is approximately the same in the five sets of data from pH 10.5 to 12.5. However, the amount of peroxide that is decomposed to oxygen decreases steadily with an increase of the pH level, and the amount of peroxide which is consumed in reaction with groundwood, in turn, increases. The percentage of the total peroxide consumed which was utilized in each of these five reactions was calculated and is presented in Table VI. The calculations were made for the 90-minute period which is shown in Figures 10 to 14.

It can be concluded from the data shown in Figures 8 to 14 and Table VI that the rates of any of the reactions involved in the consumption of peroxide are slow at pH levels 9.0 and 10.0. At pH levels from 10.5 to 12.5 the rate of total peroxide consumption is approximately constant, but
## TABLE VI

**THE EFFECT OF pH ON THE PEROXIDE CONSUMPTION OF INDIVIDUAL REACTIONS**

<table>
<thead>
<tr>
<th>pH</th>
<th>Peroxide Consumption Decomposition, %</th>
<th>Groundwood, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5</td>
<td>53</td>
<td>47</td>
</tr>
<tr>
<td>11.0</td>
<td>41</td>
<td>39</td>
</tr>
<tr>
<td>11.5</td>
<td>36</td>
<td>64</td>
</tr>
<tr>
<td>12.0</td>
<td>17</td>
<td>83</td>
</tr>
<tr>
<td>12.5</td>
<td>12</td>
<td>88</td>
</tr>
</tbody>
</table>

the ratio of peroxide decomposition to groundwood consumption of peroxide decreases markedly.

### Kinetic Analysis

**Analysis of total peroxide consumption**

In considering the kinetics of the various reactions encountered in this investigation it should be understood that analyses of the data can be based only on the change in peroxide concentration as affected by these reactions. Naturally, the nature and concentration of the organic materials in groundwood enter into the kinetics of the reaction with peroxide. The effect of these organic materials on the kinetics of this reaction can be ascribed only qualitatively in this investigation, since the mechanisms of groundwood-peroxide reactions are, as yet, largely unknown.

The reaction-rate data for total peroxide consumption were tested for possible compliance with reaction-rate equations for first-, second-, and third-order reactions, using accepted methods (see Glaeser (46)). The
total peroxide consumption rate appeared to be of the first order over a considerable portion of the bleaching time, and at all pH levels.

If a reaction is of the first order, the rate of concentration change with time, \( \frac{dc}{dt} \), satisfies the following equation (at constant volume):

\[
-\frac{dc}{dt} = kc
\]

where \( k \) is the first-order reaction-rate constant, \( t \) is time, and \( c \) is the concentration at any time. In this investigation \( t \) is expressed in minutes, and \( k \), therefore, in reciprocal minutes. Equation (3) illustrates the fact that a first-order reaction is one in which the rate of reaction is directly proportional to the concentration of the reacting material. Integration of Equation (3) gives:

\[
(4) \quad -\ln c = kt + \text{constant} \quad \text{or} \quad (5) \quad -\log c = (kt/2.303) + \text{constant}
\]

Equation (5) indicates that in a first-order reaction a straight line is produced when the logarithm of the concentration is plotted against time.

In Figure 15, residual peroxide concentration is plotted against time, using semilogarithmic paper, for the total peroxide consumption data obtained at pH level 11.5. These data are presented to demonstrate the degree to which total peroxide consumption conforms to first-order equations. The run at pH 11.5 can be considered representative of the entire series in this respect. The data at some pH levels produced less variation from a linear relationship and some slightly more. Data to be presented later (pages 110 to 116) demonstrate more conclusively that the rate of peroxide consumption is of the first order. The fact that data from these
FIGURE 15

Peroxide Consumption
pH 11.5

Starting Concentration for the First Order Reaction

Residual peroxide, g/l, (as \( \text{H}_2\text{O}_2 \))

Zero Time for the First Order Reaction

Reaction time, min.
ments will satisfy a first-order equation for at least a portion
of the reaction period indicates that only the concentration of peroxide
is important in determining the over-all rate of consumption of peroxide
this portion of the bleaching time. Therefore, the concentration
of organic material which reacts with peroxide must be unimportant
as the kinetics of the reaction are concerned. There are three
possible ways in which to account for this fact: (1) The concentration of
peroxide is equivalent (in terms of reactivity) to that of peroxide
which are being consumed at the same rate, as in a second-order reaction
involving the reactants starting at the same concentration; (2) the concentration
of organic materials is in such large excess that it does not change
significantly during the course of the reaction and therefore becomes part
of the reaction-rate constant; (3) the reaction with organic material has
been replaced during the period of the first-order reaction and only decomposi-
tion is taking place. The first reason given is not acceptable since the
concentrations of the two constituents in the bleach liquor, free hydrogen
peroxide and hydroperoxide ion, change appreciably over the pH range being
considered, and it is very unlikely that the concentration of active organic
materials changes in like amount with a change in pH. The second reason
given above is the most acceptable one since it has been demonstrated (1)
that groundwood can be bleached repeatedly with 2% sodium peroxide, and
that the brightness increase obtained each time, indicating that only a portion
of the reactive organic material is affected during a single bleaching
period under the conditions used in this investigation. The data to be
presented in Table VII demonstrate that the third reason is not tenable.

The slope of the line drawn in Figure 13 multiplied by 2.303
is the reaction-rate constant, k_1, for the first-order portion of the
rate of total peroxide consumption at pH 11.5. This constant was calculated as 0.017 min.\(^{-1}\). It must be emphasized that this specific reaction-rate constant represents the rate of total peroxide consumption only during the linear portion of the curve in Figure 15, that is, after approximately 30 minutes bleaching time when the residual peroxide concentration is less than 0.40 g./l. The limiting axes for the first-order reaction have been added to Figure 15. Within the limiting axes the data satisfy Equation (5), and the calculated value for \(k_t\) is valid.

The other runs in the series being discussed are also first order for a portion of the reaction time. The data for the runs at pH levels 10.5, 11.0, 12.0, and 12.5 also pass through the 30-minute, 0.40-g./l. residual peroxide point when plotted in the same way as the data for pH 11.5 in Figure 15. The first-order portions of the reactions at the pH levels given above all start at a point very close to that for the first-order portion of the data for pH level 11.5, and the same limiting axes can be considered to apply. First-order constants were calculated for the other four pH levels given above. Because first-order portions of the reactions at pH levels 10.5 to 12.5 start at the same point with regard to time and peroxide concentration, the values of \(k_t\) for each of these pH levels can be directly compared. The calculated values of \(k_t\) are given in Table VII. The data for all pH levels are not presented graphically at this point because further data, which are discussed in detail (page 117), include the same area of investigation. The portion of the bleaching time during which the reaction approximated first order is also indicated in Table VII. The values given for initial and final time limits in Table VII
represent the inception point and the termination point of the first-order portion of each 180-minute bleach.

### TABLE VII

**FIRST-ORDER REACTION CHARACTERISTICS AS AFFECTED BY pH**

<table>
<thead>
<tr>
<th>pH</th>
<th>Time Limits of First-Order Reaction</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial, min.</td>
<td>Final, min.</td>
<td>$k_t$, min.$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>10.5</td>
<td>30</td>
<td>180</td>
<td>0.021</td>
<td></td>
</tr>
<tr>
<td>11.0</td>
<td>30</td>
<td>180</td>
<td>0.020</td>
<td></td>
</tr>
<tr>
<td>11.5</td>
<td>30</td>
<td>180</td>
<td>0.017</td>
<td></td>
</tr>
<tr>
<td>12.0</td>
<td>30</td>
<td>150</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>12.5</td>
<td>30</td>
<td>90</td>
<td>0.017</td>
<td></td>
</tr>
</tbody>
</table>

By comparing the data given in Table VII with the curves from Figures 10 to 14, it is apparent that the first-order portion of the total peroxide consumption is not solely dependent on either the decomposition reaction or the reaction with groundwood, but includes both reactions in some cases and only the reaction with groundwood in others. At pH 9.0 the duration of the first-order reaction is from 5 to 180 minutes, starting at a concentration of 0.96 g./l. of peroxide. The value of $k_t$ for pH 9.0, under the specified conditions (this $k_t$ cannot be compared to those in Table VII for an estimation of relative reaction rate), was calculated as 0.004 min.$^{-1}$. At pH 10.0 the first-order reaction started at 20 minutes and 0.70 g./l. of peroxide and continued to the end of the bleaching period. The value of $k_t$ for the first-order portion of the total peroxide consumption at pH 10.0 was calculated as 0.012 min.$^{-1}$. In general, it was observed that the over-all rate of peroxide consumption was slowest at pH 9.0, more rapid
at pH 10.0, and most rapid for the five highest pH levels. At pH levels 10.5 to 12.5 the over-all rate of reaction was about the same, with the rate of the first-order portions of these reactions being comparable on the basis of the values of $k_4$ given in Table VII. Table VII indicates that the reaction rate is greatest at pH 10.5, with a minimum at pH 12.0.

Analysis of peroxide decomposition

The rate data for peroxide decomposition, plotted in Figures 8 to 14, show no particular kinetic order. However, when it is considered that the rate of change of peroxide concentration indicated in the Curves (D) in Figures 8 to 14 includes only a part of the total concentration change, it is evident that normal rate equations would not be likely to apply.

When peroxide decomposes to oxygen in a system containing only hydrogen peroxide and sodium hydroxide, the reaction is not first order if the sodium hydroxide concentration is not changed during the reaction period. The reason for this is evident if it is assumed that only the free hydrogen peroxide present in the alkaline solution reacts to form oxygen. In that case, the rate of decomposition would be dependent on the concentration of free hydrogen peroxide rather than the concentration of total peroxide, which includes any hydroperoxide ion present. It can be seen from Figure 1 (page 12) that there is a decrease in the fraction of free hydrogen peroxide present in the system when the concentration of total peroxide is decreased, as it would be by decomposition; thus the concentration of free hydrogen peroxide is not proportional to the concentration of total peroxide when considered over an appreciable range.
Several determinations of the rate of peroxide decomposition were made using c.p. liquor at various sodium hydroxide concentrations. These experiments were performed in the apparatus used for the bleaching experiments, and the rate of oxygen evolution was measured volumetrically according to Method 2E given on page 39. At sodium hydroxide concentrations corresponding to initial pH values up to 11.5 the reactions were apparently first order because of the relatively large concentration of free hydrogen peroxide present. However, at a concentration of sodium hydroxide corresponding to an initial pH of 12.0, the deviation from first order could be perceived. The data for the run at initial pH 12.0 are presented in Figure 16. As in Figure 15, the residual peroxide concentration is plotted against time on semilogarithmic paper, and a linear relationship indicates a first-order reaction. Curve (a) represents the rate of change in concentration of total peroxide, whereas Curve (b) represents the rate of concentration change for free hydrogen peroxide as calculated from the equilibrium equation.

It is apparent that the points for Curve (a) deviate from the straight line drawn, whereas those for Curve (b) do not, thus indicating that the rate of peroxide decomposition is dependent on the concentration of free hydrogen peroxide in solution.

The situation with regard to peroxide decomposition during bleaching is somewhat different from that described above, because the pH is controlled at a given level and the concentration of free hydrogen peroxide is always proportional to the concentration of total peroxide (see page 14). Therefore, it might be expected that the rate of decomposition during the bleaching period would be first order.
FIGURE 16

Peroxide Consumption
Initial pH 12.0
(no groundwood present)

Residual peroxide, g/l. (as H₂O₂)

Curves (a) Total peroxide
Curves (b) Free hydrogen peroxide

Reaction time, min.

30 40 60 80 100 120
If the rate of decomposition of peroxide is proportional to the concentration of free hydrogen peroxide, the following equation will define the rate:

\[ -\frac{dC_{H_2O_2}}{dt} = k_d C_{H_2O_2} \]  \hspace{1cm} (6)

where \( C_{H_2O_2} \) is the concentration of free hydrogen peroxide and \( k_d \) is the first-order reaction-rate constant for the decomposition reaction. However, because the concentration of free hydrogen peroxide is directly proportional to the concentration of total peroxide, Equation (6) can be written:

\[ -\frac{dC_{total}}{dt} = k_d C_{total} \]  \hspace{1cm} (7)

where \( C_{total} \) represents the total concentration of peroxide in solution. It should be emphasized that this equation involves only that part of the total peroxide consumption which is due to decomposition, even though it is expressed in terms of the total peroxide concentration. Equation (7) shows that the instantaneous rate of concentration change, at any specified time, which is due to the decomposition reaction and is expressed in terms of the total peroxide concentration (as in the Curves (D), Figures 8 to 14) will be proportional to the total concentration at that time. With this knowledge it is possible to test the data obtained on oxygen evolution during the bleaching period to determine whether or not the decomposition reaction is first order in the presence of groundwood, and to determine the reaction-rate constants if first-order reactions are found.

The quantity \( \frac{dC_{total}}{dt} \) was determined from the curves labeled (D) in Figures 8 to 14 by measuring the slope of a tangent to the curve at a number of points. The value of this slope, expressed in grams per liter
per minute, represents the instantaneous rate of decomposition of peroxide to oxygen for the particular time in question. The actual concentration of total peroxide for each time point is determined from the Curves (T). The values of rate and concentration for each time point are then plotted, with rate as the ordinate and concentration as the abscissa.

In Figure 17, the curve labeled (d) is a rate-concentration plot for the runs made at pH 11.0. The rates were determined by the tangent method with the first measurement made at the five-minute point and the final measurement at the 60-minute point.

It is apparent that a linear relationship exists between the rate and concentration values plotted in Figure 17, Curve (d). The slope of the line drawn should be equal to the first-order reaction-rate constant, $k_d$, for the decomposition of peroxide to oxygen. However, the line drawn through the points in Figure 17 does not start at the zero point of the graph as it should in order to conform to the rate equation, Equation (7), used in its calculation. The reason for this behavior is discussed below.

A factor which enters into the measurement of rate of oxygen evolution, and which has not been discussed previously, is the formation of carbon dioxide during the bleaching period. It was mentioned on page 54 that carbon dioxide (as sodium carbonate) was detected in appreciable amounts in the bleach liquor after the completion of a bleaching experiment. Experimental data and a discussion on carbon dioxide formation during bleaching will be found in a later section of this work (page 179 et seq.). It is sufficient to mention, at this point, that small amounts of the oxygen formed by decomposition of peroxide are consumed in alkaline oxidation of organic materials to form carbon dioxide. This reaction does not appear to
FIGURE 17

Variation of Reaction Rate with Concentration
pH 11.0

Curves (d), (d')  Decomposition reaction
Curves (e), (e')  Peroxide-groundwood reaction
be related to bleaching. It is apparent that consumption of oxygen during the bleaching period will introduce an error into the measurement of the rate of oxygen evolution, which error will also be carried over to the calculation of the rate of reaction between peroxide and groundwood.

The values of rate which are plotted in Figure 17 were obtained by taking tangents to the Curve (D) in Figure 11, as previously described. This method is very sensitive to small changes in the trend of the curve from which the rate measurement is obtained. If the rate of the decomposition reaction is considered, a decrease in the amount of oxygen evolution measured, due to carbon dioxide formation, would bring about an increase in the apparent rate of decomposition. The curve representing the relation between rate and peroxide concentration would reach zero rate at some peroxide concentration higher than zero. This is the case in Figure 17.

The error introduced by the formation of carbon dioxide can be expected to be at a minimum close to the start of the reaction period when the rate of oxygen evolution is large. Therefore, it would appear that the most reliable estimate of the value of the reaction-rate constant for the decomposition reaction could be obtained by basing the estimate on conditions found early in the bleaching period. Accordingly, it was assumed that the rate of decomposition was correct at a concentration of 0.8 g./l. of peroxide. This concentration was selected because it was reached, at pH levels above 10.0, within the first 10 minutes of bleaching time. In addition, slightly less than 25% of the peroxide had reacted, leaving ample peroxide for continued reaction at the rapid rate observed initially. The
rate of reaction at a concentration of 0.8 g./l. could have been determined directly from Curve (D) in Figure 11, but it was decided that the rate determined by the intersection of Curve (d) in Figure 17 with 0.8 g./l. peroxide concentration would give a more reliable value. The reaction-rate constant, $k_d$, for the rate of decomposition at pH 11.0 was calculated as 0.017 min.$^{-1}$ by the method described above. The curve which represents the rate-concentration relationship for the calculated value of $k_d$ is shown in Figure 17 as a dotted line labeled (d'). Curve (d') conforms to Equation (7) for first-order peroxide decomposition.

The decomposition rate constants for the other runs in this series have been estimated by the method described above. In each case a straight line was obtained for the rate-concentration plot, but this line passed through zero rate at some value of concentration greater than zero. Therefore, the rate-constant estimate was based on the rate at 0.8 g./l. of peroxide. The values for these rate constants are given in Table VIII.

**TABLE VIII**

<table>
<thead>
<tr>
<th>pH</th>
<th>First-Order Reaction-Rate Constant, $k_d$, min.$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>0.013</td>
</tr>
<tr>
<td>10.5</td>
<td>0.018</td>
</tr>
<tr>
<td>11.0</td>
<td>0.017</td>
</tr>
<tr>
<td>11.5</td>
<td>0.018</td>
</tr>
<tr>
<td>12.0</td>
<td>0.010</td>
</tr>
<tr>
<td>12.5</td>
<td>0.007</td>
</tr>
</tbody>
</table>
From the data in Table VIII it is apparent that the decomposition rate passes through a maximum as the pH is increased. This behavior is characteristic of unstabilized peroxide decomposition. Previous experiments have indicated that peroxide decomposition is stabilized by groundwood extract, and such stabilization could be expected in the case at hand. Thus, the results in Table VIII indicate that abnormal decomposition was taking place during the runs being considered. Further data of a similar nature (page 124), obtained under slightly modified experimental conditions, demonstrate that the decomposition rates given in Table VIII are abnormal, for reasons which will be discussed presently.

It should be noted that the values of rate constant in Table VIII are not comparable to those given in Table VII because somewhat different portions of the peroxide consumption reaction are considered. The values in Table VII were obtained from data taken after about 30 minutes of the bleaching period had passed. The values in Table VIII include the first 30 minutes of the bleaching period and 30 minutes, or less, additional time, depending on the point at which oxygen evolution apparently ceased. If decomposition were to continue at the rates indicated in Table VIII throughout the entire bleaching period, it would mean that the first-order portion of the total peroxide consumption data was almost entirely due to decomposition. The peroxide consumption curves in Figures 9 to 14 indicate that a large part of the peroxide is consumed in reaction with groundwood during that portion of the reaction time when total peroxide consumption is first order. Therefore, the decomposition reaction must be slower than shown in Table VIII or nonexistent, during the period when total peroxide consumption is of the first order.
Analysis of the groundwood-peroxide reaction

From information presented on the kinetics of the decomposition reaction it would appear that decomposition is kinetically of the first order. It has also been demonstrated that the total peroxide consumption data are first order over a portion of the reaction time. Therefore it can be concluded tentatively that the reaction between peroxide and groundwood has first-order dependence during some portion of the bleaching period. This conclusion is based on the fact that the peroxide-groundwood reaction occurs simultaneously with the decomposition reaction during portions of the reaction period when the sum of the peroxide consumption of the two reactions can be represented by a first-order equation. If the reaction between peroxide and groundwood is first order with respect to the total peroxide concentration, it can be expressed by the equation:

\[-dC_{\text{total}}/dt = k_0 C_{\text{total}} \quad (8)\]

where \(C_{\text{total}}\) is the total concentration of peroxide at any time, and \(k_0\) is a first-order reaction constant. The new constant, \(k_0\), has been introduced to represent the reaction of peroxide which is effective in bleaching. It can be seen that the case represented by Equation (8) is analogous to that represented by Equation (7) for the decomposition reaction. The rate factor in Equation (8) represents the rate of peroxide consumption which is due to the reaction between peroxide and groundwood. The rate of peroxide consumption by the groundwood-peroxide reaction can be determined directly at any time point by taking a tangent to one of the Curves (8) in Figures 8 to 14 and thus obtaining the instantaneous slope of the curve. The total peroxide concentration, \(C_{\text{total}}\), for the same time point is obtained from the Curves (T). If the peroxide-groundwood reaction is of the first
order, a plot of rate values from the Curves (E) against concentration values from Curves (T) (Figures 8 to 14) should provide a linear relationship according to Equation (8). Therefore a rate-concentration plot of values obtained from Figures 10 to 14 was made for pH levels of 10.5-12.5. Because of the small change in rate of the groundwood-peroxide reaction at pH levels of 9.0 and 10.0, the data taken at these pH levels were not considered. The rate-concentration relationship was established for the first 60 minutes of the bleaching period by the method given above. The relationship was linear for the data at pH levels of 11.0, 11.5, and 12.0. The data for the run at pH 11.0 are shown in Figure 17, Curve (e), with the decomposition data for the same pH level.

It will be noted from Figure 17 that Curve (e) does not pass through the origin as it should in order to satisfy Equation (8). It is evident that the error due to the formation of carbon dioxide is carried over into the calculation of the rate of the peroxide-groundwood reaction because the difference between the rate of oxygen evolution and the rate of total peroxide consumption is used to determine the peroxide-groundwood reaction rate. As demonstrated in Figure 17, the effect of this error on the rate of the peroxide-groundwood reaction is the reverse of that in the case of decomposition; that is, the rate-concentration data give a line which crosses zero rate at some point less than zero concentration. For this reason, the value of the rate constant for the peroxide-groundwood reaction can be estimated more reliably by assuming that the rate at some point early in the reaction is the correct one. This calculation was performed in the same way as for the decomposition data (page 89). The rate constant obtained was 0.012 min.\(^{-1}\). The curve which represents the rate-
concentration relationship for the calculated value of $k_e$ is shown in Figure 17 as a dotted line labeled ($e'$). Curve ($e'$) conforms to Equation (8) for a first-order reaction.

The values of $k_e$ for the three pH levels at which the peroxide-groundwood reaction could be considered first order are given in Table IX.

**TABLE IX**

<table>
<thead>
<tr>
<th>pH</th>
<th>First-Order Reaction-Rate Constant, $k_e$, min.$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.0</td>
<td>0.012</td>
</tr>
<tr>
<td>11.5</td>
<td>0.015</td>
</tr>
<tr>
<td>12.0</td>
<td>0.020</td>
</tr>
</tbody>
</table>

These values of $k_e$ in Table IX indicate that the rate of the peroxide-groundwood reaction increases with an increase in pH. Further conclusions on these data will be reserved until all the experimental results on bleaching kinetics have been presented.

As shown above, the rate of consumption of total peroxide which can be attributed to the reaction between groundwood and peroxide is proportional to the concentration of total peroxide at certain pH levels. It was demonstrated previously (page 14) that the total peroxide in an alkaline solution of hydrogen peroxide is composed of free hydrogen peroxide and hydroperoxide ion in definite proportions at any constant pH. It is not probable that both of these peroxide forms would react with groundwood, as would be necessary if the rate of peroxide consumption (due to groundwood)
were proportional to the concentration represented by the sum of the concentrations of free hydrogen peroxide and hydroperoxide ion. Therefore groundwood must react with either free hydrogen peroxide or hydroperoxide ion. It is evident from Figures 8 to 14 that the reaction between groundwood and peroxide increases greatly with an increase in pH and, consequently, with an increase in the concentration of hydroperoxide ion in the bleach liquor. Therefore, it seems reasonable to assume that groundwood reacts with the hydroperoxide ion formed in alkaline peroxide solutions. This possibility has been suggested by other investigators in the field of alkaline peroxide bleaching (9, 23). If this is the case, the first-order reaction-rate equation can be written:

\[-\frac{\text{d} \text{OOH}^-}{\text{d}t} = k \cdot \text{OOH}^- \quad (9)\]

Where \(\text{OOH}^-\) is the concentration of hydroperoxide ion. Since \(\text{OOH}^-\) is directly proportional to the total peroxide at any pH level, Equation (9) is equivalent to Equation (8), which was used to demonstrate the conformance of some of the groundwood-peroxide reaction-rate data to first-order reaction characteristics.

**Effect of Increased Peroxide Concentration**

Most of the experiments carried out in this investigation were made with 2.0% peroxide (as \(\text{Na}_2\text{O}_2\)), based on the weight of oven-dry groundwood. It was considered desirable to obtain information on the course of the various reactions occurring during the bleaching period when the concentration of peroxide was increased. Since the reactions involved in peroxide bleaching appear to be largely of first-order dependence, an increase in the
peroxide concentration could be expected to have only slight effect on
the rate of peroxide consumption at any given concentration. Evaluation
of the extent to which reaction kinetics were affected by increased
peroxide concentration could be expected to aid in characterizing the
peroxide bleaching reactions.

The effect of increasing peroxide concentration was determined
by obtaining a set of data using 4.0% peroxide (as Na₂O₂), based on the
weight of oven-dry groundwood. The runs for this experiment were made at
a pH of 11.0. This particular pH level was selected because the consumption
of peroxide by decomposition and by the reaction with groundwood were about
equal in amount for the runs made with 2.0% peroxide. Bleaching at a pH
of 11.0 also gives a desirable increase in brightness. The rate of de-
composition was determined by Method 2A, page 34, and the rate of total
peroxide consumption was determined by Method 1A, page 28. As in the
previous series of bleaches, hydrogen peroxide and sodium hydroxide were
added separately and simultaneously at the start of each run.

The data obtained for this experiment are presented graphically
in Figure 18. Oxygen evolution has been calculated in terms of total
peroxide consumption by the method described on page 80. The curves in
Figure 18 are labeled in the same manner as previous peroxide consumption
curves. The curves in Figure 18 can be compared directly with those in
Figure 11, for peroxide consumption at a pH of 11.0 with 2.0% peroxide.
The scale for residual peroxide values in Figure 18 corresponds to twice
the values of the residual peroxide scale for Figure 11.
FIGURE 18

Peroxide Consumption
pH 11.0
4.0% peroxide (as Na₂O₂)
Kinetic Analysis

A comparison of the curves in Figures 11 and 18 indicates that the total peroxide consumption was somewhat more rapid with increased peroxide concentration. It is also evident that more peroxide was consumed by decomposition at a concentration of 4.0% peroxide than at the 2.0% concentration. However, a comparison of the Curves (E), which represent the reaction between peroxide and groundwood, indicates that the course of this reaction was quite similar over most of the bleaching period.

The data obtained in the present experiment were tested for possible conformity to first-order reaction rates by the methods developed in the previous section of this work. Figure 19, Curve (a), shows a semilogarithmic plot of the residual peroxide concentration against reaction time for the experiment at hand. It can be seen that the points for Curve (a) fall close to a straight line for the last 120 minutes of the reaction period. Curve (b) shows similar data for the run at a pH of 11.0 with 2.0% peroxide (Figure 11). The data for Curve (b) were plotted with zero time at the point at which the run with 4.0% peroxide reached a concentration of 1.0 g./l. of peroxide (16 minutes on the time scale). In this way the effect of increased peroxide concentration on the rate of reaction can be compared conveniently. It is evident that the rate of reaction is about the same in both cases.

Equation (?) and the method described on page 89 were used to test the data for peroxide decomposition, Figure 18, Curve (D), for its kinetic order. Figure 20 shows the rate-concentration plot for these data. The linear relationship between rate and concentration in Figure 20 indicates
FIGURE 19

Peroxide Consumption

pH 11.0

- Curve (a) 4.0% Peroxide (as Na₂O₂)
- Curve (b) 2.0% Peroxide (as Na₂O₂)

Residual peroxide, g/L, (as Na₂O₂)

Reaction time, min. (for Curve (a))

20  40  60  80  100  120  140  160  180  200
FIGURE 20

Relation Between Rate of Decomposition and Total Peroxide Concentration

pH 11.0
4% peroxide (as Na₂O₂)
that the decomposition was of the first order for the first 60 minutes of the reaction time. Curve (d) in Figure 20 does not pass through the origin of the graph; therefore the value of $k_d$ for the data was estimated from the rate at a peroxide concentration of 1.60 g./l., as represented by Curve (d') in Figure 20. The value obtained for $k_d$ was 0.024 min.$^{-1}$. This value of $k_d$ is somewhat larger than that obtained for the run at a pH of 11.0 with 2.0% peroxide, given as 0.017 min.$^{-1}$ in Table VIII. The fact that the decomposition reaction rate was larger with 4.0% peroxide than with 2.0% peroxide explains why the amount of oxygen evolved was relatively larger with 2.0% peroxide.

The data for the rate of the reaction between peroxide and groundwood, as shown in Figure 18, Curve (B), were also tested for conformity to first-order reaction-rate equations, using Equation (8) and the method described on page 95. The points on the rate-concentration plot were not sufficiently close to a straight line to permit accurate estimation of a first-order constant.

In general, it is apparent that the course of the bleaching reactions when 4.0% peroxide is used is very similar to that observed with 2.0% peroxide, other conditions being the same. It can be concluded that the effect of concentration on the course of the reactions occurring during bleaching is small. Thus, previous indications that groundwood-peroxide reactions are of the first order with respect to peroxide concentration are further affirmed by the data on the effect of increased concentration.
Runes with Preliminary pH Adjustment Followed by Hydrogen Peroxide Addition

The results obtained from runs initiated with separate and simultaneous addition of hydrogen peroxide and sodium hydroxide indicate that during some portions of the bleaching period the reactions in the groundwood-peroxide system were of the first order with respect to the total peroxide concentration. If simultaneous reactions, first order with respect to total peroxide, were taking place, the total peroxide consumption could be expected to be first order as well. This did not prove to be the case during the initial portion of the bleaching period, even though the total peroxide consumption appeared to be composed of two first-order reactions at some pH levels. However, after approximately 30 minutes of the bleaching period had passed, the total peroxide consumption appeared to be of the first order, with both decomposition and the peroxide-groundwood reaction occurring during the first-order period. The indeterminate order of the rate of total peroxide consumption for the first 10 to 20% of the bleaching period is most probably due to erratic peroxide decomposition during this period.

The values of the decomposition reaction-rate constant, k, given in Table VIII cover a wider range than might be expected when the stabilizing effect of groundwood on decomposition in unstabilized peroxide solutions is considered. It seems quite possible that the conditions obtaining in the groundwood-peroxide mixture shortly after the simultaneous addition of hydrogen peroxide and sodium hydroxide could bring about a more rapid decomposition of peroxide than would be the case after the system had come to complete equilibrium. It was deemed advisable to modify the method used
in adding reactants to the groundwood and obtain further data on the
effect of pH on the kinetics of the reactions occurring during the peroxide
bleaching of groundwood.

In the present series of experiments five sets of data were ob-
tained at pH levels of 10.5, 11.0, 11.5, 12.0, and 12.4. These pH levels
were selected to include the range in which both decomposition and reaction
with groundwood were appreciable. Runs were made to determine the rate
of oxygen evolution using Method 23, page 38. Rate of total peroxide de-
composition was determined by Method 13, page 32. Except for the procedure
followed in adding the reactants to the groundwood slurry, the new methods
are identical with those used to obtain the data presented in Figures 8 to
14. For the present series of experiments the sodium hydroxide was added
first, and the system was allowed to come to pH equilibrium before the
hydrogen peroxide was added. Since groundwood, especially at lower pH
levels, will continue to consume sodium hydroxide for a considerable time,
the preadjustment period was several hours in duration in some cases. In
the following presentation of data, runs at various pH levels will be
designated 10.5p, 11.0p, etc., to distinguish them from runs at the same
pH level in which the pH was not preadjusted.

The data in the series of experiments being considered are pre-
sented graphically in Figures 21 through 25. The data on the rate of
oxygen evolution are expressed in terms of total peroxide consumption. The
method of calculation was discussed on page 67. The curves in Figures
21-25 are labeled in the same fashion as other curves of this type: (T)
for total peroxide consumed; (D) for peroxide decomposed to oxygen; (N) for
peroxide reacting with groundwood. Only the first 90 minutes of the 180-minute bleaching period are shown in Figures 21-25, since the reactions are almost complete in that time.

A comparison of the data presented in Figures 10-14, for experiments in which the pH was not preadjusted, with that presented in Figures 21-25 shows that preadjustment of pH has a considerable effect on the course of the various reactions. The data given for pH level 12.5 can be considered comparable to those for pH 12.4p for the purposes of this discussion. In general, the rate of peroxide consumption is slower for runs made with preadjusted pH. The difference in rate is most appreciable at pH levels of 10.5, 11.0 and 12.5. In all cases, except at a pH level of 12.0, preadjustment of pH has brought about decreased decomposition, that is, less oxygen evolved during the bleaching period. The effect of preadjustment of pH on the reaction between peroxide and groundwood is not evident from a qualitative examination of the data. In some cases the rate of the peroxide-groundwood reaction appeared to be increased by preadjustment of pH, and in others, decreased.

The effect of pH level on the course of the various reactions follows the same general trend with preadjusted pH experiments as with those not preadjusted. The data in Table X illustrate this point. The amount of peroxide decomposed and peroxide reacted with groundwood was determined from the data given in Figures 21-25 for the first 90 minutes of the bleaching period at each pH level. These values, expressed as a percentage of total peroxide consumption, are presented in Table X.
TABLE X
THE EFFECT OF pH ON THE PEROXIDE CONSUMPTION OF INDIVIDUAL REACTIONS

<table>
<thead>
<tr>
<th>pH</th>
<th>Peroxide Consumption by</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Decomposition, %</td>
<td>Groundwood, %</td>
</tr>
<tr>
<td>10.5p</td>
<td>43</td>
<td>57</td>
</tr>
<tr>
<td>11.0p</td>
<td>38</td>
<td>62</td>
</tr>
<tr>
<td>11.5p</td>
<td>23</td>
<td>77</td>
</tr>
<tr>
<td>12.0p</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>12.4p</td>
<td>10</td>
<td>90</td>
</tr>
</tbody>
</table>

The data shown in Table X are similar to those shown in Table VI for experiments made without preadjusting the pH. In both tables the percentage of peroxide consumed by decomposition shows a decrease, with an increase in pH level and, conversely, the reaction between peroxide and groundwood consumes an increased amount of peroxide.

Before considering the reaction kinetics of the present data, the effect of preadjustment of pH on the rate of brightness increase should be mentioned. Brightness and color change during bleaching will be discussed in detail in a separate section; however, the following facts are of interest at this point. High sodium hydroxide concentration has been found to have an adverse effect on brightness development. This adverse effect might have been expected to be especially evident where groundwood was in contact with alkali prior to adding peroxide; however, at pH levels below 12.0p the change of brightness with time followed the same course whether the pH was preadjusted or not. From the above fact, and from other information to be presented later (page 166), it was concluded that the reactions involved in groundwood bleaching were essentially unchanged by pH preadjustment.
Kinetic Analysis

Analysis of total peroxide consumption

The rate of total peroxide consumption was tested for conformity to first-order reaction-rate equations by plotting residual peroxide against time on semilogarithmic paper, a method which was discussed on page 81. Figures 26-30 show the results which were obtained with total peroxide consumption data from runs at pH levels 10.5p through 12.4p. A linear relationship was obtained for pH levels 10.5p, 11.0p, 11.5p, and 12.0p. This linear relationship holds, in each of the four cases, over at least the 90-minute period which is shown in Figures 21-24, and represents a total peroxide consumption of over 90% of the initial peroxide concentration. Therefore, it can be concluded that total peroxide consumption is of the first order with respect to peroxide during the significant portion of the bleaching period. Deviations from first order during consumption of the last 10% of peroxide can be considered insignificant. The data for pH level 12.4p, which vary from first order, will be discussed later.

The fact that total peroxide consumption is of the first order indicates that the reactions involved in total peroxide consumption are also first order with respect to peroxide, or can be represented by first-order equations. Previous data have indicated (pages 93, 97) that total peroxide consumption can be attributed to two reactions: (1) decomposition, apparently first order with respect to free hydrogen peroxide, and (2) reaction with groundwood, apparently first order with respect to hydroperoxide ion. Because both free hydrogen peroxide and hydroperoxide-ion concentrations
FIGURE 30
Peroxide Consumption
pH 12.4p

FIGURE 31
Peroxide Consumption
pH 11.0p
(Sodium silicate added)
are directly proportional to total peroxide concentration at a given pH level, the two reactions listed above must also be first order with respect to total peroxide. Therefore, the two reactions could combine to produce a total peroxide consumption rate of the first order.

First-order reaction constants, \( k_t \), can be calculated from the slopes of the curves shown in Figures 26-29. The first-order constants for total peroxide consumption from experiments at pH levels of 10.5p to 12.0p are listed in Table XI.

**TABLE XI**

**THE EFFECT OF pH ON FIRST-ORDER REACTION-RATE CONSTANTS FOR TOTAL PEROXIDE CONSUMPTION**

<table>
<thead>
<tr>
<th>pH</th>
<th>First-Order Reaction-Rate Constant, ( k_t ), min.(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5p</td>
<td>0.020</td>
</tr>
<tr>
<td>11.0p</td>
<td>0.022</td>
</tr>
<tr>
<td>11.5p</td>
<td>0.025</td>
</tr>
<tr>
<td>12.0p</td>
<td>0.029</td>
</tr>
</tbody>
</table>

It is evident, from the values of \( k_t \) in Table XI, that the over-all reaction rate increases as the pH is increased. The values of \( k_t \) found for the experiments at pH levels of 9.0 and 10.0 can be compared with the values of \( k_t \) given in Table XI, because total peroxide consumption at these pH levels was approximately first order for the entire reaction time. As listed in Table VII, \( k_t \) for pH 9.0 was 0.004 min.\(^{-1} \), and \( k_t \) for pH 10.0 was 0.012 min.\(^{-1} \). Thus it can be concluded that the rate of peroxide consumption was increased markedly by increasing the pH from 9.0 to 12.0; the rate constant at pH 12.0p was over seven times that at pH 9.0.
Analysis of individual reactions

Since the rate of reaction of total peroxide is clearly of the first order for the present data, an analysis of the individual reactions should provide more reliable information than did the data taken without preadjustment of pH. A previous consideration of the rates of the decomposition reaction (page 93) and the reaction between peroxide and groundwood (page 97) indicated that these reactions were of the first order with respect to total peroxide concentration. The present data were tested for conformity to the first-order equations. The variation of rate of total peroxide consumption with total peroxide concentration was calculated for the data from pH levels of 10.5p, 11.0p, 11.5p and 12.0p. Calculations were made using Equation (7) and the method developed on page 89 for the decomposition reaction, and Equation (8) and the method developed on page 95 for the reaction between peroxide and groundwood. It should be noted that the graphs used in determining the instantaneous rates according to the methods given were approximately four times the size of the graphs reproduced in this work. Greater accuracy was obtained by the use of the larger graphs. The rate-concentration calculations cover the first 60 minutes of the bleaching period for the groundwood-peroxide reaction at all pH levels, and the decomposition reaction at pH levels of 10.5p and 11.0p. The first 40 minutes are covered for the decomposition reaction at pH levels of 11.5p and 12.0p. Approximately 70% of the total peroxide was consumed during the time interval covered by the rate-concentration calculations. The results of these calculations are presented graphically in Figures 32 through 35 (note that the ordinate scale in Figure 35 is double that of Figures 32-34). The best straight line has
FIGURE 32

Variation of Reaction Rate with Concentration

$\text{pH 10.5p}$

Curves (d), (d') Decomposition reaction

Curves (e), (e') Peroxide-groundwood reaction
FIGURE 33
Variation of Reaction Rate with Concentration
pH 11.0p

Curves (d), (d') Decomposition reaction
Curves (e), (e') Peroxide-groundwood reaction
FIGURE 35

Variation of Reaction Rate with Concentration
pH 12.0p

Curves (d), (d') Decomposition reaction
Curves (e), (e') Peroxide-groundwood reaction
been drawn through the points calculated for the decomposition reaction, labeled (d), and for the peroxide-groundwood reaction, labeled (e). At pH 10.5p the initial point was not considered in drawing the peroxide-groundwood curve. This point appears to be superficially high, probably because the system had not yet reached complete equilibrium.

The fact that a reasonably linear relationship exists for each of the rate-concentration plots shown in Figures 32-35 indicates that both the decomposition reaction and the reaction between peroxide and groundwood are of the first order for the pH levels being considered. The first-order reaction-rate constant for each reaction should be equivalent to the slope of the line drawn through the calculated rate-concentration points. An examination of Figures 32-35 shows that the rate-concentration curves do not pass through the zero point as they should in order to satisfy the first-order equation used in their calculation. It is evident that the error arising from the formation of carbon dioxide is responsible, as before, for the deviation of the curves from their theoretical direction through the origin of the plot.

It is possible, with the present data, to determine the reliability of values of $k_d$ and $k_e$ as estimated from the rate at a given concentration early in the reaction period (the method used in previous estimates of $k_d$ and $k_e$). With this purpose in mind, the values of $k_d$ and $k_e$ were calculated in two ways for pH levels of 10.5 to 12.0. In the first case, the slope of the curves (d) and (e) was taken as the value of the constant. These values represent the result of plotting rate-concentration points calculated by the methods specified and measuring the slope of the straight line obtained. These
values are not true first-order constants because the line from which they were calculated does not pass through the origin in Figures 32-35. These constants have been termed $K_d$ for decomposition and $K_e$ for the peroxide-groundwood reaction to differentiate them from true rate constants.

The second values for $K_d$ and $K_e$ were determined, as with previous data, by assuming that the rate of each of the reactions was most accurately measured at some point early in the reaction period. The concentration of 0.8 g./l. peroxide was found to be satisfactory because it was reached, at all pH levels, in about 10 minutes after the start of the bleaching. At this point the system should have had time to reach equilibrium. As before, it was decided that the rate determined by the intersection of a (d) or an (e) curve from Figures 32-35 with 0.8 g./l. peroxide concentration would give a more reliable rate value than a direct determination from the slope of Curves (b) and (d) in Figures 21-24. Accordingly, the rate-constant values were obtained from Figures 32-35 and dotted lines (d') and (e') were placed on Figures 32-35 to represent the rate-concentration relationship for the calculated value of $K_d$ and $K_e$. Constants calculated in this manner are true first-order constants because they satisfy Equations (7) and (8).

Table XII contains the rate constants for decomposition and for the peroxide-groundwood reaction as calculated by both methods. In addition, the sum of the constants for each method and at each pH level is given in Table XII. Values of $K_e$ for the same data are placed in Table XII for reference.
### Table XII

**First-Order Reaction-Rate Constants for the Individual Reactions**

<table>
<thead>
<tr>
<th>pH</th>
<th>$k_d$</th>
<th>$k_a$</th>
<th>$k_d+k_a$</th>
<th>$k_t$</th>
<th>$k_d+k_a$</th>
<th>$k_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5p</td>
<td>0.009</td>
<td>0.009</td>
<td>0.018</td>
<td>0.009</td>
<td>0.010</td>
<td>0.019</td>
</tr>
<tr>
<td>11.0p</td>
<td>0.015</td>
<td>0.010</td>
<td>0.025</td>
<td>0.011</td>
<td>0.012</td>
<td>0.023</td>
</tr>
<tr>
<td>11.5p</td>
<td>0.015</td>
<td>0.013</td>
<td>0.028</td>
<td>0.010</td>
<td>0.016</td>
<td>0.026</td>
</tr>
<tr>
<td>12.0p</td>
<td>0.016</td>
<td>0.016</td>
<td>0.032</td>
<td>0.011</td>
<td>0.019</td>
<td>0.030</td>
</tr>
</tbody>
</table>

Consideration of the values of the first-order constants given in Table XII in the light of other information available on the rates of the two reactions indicates that $k_d$ and $k_a$ are the most reliable estimates of the rate constants. Because both the individual reactions are first order with respect to total peroxide concentration, any difference in the reaction rates of the two reactions must be due to differences in the specific reaction-rate constant. In Table XII the values obtained for $k_d$ are the same as, or greater than, the values of $k_a$; therefore the decomposition reaction would be expected to predominate in the amount of total peroxide consumed. The data given in Figures 21-24 and in Table X indicate that the reaction between peroxide and groundwood is the predominating one; thus the peroxide-groundwood-rate constant should be greater than the decomposition-rate constant, as is the case with the values of $k_a$ and $k_d$ in Table XII.

The reliability of the values of the decomposition- and peroxide-groundwood-rate constants in Table XII can be checked further by the fact that the sum of these two constants should equal $k_t$ as given in Table XII. It is evident that $k_t$ must equal $k_d + k_a$ when it is considered that the rate of total peroxide consumption is the sum of the rates of peroxide consumption.
by decomposition and peroxide consumption by reaction with groundwood. Therefore, (from Equations (7) and (8)):

\[
\frac{dg_{\text{total}}}{dt} = k_d g_{\text{total}} + k_e g_{\text{total}} = k_{\text{t}} g_{\text{total}} \quad (10)
\]

By comparing the value for the sum of \( k_d \) and \( k_e \) with the value of \( k_t \) (which can be considered accurate) for each pH level in Table XII, it can be seen that at pH levels of 11.0p, 11.5p, and 12.0p, the sum of the rate constants of the individual reactions is too high by 0.003 min.\(^{-1}\). At pH 10.5p the sum of the constants is lower than \( k_t \) by 0.002 min.\(^{-1}\). The value of the sum of \( k_d \) and \( k_e \) compared with \( k_t \) differs by only 0.001 min.\(^{-1}\) for each pH level shown in Table XII.

It should be noted in Figures 32-35 that the points for Curves (d) and (e) in the vicinity of 0.8 g./l. peroxide concentration conform as well as or better than at any other concentration with Curves (d') and (e'), respectively, indicating that the rate at this point was correctly assumed to be relatively free from error. It can be concluded that the values of \( k_d \) and \( k_e \) given in Table XII represent as good an estimate as could be obtained of the relation of the specific rate of decomposition to the specific rate of reaction with groundwood.

It is interesting to calculate the amount of error in the measurement of oxygen evolution that is necessary to create a certain variation in the value of \( k_e \). The data for the experiment at pH 12.0p, where the difference in \( k_d \) as calculated by the two methods discussed above is the largest, can be taken as an example. A value of 0.019 min.\(^{-1}\) was obtained from the rate-concentration curve in Figure 35, and a value of 0.011 min.\(^{-1}\)
was calculated from the rate of decomposition at 0.8 g./l. peroxide. From Figure 24, when oxygen evolution had ceased at the end of 45 minutes' bleaching time, the decomposition reaction had accounted for 31% of the total peroxide consumption. The relation between $k_d$ and $k_o$ for pH 12.0p (Table XII) indicates that the amount of peroxide decomposed to oxygen should have been $11/30$ of the total peroxide consumed, or 37%. It is evident that the small difference between theoretical and actual oxygen evolution is responsible for an error in $k_o$ of over 40%.

The values of $k_d$ from Table XII indicate that the rate of oxygen evolution is approximately constant over the pH range considered. This result is compatible with the information previously presented on the stabilising effect of groundwood extract on unstabilised peroxide solutions. It has been suggested that the relatively poor agreement of the rate of total peroxide consumption with first-order equations, in those experiments where the pH had not been preadjusted, was due to erratic peroxide decomposition. On the basis of the data presented for runs at a preadjusted pH, this supposition seems to be justified.

It can be concluded, from the values of $k_d$ and $k_o$ in Table XII, that the over-all increase in the rate of peroxide consumption with increased pH is due almost entirely to an increase in the rate of the reaction between peroxide and groundwood. The agreement between $k_o$ from Table IX and $k_o$ from Table XII should be noted. It will be demonstrated in a later section of this work that the increase in the rate of the peroxide-groundwood reaction is reflected in the amount and rate of brightness increase (page 138 et seq.).
Since the only condition which was varied during the experiments in this section was the pH, it seems safe to assume that the reaction between peroxide and groundwood is catalysed by the hydroxyl ion. There is no other apparent reason for the specific reaction-rate constant for the reaction between peroxide and groundwood to increase with an increase in pH. The reaction rate constant, $k_2$, is almost directly proportional to pH over the range shown in Table XII. The decomposition reaction is also catalysed by hydroxyl ion; however the specific reaction rate does not depend on the pH level, as demonstrated in this work (page 62 and Table XII), and by other investigators (38, 39).

Analysis of the experiment at pH 12.4p

The data for the experiment made at pH level 12.4p are shown in Figure 25. It is evident that the decomposition reaction is at a minimum at this high pH level, and that the reaction between groundwood and peroxide is predominant.

In Figure 30, the semilogarithmic plot of residual peroxide against time for the data being discussed indicates that the reaction was not first order over the major portion of the reaction period, as were the runs at lower pH levels. However, after the first 40 minutes of the bleaching period, the curve in Figure 30 becomes practically linear and a value of the rate constant, $k_t$, can be estimated. Such an estimation indicates that $k_t$ for the latter portion of the bleaching period is about 0.014 min.$^{-1}$. This value of $k_t$ represents a first-order reaction with zero time at the 30-minute point of Figure 30 and a starting concentration of 0.56 g./l.
peroxide. A comparison of the first-order constant at pH 12.4p with the constants for the other pH levels in Table XI indicates that the first-order reaction at pH 12.4p was appreciably slower than at any other pH. A qualitative comparison of the initial reaction rate at pH 12.4p, Figure 30, with the reaction rates for the other pH levels in Figures 26-29 indicates that this initial reaction was no more rapid than the reaction at any other pH level.

A first-order reaction-rate constant was estimated for the decomposition reaction by determining the rate of peroxide consumption due to decomposition at 0.8 g./l. total peroxide concentration. The rate value was obtained by taking a tangent to the Curve (D) in Figure 25, and the value of \( k_d \) was calculated as 0.003 min.\(^{-1}\). This value, although it cannot be considered exact, indicates that the decomposition reaction is very slow at pH 12.4p.

The first-order constant for the peroxide-groundwood reaction was determined as 0.015 min.\(^{-1}\) using the intercept of the straight-line rate-concentration plot with 0.8 g./l. peroxide. The rate-concentration plot for pH level 12.4p is not included because it approximates, by another method, the first-order reaction portion of the peroxide consumption plot in Figure 30 for this pH level. It is evident that the rate of total peroxide consumption and the rate of peroxide consumption by groundwood should be approximately the same during most of the bleaching period because oxygen evolution appears to stop at an early point in the reaction period.
There are two explanations which might be advanced to account for the difference in the course of reaction between the experiment at pH 12.4p and those experiments which were made at lower pH levels. It has been suggested that the reaction between peroxide and groundwood is catalysed by hydroxyl ion. It is possible, therefore, that some inhibitor might be present at pH 12.4p that is not present at lower pH levels, and that such an inhibitor could decrease the rate of the catalysed reaction.

Another possible explanation lies in the fact that the hydroperoxide-ion concentration at pH 12.4p is approximately 80% of the total peroxide concentration. It is possible that, under this condition, the concentration of organic material with which the peroxide reacts cannot be neglected in its effect on the rate of the peroxide-groundwood reaction. As will be pointed out in a later section of this work, sodium hydroxide will react with groundwood and affect a color change. It is possible that both peroxide and hydroxide react with the same portion of the groundwood in bringing about color changes. In this case the concentration of reactive material in the bleach liquor could be considered to include the hydroperoxide-ion concentration and the hydroxide concentration, and thus to increase rapidly with increasing pH. The total concentration of these two materials is 0.036 mole per liter at pH 12.4, as compared to 0.018 mole per liter at pH 12.0 and 0.008 mole per liter at pH 11.5. If the concentration of the organic reactant in groundwood entered into the kinetics of the peroxide consumption reaction, the rate of peroxide consumption could be expected to decrease and also to differ from a first-order relationship. This is the case with the experimental data obtained at pH 12.4p.
RUNS AT PREADJUSTED pH 11.0 WITH ADDED SODIUM SILICATE

Sodium silicate is added to commercial peroxide bleach liquors to increase the stability of the solution. Sodium silicate is the salt of a strong base and a weak acid which hydrolyses in solution to release hydroxyl ions, and acts as a buffer salt when bleaching without controlling the pH level. When the pH level is controlled, as in the present experiment, this buffer action is not important. There is a possibility that sodium silicate could enter into chemical reaction with one or both of the components of the groundwood-peroxide system and thereby complicate a kinetic analysis of groundwood-peroxide reactions. It was for this reason that the simplest possible peroxide bleach liquor was used for most of the experiments in this investigation. However, the course of the bleaching reaction with added silicate is of interest from the commercial standpoint, and therefore the present experiment was carried out.

The rate of oxygen evolution was determined by Method 2B, page 96, and the rate of peroxide consumption was determined by Method 1D, page 32. One modification was made in the methods named in carrying out the present experiment. In each case, 9% (based on the weight of oven-dry groundwood) of 40% H2O, sodium silicate was added with the sodium hydroxide needed for preadjusting the pH to 11.0. The results of the present experiment are presented graphically in Figure 36, which is similar to previous presentations of this type of data. The full 180-minute bleaching period is shown.

The data in Figure 36 can be compared with those shown in Figure 22, which represents data taken under the same experimental conditions without
the presence of sodium silicate. A qualitative comparison of these figures indicates that the rate of total peroxide consumption was considerably slower in the presence of silicate. As might be expected, the rate and amount of oxygen evolution is less in the presence of silicate. The best agreement between the curves in Figures 22 and 36 lies with the (E) curves, although the rate of reaction between peroxide and groundwood was somewhat slower in the presence of sodium silicate.

Kinetic Analysis

The residual peroxide concentration is plotted on semilogarithmic paper, in Figure 31, where it can be compared with similar plots for those runs which were made without added sodium silicate. It is apparent from a comparison of Figures 26-31 that the addition of silicate retarded the total peroxide consumption. The rate of peroxide consumption with added sodium silicate was considerably slower than in any case where silicate was not added.

It is evident from Figure 31 that the initial portion of the reaction period does not conform to the first-order relationship. However after about 30 minutes of the bleaching period has passed, the reaction rate can be represented by the straight line which has been drawn in Figure 31. The reaction-rate constant which was calculated from the slope of this line is 0.008 min.\(^{-1}\) for a first-order reaction with zero time at the 30-minute point in Figure 31 and a starting concentration of 0.67 g./l. peroxide.

Some explanation of the deviation from first order of the data under consideration can be obtained from a figure showing the variation of reaction
rate with total peroxide concentration. Figure 37 gives the rate-concentration relationship for the decomposition reaction and the reaction between peroxide and groundwood. From Figure 37 it is apparent that the decomposition reaction data cannot be adequately represented by a straight line. For purposes of comparison, a first-order constant, $k_d$, for the decomposition was estimated from the rate of decomposition at 0.8 g./l. The value of 0.003 min.$^{-1}$ which was obtained is represented by curve (d') in Figure 37. It should be noted that the rate of the decomposition reaction is much slower in the presence of sodium silicate than in its absence, and therefore the error in evaluation of decomposition rate which is produced by the formation of carbon dioxide would be greater in this case than where the decomposition rate was rapid. The increased error would also carry over into the evaluation of the rate of the reaction between peroxide and groundwood. The rate-concentration relationship for the reaction between peroxide and groundwood is not linear until a concentration of about 0.5 g./l. is reached. For values of concentration below 0.5 g./l. the relationship is linear and the reaction rate constant, $k_e$, for the reaction is 0.005 min.$^{-1}$, whether the slope of the line (e) through the plotted points or the slope of the line (e') based on the estimated rate at 0.8 g./l. is used. At concentrations above 0.5 g./l. it would appear that the reaction-rate constant for the reaction between peroxide and groundwood was larger than 0.005 min.$^{-1}$. The rate of brightness increase for these data, as presented on page 171, indicates that the bleaching reaction was not abnormally rapid during the initial reaction period. It is probable that the initial reaction rate for the groundwood-peroxide reaction is superficially high because of the error arising from carbon dioxide formation.
FIGURE 37

Variation of Reaction Rate with Concentration
pH 11.0p
(Sodium silicate added)

Curves (d), (d') Decomposition reaction
Curves (e), (e') Peroxide-groundwood reaction
It is interesting to note that the sum of values of $k_0$ and $k_d$, estimated above as 0.005 and 0.003 min.$^{-1}$ respectively, is equal to the value of 0.008 min.$^{-1}$ which was obtained for $k_d$ during that portion of the total peroxide consumption which conformed to first order.

In considering the reactions occurring during peroxide bleaching of groundwood in the presence of sodium silicate, two things are of interest: the deviation of the total peroxide consumption data from first order during the initial period of the reaction, and the comparative reduction in all reaction rates.

It seems likely that the primary reason for the deviation of the total peroxide consumption data from first order during the initial period of the reaction is the nonconformance of the decomposition reaction to first-order equations. The situation can be considered analogous to that which occurs when hydrogen peroxide and sodium hydroxide are added to groundwood separately and simultaneously, thus producing a more rapid decomposition reaction which is due to the temporarily unstable condition of the peroxide solution. The rate of decomposition of a sodium silicate-stabilised peroxide solution is much slower than with unstabilised solutions. Therefore, the rate of decomposition during the initial portion of the reaction period in the presence of sodium silicate would need to be only slightly more rapid than the value after the system had come to equilibrium in order to produce a large change, percentagewise, in the value of $k_d$, and consequently in conformance with the first-order equations.

It has been mentioned previously that the reaction between peroxide and groundwood, and the decomposition reaction as well, appear to be
catalysed by hydroxyl ion. If sodium silicate exerts a negative effect on the hydroxyl-ion catalysis of peroxide decomposition, as has been shown, it is reasonable to expect that the same negative effect will be exerted on the hydroxyl ion-catalysed reaction between peroxide and groundwood. It is evident, from a comparison of the reaction-rate constants estimated for the individual reactions in the presence of sodium silicate with those presented in Table XII for pH 11.0p, that both decomposition and the reaction between peroxide and groundwood are less rapid when sodium silicate is added to the bleach liquor. It should be mentioned at this point that data to be presented on the rate and amount of brightness increase (page 171) indicate that the presence of sodium silicate in the bleach liquor does not change the characteristics of the brightness-producing reaction.

SUMMARY

It seems well to summarise briefly, at this point, the information which has been obtained in this investigation of the kinetics of alkaline peroxide bleaching. It has been demonstrated that, under properly selected experimental conditions, the rate of total peroxide consumption is of the first order with respect to peroxide concentration. During the bleaching period, some peroxide decomposes to form oxygen, and such decomposition contributes to the total peroxide consumption. Therefore, peroxide can be considered as consumed in two ways during bleaching, by decomposition and by reaction with organic materials present in the peroxide-groundwood system. It has been shown that both of the reactions occurring during groundwood
bleaching are first order with respect to total peroxide concentration under conditions specified in the present investigations. First-order reaction-rate constants at several pH levels have been estimated for total peroxide consumption, decomposition, and the peroxide-groundwood reaction. It has been shown that there is an increase in rate of total peroxide consumption with an increase in pH which appears to be due to a corresponding increase in the rate constant of the peroxide-groundwood reaction.

Alkaline peroxide solutions, in the pH range considered, contain peroxide as free hydrogen peroxide and as hydroperoxide ion. The amount of these two constituents varies with pH. It has been demonstrated that it is the free hydrogen peroxide which decomposes to form oxygen. Experimental results have also indicated that hydroperoxide ion is the active bleaching agent in the bleach liquor, a fact which is more conclusively demonstrated by data presented in a following section (page 172).
BRIGHTNESS AND COLOR CHANGE

This section of the experimental data obtained in the present investigation concerns those changes in brightness and color of groundwood pulp which occur during the bleaching process. Because the purpose of reacting groundwood with peroxide is to increase the brightness of the pulp, the data presented previously on the kinetics of peroxide bleaching have little practical value unless they can be related to brightness increases. The discussion to follow brings out the relationships between peroxide consumption and brightness increase, as well as other information of importance with regard to groundwood color changes.

EXPERIMENTS WITH CONTROLLED pH

The data on brightness development during bleaching which will be presented first are those which were obtained from runs initiated with separate and simultaneous addition of hydrogen peroxide and sodium hydroxide. These data were obtained at controlled pH levels from 9.0 to 12.5. Peroxide consumption curves and a general discussion for these data will be found on pages 73 to 96, Figures 8-14. These data have been selected for primary consideration in this section for reasons given below. The pH range covered in this series of experiments was the widest range used in connection with the same experimental procedure. The experiments made with preadjusted pH (pages 105 to 129) gave more reliable information on the kinetics of the reactions involved in bleaching than the experiments now being considered with respect to brightness development. However, as will be demonstrated (page 166 et seq.), preadjustment of pH produces an exaggerated adverse effect on pulp brightness at those pH levels where the action of
sodium hydroxide on pulp color is appreciable. Experiments made without
preeadjusting the pH also show this adverse effect at high pH levels, but
only to an extent which can be considered normal for such conditions. Data
presented on page 166 indicate that the course of brightness development
is the same whether or not the pH is preeadjusted in those cases where the
effect of sodium hydroxide on color is not large. The information de-
veloped in the section of this work dealing with reaction kinetics indicates
that the same general conclusions apply to the kinetics of peroxide bleach-
ing whether the pH is preeadjusted or not. Therefore a discussion of the
present data on brightness change in relation to bleaching kinetics need
not be restricted to the relation between brightness development and re-
action kinetics for each specific experimental condition. In addition it
should be mentioned that the experimental conditions used in obtaining the
brightness data presented below (Method 1A, page 29) are similar to those
used in many commercial bleaching operations.

Development of G.E. brightness during the 180-minute reaction
period is shown in Figures 38-44 for runs at pH levels from 9.0 to 12.5.
The procedure used in preparing and analysing brightness samples is given
on page 21. It should be noted that the actual brightness values are given
in Figures 38-44 and not the brightness increase, as is often the case
with data of this type. In Figures 38 and 39 the G.E. brightness scale
extends from 54.0 to 60.0%, whereas in the remaining figures the range is
55.0 to 61.0%.

It can be observed from Figures 38-44 that a trend of brightness
development is clearly indicated in each case, as shown by the curve drawn
for each figure. The fact that individual brightness values depart rather widely from the curves drawn demonstrates that brightness change by itself would not serve as a satisfactory means for following the course of the reaction between peroxide and groundwood with exactness.

The brightness value for the unbleached pulp can be taken as 55.4% for each case. This value was obtained by preparing a brightness sample from unbleached pulp to be processed with each set of brightness samples made during the present investigation (see page 26). In this way 38 measurements were made of the brightness of the unbleached pulp, the average value of which was 55.4% G.B. brightness. Because of the variation in brightness of individual samples of groundwood pulp, this average brightness can be considered a more reliable value for the brightness at zero time in Figures 38-44 than the value obtained from the unbleached samples processed with each run. There was no measurable brightness drop for the stored pulp during the period of this investigation.

The data in Figure 38 indicate that the treatment given the pulp before adding bleach liquor tends to lower the brightness slightly. At pH 9.0 bleaching is at a minimum, and the first few brightness samples obtained were of lower brightness than the unbleached pulp.

Because of the loss of peroxide through decomposition of the unstabilized bleach liquor used in this investigation, the brightness increase which was obtained under the experimental conditions used was somewhat less than would be obtained commercially. The maximum brightness increase obtained in the experiments being discussed was 5.5 points at pH 11.0, as compared with
an 8.9-point increase obtained with stabilized liquor under the same experi-
mental conditions (see page 48).

Considerable information on the effect of pH on brightness de-
velopment can be obtained from a comparison between the sets of data shown in Figures 38-44. Such a comparison must be largely qualitative because brightness development is affected by factors other than pH alone, as will be shown presently. Such complicating effects are not indicated in a simple plot of brightness against reaction time. One general observation that can be made is that the brightness values obtained pass through a maximum as the pH is increased. For the experimental conditions used, this maximum is reached at pH 11.0. Another evident fact is that brightness passes through a maximum during bleaching at each pH level, except 9.0. The time required to reach this maximum brightness decreases as the pH is increased. These observations are more easily evaluated from the data in Table XIII. These data were selected from the curves in Figures 38-44. The curves were drawn, as fairly as possible, through the experimental brightness values at each pH level. In Table XIII, figures are given for time to reach maximum bright-
ness (to the closest 10 minutes), and for the brightness value at the maximum point of each curve.

The maximum brightness values given in Table XIII indicate that there is not a large difference between the brightness obtained at pH levels 10.0 to 12.5. However the fact that differing amounts of peroxide entered into reaction with groundwood to produce the given brightness increases must be considered. Also included in Table XIII are values for the amount of per-
oxide which reacted with groundwood up to the point of maximum brightness. These
### TABLE XIII

**ANALYSIS OF BRIGHTNESS DEVELOPMENT**

<table>
<thead>
<tr>
<th>pH</th>
<th>Time to Reach Maximum Brightness, min.</th>
<th>Effective Peroxide Consumption, g./l.</th>
<th>Maximum Brightness, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0</td>
<td>180 (plus)</td>
<td>0.10</td>
<td>57.1</td>
</tr>
<tr>
<td>10.0</td>
<td>130</td>
<td>0.33</td>
<td>59.3</td>
</tr>
<tr>
<td>10.5</td>
<td>110</td>
<td>0.47</td>
<td>60.2</td>
</tr>
<tr>
<td>11.0</td>
<td>80</td>
<td>0.53</td>
<td>60.7</td>
</tr>
<tr>
<td>11.5</td>
<td>70</td>
<td>0.53</td>
<td>60.2</td>
</tr>
<tr>
<td>12.0</td>
<td>40</td>
<td>0.56</td>
<td>60.4</td>
</tr>
<tr>
<td>12.5</td>
<td>20</td>
<td>0.48</td>
<td>59.2</td>
</tr>
</tbody>
</table>

Values were taken from the Curves (3) in Figures 8-14. From a comparison between effective peroxide consumed and the respective brightness obtained it is evident that more peroxide is required to effect a given brightness increase at a high pH than at a low pH. Further data on the relation between peroxide consumption and brightness increase is given on page 161.

The primary reason for the difficulty encountered in maintaining bleaching efficiency at a high pH level is the action of sodium hydroxide on groundwood pulp color. As will be demonstrated conclusively by a study of the spectral reflectance curves of groundwood pulp bleached at various pH levels (page 149 et seq.), sodium hydroxide reacts to produce a yellow color in groundwood, the effect being more pronounced as the hydroxyl-ion concentration is increased. Because O.E. brightness is a measure of reflectance in the blue end of the visible spectrum, it could be expected to be adversely affected by increasing the yellowness of the pulp. The action of sodium hydroxide also accounts for the decrease in brightness which was
observed during the last portion of the bleaching period at most pH levels. A comparison of the peroxide consumption curves with the brightness development curves for each pH level indicates that brightness reversion is not appreciable until most of the peroxide has been consumed. When it is considered that sodium hydroxide is continually replenished during the bleaching period in order to maintain the pH level, while peroxide is gradually consumed, brightness reversion could be expected to occur toward the end of the bleaching period as the proportion of hydroxide to peroxide becomes larger.

It is apparent that any specific measurements of the variation of the rate of brightness increase with pH would be complicated by the adverse effect of sodium hydroxide on brightness development. However the data given in Figures 38-44 show clearly that brightness development is more rapid as the pH is increased. It is evident that the increase in specific reaction rate between peroxide and groundwood with increasing pH level (demonstrated on page 124) is responsible for the observed increase in rate of brightness development with increasing pH level. The time to reach maximum brightness can be considered as a rough measure of the reaction rate at each pH level. The values for time to reach maximum brightness as given in Table XIII show a continuous decrease with increase in pH level, indicating a corresponding increase in rate of brightness development.

EXPERIMENTS WITH THE pH UNCONTROLLED

Two experiments, at initial pH 10.5 and 11.5, were made with the pH uncontrolled. The kinetics of these experiments were discussed on pages 65 to 71 of the previous section of experimental data. The peroxide con-
sumption for these runs is given in Figures 5 and 6. The variation of pH during the reaction period is shown in Figure 7.

Brightness development for the run made at initial pH 10.5 is shown in Figure 45, and for the run made at pH 11.5, in Figure 46. Brightness development for runs at pH level 10.5 (Figure 40) and 11.5 (Figure 42) are shown as dotted curves in Figures 45 and 46, respectively, for reference purposes.

Information made available by the previously discussed investigation of bleaching kinetics can be utilized in interpreting the present data. It is evident from Figure 45 that a higher brightness was obtained by bleaching at pH 10.5 (Curve (b)) than by allowing the pH to follow its natural downward course during bleaching (Curve (a)). Reference to the peroxide consumption in the two cases (Figures 5 and 10) shows that the reaction between peroxide and groundwood consumed far less peroxide when the pH was not controlled than when a pH level was maintained. The reason for the difference in effective peroxide consumption in the two cases is evident when it is considered that the pH dropped from 10.6 to 8.4 during the run at uncontrolled pH (Figure 7, Curve (a)). This pH drop would result in a decrease in the specific reaction rate between peroxide and groundwood and, consequently, less bleaching and more decomposition (the decomposition rate has been demonstrated to be much less affected by pH level than the rate of the peroxide-groundwood reaction). It should be noted that there is little indication of brightness reversion in the data given in Figure 46, Curve (a). This result may be ascribed to the fact that the hydroxyl-ion concentration was very low toward the end of the bleaching period.
FIGURE 45

Brightness Development
Initial pH 10.5

Curve (a) pH uncontrolled
Curve (b) pH controlled

FIGURE 46

Brightness Development
Initial pH 11.5

Curve (a) pH uncontrolled
Curve (b) pH controlled
A comparison of Curves (a) and (b) in Figure 46 indicates that, in this case, the pulp was bleached to a higher brightness by not controlling pH than by maintaining the initial pH of 11.5 at the same level during the bleaching. During the course of the run with uncontrolled pH, the pH dropped from 11.5 to 10.0 (Figure 7, Curve (b)). Experiments at controlled pH levels have shown that the specific reaction rate between peroxide and groundwood is sufficiently large to produce effective bleaching over the range from pH 11.5 to 10.0. From Curve (a) in Figure 46 it can be determined that the maximum brightness of 60.8% was reached after about 160 minutes of bleaching. Effective peroxide consumption at that point, from Curve (b), Figure 6, was 0.47 g./l. as compared with 60.2% brightness from 0.53 g./l. peroxide at pH level 11.5 (Table XIII). Thus, a higher brightness was obtained with less peroxide when the pH was not controlled. This result can be attributed to the fact that the pH was high enough during the first portion of the run to produce a rapid reaction between peroxide and groundwood and remained high enough during the run to maintain the specific reaction rate for the peroxide-groundwood reaction at a point where appreciable bleaching would continue. At the same time, the drop in pH during the run served to minimize brightness reversion which has been shown to be more serious at higher pH levels.

It should be noted that the data presented above on brightness development during runs with uncontrolled pH were obtained under experimental conditions which are comparable to commercial bleaching. It is evident from the above discussion why bleaching efficiency depends, to a large extent, on the pH conditions which prevail during the reaction period.
COLOR CHANGE DURING BLEACHING

Up to this point only changes in G.E. brightness have been used to demonstrate the effect of peroxide bleaching on the color of groundwood pulp. G.E. brightness represents the percentage reflectance obtained over a small portion of the visible light spectrum. The wavelength range utilized in making G.E. brightness determinations is centered on 457 mmu, and may be considered as the reflectance of monochromatic light at that wavelength. Normally, G.E. brightness measurements would provide sufficient information to permit evaluation of bleaching effectiveness. In the present case, however, a study of the effect of peroxide bleaching on reflectance over the entire range of visible light provides further useful information. This investigation was carried out by obtaining the spectral reflectance curves for the same samples used in measuring brightness development during bleaching. Brightness data for the samples to be considered here were given in Figures 36 to 44, and were discussed in the preceding pages of this section. For determination of brightness development during bleaching, 15 brightness samples were taken during the reaction period. At each pH level (except 9.0) three of the 15 brightness samples were also used to determine the change in spectral reflectance of the groundwood pulp during bleaching. The spectral reflectance of these samples was obtained on a General Electric Recording Spectrophotometer (hereafter abbreviated as GEERS) according to the procedure on page 21. The three samples from each experiment which were used for the determination of GEERS curves were: (1) the sample taken closest to 15 minutes after the start of the run; (2) the sample having the maximum brightness value (in cases where two samples had the maximum value, the first-taken sample
was used; and (3) the final sample, taken at the end of the 180-minute bleaching period. In all cases the sample having maximum brightness was obtained at some time after the 15-minute sample and before the 180-minute sample. In addition, a GERS curve was obtained for the sample of unbleached groundwood which was processed with the bleached groundwood samples from each run. At pH level 9.0, only the unbleached and the final samples were used for reflectance curves because of the small reflectance change at this pH level. The reflectance curves for pH levels 9.0 to 12.5 are given in Figures 47 to 53.

To interpret the data presented in the GERS curves it should be explained that an increase in reflectance at 457 mmu corresponds to an increase in G.E. brightness, and is a desirable result in bleaching. However, peroxide bleaching of groundwood also increases the reflectance over the entire wavelength range as shown in Figures 47-53. The fact that the reflectance in each case is lower in the vicinity of 450 mmu (in the blue area of the spectrum) than it is in the vicinity of 600 mmu (in the yellow area of the spectrum) is responsible for the yellow cast which is characteristic of groundwood pulp.

If the reflectance increase which is due to the reaction of peroxide bleach liquor with groundwood is larger from 550 to 700 mmu than it is in the area near 457 mmu, it can be considered as an undesirable increase in the yellow cast of groundwood pulp, even though the G.E. brightness be increased. It is apparent from Figures 47 to 53 that such an increase in yellow cast is obtained in each case. Therefore it is the relation between increase in brightness and increase in yellow cast which must be considered in evaluating the effect of alkaline peroxide bleaching on groundwood.
FIGURE 47

Reflectance Curves
pH 9.0

WAVELENGTH IN MILLIAMETERS

Samples

Unbleached

Bleached 180 minutes
Reflectance Curves
pH 10.0

Samples
- Unbleached
- Bleached 15 minutes
- Maximum brightness
- Bleached 180 minutes
FIGURE 50
Reflectance Curves
pH 11.0

Samples
- Unbleached
- Bleached 15 minutes
- Maximum brightness
- Bleached 180 minutes
FIGURE 51
Reflectance Curves
pH 11.5

Samples
- Unbleached
- Bleached 15 minutes
- Maximum brightness
- Bleached 180 minutes
samples were analyzed because of the small degree of color change obtained, it can be seen that the reflectance in the yellow portion of the spectrum has increased to a greater extent than that in the blue portion of the spectrum during the course of the bleaching reaction.

At pH 10.0 the reflectance in the blue end of the spectrum is approximately equal for the maximum brightness and final samples, but the final sample shows a slightly greater reflectance in the yellow portion of the spectrum. The peroxyde-groundwood reaction continued to increase reflectance in the yellow portion after a maximum reflectance had been reached in the blue portion of the spectrum.

The results at pH 10.5 and 11.0 are quite similar. In each case the maximum brightness sample has the greatest reflectance in both the blue and yellow portions of the spectrum, but the final sample shows a greater decrease in reflectance in the blue than in the yellow. At these two pH levels it appears that the peroxyde-groundwood reaction stopped at about the maximum brightness point. A check of the time to maximum brightness against residual peroxyde for all pH levels (Figures 9-14) indicates that there was less residual peroxyde at pH 10.5 and 11.0 at the time of maximum brightness attainment than at other pH levels.

At pH 11.5 the maximum brightness and final sample curves intersect in the vicinity of 457 mm, giving the same brightness, but the final sample has appreciably less reflectance in the blue-violet region of the spectrum and more in the yellow region than does the maximum brightness sample. These data illustrate how pulp color can vary without change in G.E. brightness.
At pH 12.0 and 12.5 the shift in color toward yellow is very evident. The reflectance in the blue region is considerably lower for the final sample than for the maximum brightness sample in both cases. Reflectance of the final sample in the yellow region of the spectrum is greater than that of the maximum brightness sample, indicating a continuation of the groundwood-peroxide reaction at these pH levels after apparent cessation of bleaching, as measured by brightness. The final sample at pH 12.5, which was subjected to the most alkaline conditions used in this investigation, was distinctly yellow in visual appearance as compared to the unbleached pulp.

It is evident from the above discussion that the observed maximum in G.E. brightness during the bleaching period is due to a shift toward a yellow color. This yellow color is caused by the reaction of sodium hydroxide with groundwood. The degree of color shift increases with pH.

A comparison of the GERS curves for the 15-minute samples is also interesting. A careful examination of Figures 47 to 53 indicates that, after 15 minutes' bleaching time, the reflectance increase in the blue region of the spectrum is about the same as, or more than, the reflectance increase in the yellow region at all pH levels below 12.5. Reflectance at wavelengths of 457 and 600 mm were used in making this comparison. This fact infers that the peroxide-groundwood reaction is at least equal to, if not predominant over, the hydroxide-groundwood reaction at the start of the bleaching period, in so far as their respective effects on pulp color are concerned.
Further confirmation of the fact that the rate of the peroxide-groundwood reaction increases with pH level can be obtained from the GERS curves. A comparison between the several sets of curves of the overall reflectance increase for the first 15 minutes of bleaching shows that the amount of such increase becomes greater as the pH level is increased. This effect must be due to an increased peroxide-groundwood reaction rate.

The permanence of the yellow color is a matter of interest in considering the color change during bleaching. When bleached groundwood samples (as a slurry) are alkaline, a distinct yellow color can be observed. Handsheets made from alkaline groundwood are yellow and of low brightness; the higher the alkalinity, the lower the brightness. If the slurry is acidified to some intermediate pH (pH 5 was used in preparing brightness samples in this work), the yellow color apparently disappears. However, the GERS data presented above show that at least part of the yellow color is irreversibly formed, as far as the methods used in preparing brightness samples for this investigation are concerned (see Method 1A, page 28).

THE RELATION OF BRIGHTNESS INCREASE TO PEROXIDE CONSUMPTION

The amount of brightness increase which can be obtained from a given amount of peroxide is a matter of interest in relation to bleaching effectiveness. The relation of the two factors, G.E. brightness increase and peroxide consumption, is shown in Figures 54 to 57 for pH levels 10.0 to 11.5, respectively. These data were obtained from the runs shown in Figures 39 to 42 for brightness development, and Figures 9 to 12 for peroxide consumption. The color change during the reaction time for these data is shown by the GERS curves in Figures 48 to 51.
Brightness Increase as a Function of Peroxide Consumption
pH 10.0

Curve (a) Effective peroxide
Curve (b) Total peroxide

Brightness Increase as a Function of Peroxide Consumption
pH 10.5

Curve (a) Effective peroxide
Curve (b) Total peroxide
The brightness increases plotted in Figures 54 to 57 represent the difference between 55.4% O.E. brightness (for unbleached pulp) and brightness values in Figures 39 to 42. The amount of peroxide consumed up to the time point determined by each of the brightness samples was calculated from the peroxide consumption curves for the same pH level. Both the consumption of total peroxide from the Curves (T), Figures 9-12, and effective peroxide from the Curves (E), Figures 9-12, are plotted against brightness increase. The data for the run at pH 9.0 are not presented because the (E) curve in Figure 8 is not sufficiently accurate to permit its use. The data for the runs at pH 12.0 and 12.5 are not presented because of the large brightness reversion effect at these pH levels. This reversion effect obscures the brightness-peroxide consumption relationship. Because of the reversion effect, the values plotted in Figures 54-57 include only the brightness increases up to maximum brightness in each case. An indication of the relation of peroxide consumption to the drop in brightness after reaching the maximum would have no significance.

One fact that is apparent from a consideration of Figures 54-57 is that the effective peroxide consumption, Curves (a), is more directly related to brightness increase than is the total peroxide consumption, Curves (b). Since total peroxide consumption includes decomposition, which does not contribute to bleaching, this result could be anticipated.

At pH 10.0, where the reversion effect due to alkali is small, the relation between effective peroxide consumed and brightness increase is almost linear, and less peroxide is necessary to obtain a given brightness than at other pH levels. The amount of effective peroxide necessary to
produce a given brightness increase is about the same for pH levels 10.5, 11.0, and 11.5. From the Curves (a) in Figures 55-57 it would appear that the first 0.1 g./l. of effective peroxide produced a larger brightness increase than subsequently consumed peroxide. There is no reason to believe that this could not be the case. However, it is also possible that alkaline reversion partly counteracts the true bleaching reaction, thus contributing to the deviation of the relation between brightness increase and effective peroxide consumption from the linearity indicated at pH 10.0.

A comparison of Figure 55 for pH 10.5 with Figures 56 and 57 for pH 11.0 and 11.5 indicates that slightly more peroxide was required at the lower pH level to obtain a given brightness increase. This fact is contrary to what could be expected on the basis of previously presented information on the effect of pH on pulp color. It should be noted, however, that the maximum brightness at pH 10.0 was reached after about 30 minutes' more bleaching than at pH 11.0 and 11.5. Therefore, the pulp at pH 10.0 was in contact with sodium hydroxide over a relatively long period during which residual peroxide concentration (as can be observed from Curve (b), Figure 55) was appreciably lower than at pH 11.0 and 11.5. As pointed out previously, such conditions encourage brightness reversion.

It is evident that the exact relation between peroxide consumption and bleaching, as measured by brightness increase, is difficult to determine because of the factors which influence brightness development. However, it can be concluded that, with the experimental methods used in this investigation, a given amount of effective peroxide will produce approximately the same brightness increase at all pH levels where alkaline reversion is not excessive.
THE EFFECT OF PREADJUSTMENT OF pH ON BRIGHTNESS DEVELOPMENT

The data for brightness development of runs at 11.0p and 11.5p, made with the pH preadjusted, are presented graphically in Figures 58 and 59, respectively. The purpose of presenting these data is to demonstrate that the course of the bleaching reaction is the same for runs at the same pH, whether or not the pH is preadjusted. The peroxide consumption data for the run at 11.0p is shown in Figure 22, and that for 11.5p in Figure 23. The curve from Figure 41, showing the brightness development at pH 11.0 with pH not preadjusted, has been included in Figure 58 for purposes of comparison. Similarly, the curve for pH 11.5, Figure 42, is shown in Figure 59.

It is apparent from Figure 58, pH 11.0, that the course of brightness development is almost identical for the two curves shown. Curve (a) can be considered directly comparable to Curve (b) because almost the same amount of effective peroxide was used in each case, as shown by Tables VI and X.

A comparison of the two curves in Figure 59, pH 11.5, indicates that the rate of brightness development is slightly less with preadjusted pH during the first portion of the bleaching period than with the pH not preadjusted. In addition, reference to Tables VI and X shows that 77% of the total peroxide was effective in bleaching in the run at pH 11.5p, and only 64% was effective in the run at pH 11.5. On this basis a slightly greater brightness development could have been expected from the run with preadjusted pH. It can be surmised that alkaline reversion, due to treat-
FIGURE 58

Brightness Development
pH 11.0p

Curve (a) pH preadjusted
Curve (b) pH not preadjusted

FIGURE 59

Brightness Development
pH 11.5p

Curve (a) pH preadjusted
Curve (b) pH not preadjusted
ment of the groundwood pulp with sodium hydroxide before adding the peroxide, has some effect on the brightness development at pH level 11.5. However, it can be seen that brightness development has not been essentially altered by preadjustment of pH at this pH level. The CMRS curves for these two pH levels show that preadjustment of pH has no appreciable effect on color change during bleaching.

At pH 12.0p and 12.4p alkaline reversion due to preadjustment of pH had proceeded far enough to affect the development of brightness. Although the CMRS curves for these pH levels indicated that reflectance in the yellow end of the spectrum was increased almost the normal amount during the bleaching period, the brightness level attained was about equal to that for unbleached pulp.

It can be concluded from the above discussion that preadjustment of pH has only a small effect on the brightness development during bleaching at pH levels below 12.0p, that is, where the alkaline reversion effect is not excessive.

THE EFFECT OF INCREASED CONCENTRATION OF PEROXIDE ON BRIGHTNESS DEVELOPMENT

The brightness development for the experiment made at pH 11.0 with 4.0% peroxide (based on weight of oven-dry groundwood) is shown in Figure 60. Figure 42, for the run at pH 11.0, 2.0% peroxide, is reproduced on the same page for comparison. These runs were made with the pH not preadjusted. The peroxide consumption data for the run with 4.0% peroxide are shown in Figure 18, page 100.
It is apparent from a comparison of Figures 42 and 60 that the increased peroxide concentration did not produce a proportional increase in brightness. The maximum brightness attained was 62.6% (from the curve) as compared to 60.7% attained with half the initial peroxide concentration at the same pH. In terms of the relation between brightness increase and effective peroxide consumption, the run with 4.0% peroxide gave an increase of 7.3 points brightness for 0.98 g./l. effective peroxide as compared to a 5.5-point increase for 0.48 g./l. effective peroxide with 2.0% peroxide. These data confirm the fact which has been pointed out by other investigators (2, 9), that increasing the initial peroxide concentration does not give a proportional increase in brightness. The reason for this fact is evident when it is considered that the decolorization of a given amount of colored material will produce a greater increase in reflectance when the initial reflectance is low than when the initial reflectance is high.

The rate of brightness development as judged qualitatively for the run at 4.0% peroxide is more rapid than for the run at 2.0% peroxide, but is not twice the 2.0% rate, as might be expected. This result is partly due to the fact that the specific rate of decomposition was greater with 4.0% peroxide than with 2.0% peroxide, thus making the concentration of effective peroxide relatively less at any time point for the run with 4.0% peroxide. Another factor contributing to the relatively lower rate of brightness development with 4.0% peroxide is the decrease in bleaching effectiveness with increase in brightness level, as discussed above.

The GERS curves for these data showed that there was no essential difference in the color change obtained during bleaching with 4.0% peroxide, as compared with previous runs made with 2.0% peroxide.
It can be concluded from the above discussion that the results of this experiment on the effect of increased peroxide concentration on brightness development during bleaching are in accord with previously presented information on reaction kinetics and brightness development.

THE EFFECT OF ADDED SODIUM SILICATE ON BRIGHTNESS DEVELOPMENT

Brightness development during bleaching is shown in Figure 61, for the experiment with added sodium silicate that was previously discussed on pages 130 to 136 with regard to reaction kinetics. The peroxide consumption data for this experiment are given in Figure 36. This experiment was carried out at a preadjusted pH of 11.0 with 5% of 40° Bé sodium silicate (based on weight of oven dry groundwood) added. Method 1B, page 32, was followed.

The most important result of adding silicate is apparent when the course of brightness development shown in Figure 61 is compared with that for the run at pH 11.0 shown in Figure 42 (reproduced on the same page for reference). It is evident that the rate of brightness development has been decreased by the addition of silicate. There can be little doubt that this decrease in rate of brightness development is due to the low specific reaction rate that was calculated for the groundwood-peroxide reaction for these data. The value of \( k_0 \) for the present data was estimated at 0.005 min\(^{-1}\), as compared to the value of 0.012 min\(^{-1}\) which was calculated for the experiment made at pH 11.0 without added silicate. As mentioned before, an exact measure of the rate of brightness increase cannot be made because of the nonmeasurable factors which affect pulp brightness. However, on a qualitative basis the results obtained for the rate of brightness development
in the presence of silicate can be considered as confirmation of the kinetic relationships previously established for these data.

It can be observed that the final brightness value in Figure 61 is also the maximum value attained during the run. It can be assumed that some further brightness increase would have taken place had the run been continued. The amount of effective peroxide necessary to give the observed brightness increase of 4.8 points was 0.64 g./l. At pH 11.0, without added silicate, a brightness increase of 5.5 points was obtained with 0.48 g./l. effective peroxide. A comparison of the CMRS curves for the two sets of data indicated that the maximum brightness sample with added silicate had a more pronounced yellow cast than the maximum brightness sample without silicate. This increased yellow cast and the related increase in effective peroxide consumption for a given brightness increase can be ascribed to alkaline reversion taking place during the relatively long reaction period necessary to reach maximum brightness in the presence of sodium silicate (180 minutes with silicate as compared to 50 minutes without).

It can be concluded that, with the exception of decreasing the rate of brightness development, the presence of sodium silicate in the bleach liquor does not have any abnormal effect on the relation of peroxide consumption to brightness increase, or on the color changes occurring during bleaching.

THE EFFECT OF INCREASED HYDROPEROXIDE-ION CONCENTRATION ON BRIGHTNESS DEVELOPMENT

A phase of the present investigation which has not been discussed as yet is the effect of increased hydroperoxide-ion concentration on bright-
ness development. It is evident that there is no way to increase the hydroperoxide-ion concentration at a given pH level because the alkaline peroxide solution is in equilibrium with respect to hydroperoxide-ion and free hydrogen peroxide. The only way in which the hydroperoxide-ion concentration can be increased is by the addition of a concentrated alkaline peroxide solution to the groundwood slurry at the start of the bleaching period instead of by the addition of hydrogen peroxide and sodium hydroxide separately. In this way the concentration of hydroperoxide-ion will be higher than the equilibrium value for the short period until equilibrium is reached.

An experimental bleach was carried out with a high initial hydroperoxide-ion concentration, using Method 1D, page 33. The concentrated peroxide solution added as bleach liquor at the beginning of the reaction period was 1 M with respect to sodium hydroxide and contained about 25 g./l. peroxide (calculated as sodium peroxide). Under these conditions an alkaline peroxide solution is almost 100% hydroperoxide ion. Because of the special nature of the experiment, a pH level could not be selected in advance. The pH level maintained in this experiment was 11.8, which was the pH value obtained after adding the bleach liquor. The equilibrium concentration of hydroperoxide ion at pH 11.8 is 50.2% of the total peroxide concentration. Thus the hydroperoxide-ion concentration would drop from over 1.0 g./l. to about 0.5 g./l. (as Na₂O₂) during a short time at the start of the bleaching period.

The brightness development data for the run with high initial hydroperoxide-ion concentration is shown in Figure 62. Figure 43, for brightness development at pH 11.5, and Figure 44, for brightness development
FIGURE 62
Brightness Development
pH 11.8
(With high initial hydroperoxide-ion concentration)

FIGURE 44
Brightness Development
pH 12.0
(Repeated for reference)

FIGURE 43
Brightness Development
pH 11.5
(Repeated for reference)
at pH 12.0, are shown on the same page for reference. It is apparent
that the rate of brightness increase for the run at pH 11.8 is at least
as large as that at pH 12.0, and larger than that at pH 11.5. It should
be noted that a brightness value of 61.3% was attained in 20 minutes,
which is over one point higher than the brightest 20-minute sample for
any other run made in the present work with the same peroxide concen-
tration (60.1% at pH 11.0p), and is close to the value of 61.7% obtained
with 4.0% peroxide at pH 11.0. The value of 61.3% attained at the 60-
minute point represents the maximum individual brightness value obtained
with o.p. liquor in a run made with 2.0% peroxide. The maximum value of
brightness as obtained from the best curve through the points in Figure 62
is 61.2%. This value can be compared with 60.8%, which was the highest
maximum value (taken from the drawn curve) for any other bleach made with
2.0% peroxide. The value of 60.8% was attained in the run made at initial
pH 11.5 with the pH uncontrolled, and in the runs made at pH levels 11.0
and 11.0p.

The technique used in carrying out the present experiment was
not readily adaptable to the method used for determining oxygen evolution
during bleaching. Therefore only the total peroxide consumption data were
obtained, and it is not possible to calculate the relation between effective
peroxide consumption and brightness increase.

The total peroxide consumption data for the present experiment,
given in Figure 63, show that the total peroxide concentration dropped to
0.88 g./l. from the initial concentration of 1.05 g./l. in the first two
minutes of the reaction period. This concentration decrease is the largest
obtained in the first two minutes for any run made with 2.0% peroxide during the present investigation. The total peroxide consumption became first order after about 30 minutes of the reaction period had passed. The concentration at the 30-minute point was 0.42 g./l. peroxide. The first-order portion of the reaction period is comparable, therefore, to the first-order portion of other runs made with the pH not preadjusted, as discussed on page 85. The value for $k_t$ was calculated for the first-order portion of the present data as 0.014 min.$^{-1}$. This value is equal to that for the run at pH 12.0, as shown in Table VII. A comparison of the brightness development curve for pH 12.0, Figure 44, with that for the present run made at pH 11.8 with high initial hydroperoxide-ion concentration, Figure 62, shows that the trend of the two curves is very similar except for the difference in brightness level attained.

The GRHS curves for the run at pH level 11.8 with high initial hydroperoxide-ion concentration showed approximately the same amount of yellow cast as the data for the run at pH 12.0.

It can be concluded from the information presented on the effect of a high initial hydroperoxide-ion concentration on brightness development and peroxide consumption, that hydroperoxide ion is the active bleaching agent in peroxide bleach liquor. A bleaching reaction which is started with high initial hydroperoxide-ion concentration differs from a reaction started with low initial hydroperoxide-ion concentration (other conditions being comparable) in that it shows a more rapid initial peroxide consumption accompanied by a brightness increase which is appreciably larger and apparently more rapid.
SUMMARY

The information on brightness and color change during bleaching is briefly summarized below.

The increase in the reaction rate of the peroxide-groundwood reaction with increasing pH level (as demonstrated in a previous section of this work) is reflected by an increase in the rate of brightness development with increasing pH level.

Maximum bleaching effectiveness is not attainable at high pH levels because of brightness reversion produced by the reaction of sodium hydroxide with groundwood.

The alkaline reversion effect is minimized by permitting the pH to follow its natural course during the reaction period.

Spectral reflectance curves show that the color of groundwood pulp shifts toward yellow as bleaching progresses. This color shift is more pronounced at higher pH levels. Peroxide consumption by the groundwood-peroxide reaction does not always produce a brightness increase. However, such peroxide consumption is shown to give a reflectance increase in the yellow region of the spectrum.

The brightness increase which can be obtained with a given amount of effective peroxide is approximately constant for those pH levels (below 12.0) where the alkaline reversion effect is not excessive.

The course of brightness development is essentially unchanged by increasing the peroxide concentration of the bleach liquor; such an increase
results only in the attainment of a higher brightness level.

The presence of sodium silicate in the bleach liquor decreases the rate of brightness development without producing abnormal effects on the brightness and color of the pulp.

Bleaching with liquor which is initially high in hydroperoxide-ion content produces relatively higher pulp brightness at a rate which appears to be more rapid than that observed when bleaching with liquor of low hydroperoxide-ion content.

THE FORMATION OF CARBON DIOXIDE DURING BLEACHING

It was mentioned in the discussion of oxygen evolution and its measurement (page 53) that bleach liquor contained an appreciable amount of sodium carbonate at the end of the bleaching period. The quantity of sodium carbonate found in conjunction with the complete gas analysis discussed on pages 51 to 54 was considerably more than could be accounted for by absorption of carbon dioxide from the air present in the reaction vessel, or any other minor source. Carbonate-free sodium hydroxide, hydrogen peroxide, distilled water (heated to 80°C. during groundwood preparation) and groundwood are the materials which are combined at the start of each bleach with c.p. liquor. It is obvious that any appreciable quantity of sodium carbonate found at the end of the bleaching period must be formed from the organic materials in groundwood.

Since groundwood is the only carbon-containing material in the bleaching system, it is reasonable to assume that the formation of sodium
carbonate during bleaching is due to the production of carbon dioxide by the oxidation of organic material, and the subsequent reaction of the carbon dioxide with sodium hydroxide. Because the measurement of the amount of sodium carbonate in the bleach liquor is carried out by acidifying the alkaline liquor and then absorbing and weighing the evolved carbon dioxide, the data presented in this section will be considered in terms of carbon dioxide without reference to its subsequent conversion, during bleaching, to the sodium salt.

POSSIBLE OXYGEN SOURCES FOR CARBON DIOXIDE FORMATION

A detailed consideration of the reaction or reactions involved in the production of carbon dioxide by the oxidation of the organic materials in the bleaching system is not in the realm of this investigation. However, some general information on organic oxidations is helpful in considering the case at hand. It should be mentioned that no effort was made in this investigation to remove the sugars and other low-molecular weight carbohydrates that are normally present in groundwood pulp. Naturally these materials are more reactive than the cellulosic compounds, of which groundwood is composed in large part. In addition to low- and high-molecular weight carbohydrates, the lignin and other noncarbohydrate compounds can also conceivably react with oxidizing agents to form carbon dioxide.

There are two oxidizing systems which must be considered with regard to carbon dioxide formation; one is alkaline peroxide and the other is molecular oxygen in alkaline solution. There is no doubt that alkaline peroxide is responsible for much of the organic oxidation which takes place during bleaching, and probably contributes to the formation of carbon dioxide.
However, the oxidation which is of greatest interest at this point is that which is produced by oxygen in alkaline solution. Such oxidation would utilize oxygen formed during peroxide decomposition, thus causing a measurement of the amount of oxygen produced by decomposition to be superficially low. The error in the measurement of oxygen evolution has been discussed previously in its relation to the calculation of kinetic relationships in the peroxide-groundwood system. Fortunately, this error is small enough to allow useful kinetic information to be obtained.

In a general survey of carbohydrate oxidation by Pigman and Goepp (47) it is pointed out that alkaline oxygen will oxidise carbohydrate materials, resulting in the formation of carbon dioxide and organic acids. Raff and Tomlinson (48) demonstrate that certain lignins are oxidised by alkaline oxygen. Therefore it can be assumed that the organic materials present in groundwood slurry are susceptible to oxidation by an alkaline oxygen solution. The fact that a reaction of groundwood with alkaline oxygen will not produce bleaching is indicated by the work of Simon and Drelich (42) on the alkaline peroxide bleaching of raw and bleached cotton. This fact was confirmed by reacting groundwood with alkaline oxygen at a pH of 11.0 (where alkaline reversion is not excessive). No brightness increase was obtained in the normal bleaching time of 180 minutes.

An experiment was carried out to evaluate the effect of the two oxidation reactions on the formation of carbon dioxide. The detailed procedure for this experiment is given on page 42. Three samples of 1% groundwood slurry (500 ml. each) were adjusted to pH 11.5. One sample
was not treated further, one was saturated with gaseous oxygen, and sufficient peroxide was added to the third to give a concentration of 1.0 g./l. (calculated as Na₂O₂). The samples were permitted to remain at about 25°C. for 12 hours. A blank, consisting of 500 ml. of 1% groundwood slurry at pH 6.5, was maintained under similar conditions. At the completion of the reaction period the carbon dioxide content of each of the samples was measured by the method given on page 24. The results of this experiment are given in Table XIV.

**TABLE XIV**

**THE OXIDATION OF GROUNDWOOD TO FORM CARBON DIOXIDE**

<table>
<thead>
<tr>
<th>Sample Treatment</th>
<th>pH Initial</th>
<th>pH Final</th>
<th>Carbon Dioxide Formed, g.</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>6.5</td>
<td>6.5</td>
<td>0.004</td>
</tr>
<tr>
<td>Made alkaline</td>
<td>11.5</td>
<td>11.1</td>
<td>0.024</td>
</tr>
<tr>
<td>Made alkaline and oxygen added</td>
<td>11.5</td>
<td>11.0</td>
<td>0.036</td>
</tr>
<tr>
<td>Made alkaline and peroxide added</td>
<td>11.5</td>
<td>10.3</td>
<td>0.048</td>
</tr>
</tbody>
</table>

The data in Table XIV show that carbon dioxide is formed by oxidation of groundwood. All samples that were made alkaline showed an appreciable production of carbon dioxide. Since the sample which was made alkaline (with no further treatment) reacted to produce carbon dioxide, it is reasonable to assume that the oxygen which was present in the pulp as absorbed and adsorbed air was sufficient to give the observed oxidation effect. Addition of gaseous oxygen served to increase the amount of carbon dioxide formed from alkaline groundwood by about 50%, and addition of peroxide produced twice as much carbon dioxide as was obtained with the
alkaline, but otherwise untreated, sample. It can be concluded from
the data in Table XIV that alkaline oxygen will oxidize groundwood to
form carbon dioxide. These data also indicate that alkaline peroxide
oxidation of groundwood will produce carbon dioxide. However, it must
be considered that at least part of the carbon dioxide formed in the
peroxide-containing sample is due to the alkaline oxygen introduced into
the system by adsorbed air and peroxide decomposition. The possibility
that all carbon dioxide formation is due to alkaline oxygen oxidation
cannot be precluded.

A simple calculation showed that the pH drop observed with each
of the alkaline samples in Table XIV was larger than could be accounted
for by carbon dioxide formation. It is apparent that other factors, such
as formation of organic acids (formic, acetic, etc.), increase in organic
acidity (as found by Jones (2)), and saponification of acetyl groups in
the pulp, also contribute to the pH drop which is observed during peroxide
bleaching with uncontrolled pH.

THE AFFECT OF CARBON DIOXIDE FORMATION ON OXYGEN EVOLUTION

In order to determine the magnitude of carbon dioxide formation
during actual bleaching, a series of carbon dioxide determinations was
made, using the procedure given on page 24, on the liquor from the runs
made with preadjusted pH. The peroxide consumption data for the four
experiments which were considered, pH levels 10.5 to 12.0, are given in
Figures 21-24, and discussed on page 73 et seq. The liquor from runs
for the determination of oxygen evolution was used for carbon dioxide analysis
because the absorption of oxygen from the air above the slurry could be
measured by the change in volume of the closed system. The use of this series of experiments for the investigation of the formation of carbon dioxide has a disadvantage in that the alkaline groundwood was exposed to air for some time before the system was sealed and the peroxide added. For this reason it must be assumed that an indeterminate amount of carbon dioxide formation took place before the run was started. However, all runs were made with the same procedure, and the indeterminate oxidation could be expected to be fairly uniform in all cases.

The results of the series of carbon dioxide determinations is given in Table XV. The amount of carbon dioxide found at each pH level is expressed as grams and represents the total carbon dioxide for the 1000 grams of 5% groundwood slurry. The gaseous volume under S.T.P. is also included in Table XV for purposes of comparison with the volume of oxygen evolved during bleaching. Also shown in Table XV is the amount of oxygen evolved during the bleaching period, as measured by the maximum expansion of the closed system, and the amount of gas that was absorbed by the groundwood slurry after oxygen evolution had apparently ceased, as measured by contraction of the system after maximum volume has been reached. It should be mentioned that 144 ml. of oxygen would be formed by the total decomposition of the peroxide present in the system. The quantity of effective peroxide used in bleaching is also shown, as grams of Na₂O₂. The determination listed at pH 11.7 is a blank run that was carried out using the same procedure as in the other experiments, but omitting addition of peroxide at the start of the run.
<table>
<thead>
<tr>
<th>pH</th>
<th>Carbon Dioxide Formed, g.</th>
<th>Oxygen Evolved, ml.</th>
<th>Oxygen Absorbed, ml.</th>
<th>Effective Peroxide Used, g.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5p</td>
<td>0.116</td>
<td>58</td>
<td>0</td>
<td>0.50</td>
</tr>
<tr>
<td>11.0p</td>
<td>0.195</td>
<td>48</td>
<td>7</td>
<td>0.65</td>
</tr>
<tr>
<td>11.5p</td>
<td>0.164</td>
<td>34</td>
<td>9</td>
<td>0.74</td>
</tr>
<tr>
<td>12.0p</td>
<td>0.162</td>
<td>33</td>
<td>13</td>
<td>0.75</td>
</tr>
<tr>
<td>11.8p</td>
<td>0.071</td>
<td>(blank determination)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The data in Table XV indicate that there is no particular correlation between the amount of carbon dioxide formed and the other factors shown in the table. It is interesting to note that almost the same amount of carbon dioxide was formed at pH 11.5 and 12.0, where the amounts of oxygen evolved and effective peroxide used were approximately equal. This observation would indicate that pH (above a certain level) has little effect on carbon dioxide formation. The amount of carbon dioxide formed during the blank run cannot be directly compared with the carbon dioxide formation in the other cases because of the different pH levels involved. However, the blank determination does indicate that a large amount of the carbon dioxide formed at each pH level can be attributed to oxidation other than that produced by the bleach liquor.

The data on the absorption of oxygen indicate that more oxygen is absorbed at higher pH levels. However, the amount of absorption is influenced by the time at which oxygen evolution stops. Thus, for the runs shown in Table XV the amount of time for absorption to take place increased with increasing pH.

Some interesting calculations on the magnitude of carbon dioxide absorption during an oxygen evolution experiment can be based on the amount of absorption which occurs after apparent cessation of oxygen evolution. The volume change of the sealed system during a run is shown in Figure 64 for the three runs in Table XV during which absorption took place. The data plotted in this figure are the same as those plotted in Figures 22–24 for the Curves (D), with the addition of the points representing the loss in volume which occurs after reaching maximum oxygen evolution.
Evolution and Absorption of Gas During Bleaching

Volume of evolve gas, ml.

- Curve (a) pH level 11.0
- Curve (b) pH level 11.5
- Curve (c) pH level 12.0

Reaction time, min.
The data at pH 12.0 serve as the best examples of the error which is due to carbon dioxide formation, because it represents the largest amount of absorption. The error due to carbon dioxide has been discussed for the experiment at pH 12.0 (page 125) in a different sense than will be considered here.

Examination of the curves in Figure 64 indicates that absorption of gas proceeds in a regular manner with continuing time after maximum oxygen evolution has been reached. A check of Curve (c) shows that 10.6 ml. of gas were absorbed in the last 90 minutes of the bleaching period. Neglecting the absorption of carbon dioxide from the air present in the reaction vessel (the gas analysis described on page 52 showed that 4 ml. of carbon dioxide were absorbed over the entire reaction period; total absorption of the carbon dioxide present in the reaction vessel would give only 8 ml.) it can be assumed that the volume of 10.6 ml. represents oxygen absorbed and reacted. It is evident that some oxygen should have been evolved due to peroxide decomposition during the final 90-minute period. Curve (f) in Figure 24 shows that the residual peroxide at the 90-minute point was 0.08 g./l., or 0.076 gram. Of this amount, 0.066 gram reacted during the final 90 minutes of reaction time. It can be assumed, based on the relation of $k_d$ to $k_d + k_o$ from Table XII, that 11/30 of the 0.066 gram of peroxide was decomposed to form 3.5 ml. of oxygen. It can be seen that possible small errors in the values of $k_d$ and $k_o$ are not of large consequence. The sum of oxygen evolved and oxygen absorbed during the final 90-minute period of the bleach gives the total molecular oxygen which was consumed in alkaline oxygen oxidation. This sum is 14.1 ml.
For the present it can be assumed that the absorption of oxygen from the gas in the reaction vessel took place at the same rate during the first portion of the bleaching period as it did during the last portion. Therefore a value of 7.1 ml. can be taken as the amount of oxygen which was absorbed during the initial 45 minutes of the bleaching period, that is, up to the point of maximum oxygen evolution. Thus the observed value for oxygen evolution up to 45 minutes must be 7.1 ml. less than the true value. The observed value of 33.4 ml. can be corrected to a true value of 40.5 ml. by adding 7.1 ml.

The total peroxide consumed during the first 45 minutes of the reaction period (from Curve (2), Figure 24) was 0.78 g./l., or 0.74 gram. If the values of $k_d$ and $k_o$ for pH 12.0 in Table XII are correct, the amount of peroxide decomposed at the end of 45 minutes should be 11/30 of the total peroxide consumption, or 0.27 gram. The corrected volume of oxygen evolved, 40.5 ml., would be obtained by decomposition of 0.28 gram of peroxide.

Similar calculations were carried out for pH 11.0 and 11.5. It was determined that, at pH 11.5, corrected oxygen evolution at 60 minutes (the point of maximum oxygen evolution) could be accounted for by the decomposition of 0.30 gram of peroxide. The ratio of the rate of decomposition to the total of decomposition rate and groundwood-peroxide reaction rate also indicated that 0.30 gram of peroxide was used in decomposition up to the 60-minute point. For pH 11.0 it was determined that corrected oxygen evolution represented 0.44 gram of peroxide, as opposed to the decomposition of 0.41 gram of peroxide indicated by the rate-constant ratio.
The calculations given above show that the weight of peroxide used in decomposition (up to the point where rate of evolution could no longer be measured) can be arrived at by two unrelated methods. One method depends upon correcting the amount of oxygen evolution for oxygen absorbed during the reaction period, and the other depends on the values of the reaction-rate constants as calculated with the error in reaction-rate measurements caused by carbon dioxide formation taken into account. As can be seen, the values obtained by the two methods check closely.

The above calculations can be taken as further indication that the values of the reaction-rate constants which were calculated for the individual peroxide bleaching reactions (k_e and k_d in Table XII) are reliable. It should be noted in Table XII that the same value of k_d was obtained at pH 10.5, whether or not carbon dioxide formation was taken into account. The inference that no correction is needed is borne out by the data in the present section, which indicate that insufficient oxygen was absorbed during the run at pH 10.5 to make a correction possible.

The calculations considered above also confirm the assumption which was made at the start of the calculations that the oxygen absorption rate is approximately the same over the entire reaction period. It is interesting to note that the volume absorbed during the entire bleaching period was calculated as 14.5 ml. at pH 11.0, 12.6 ml. at pH 11.5, and 14.1 ml. at pH 12.0. These values indicate that the absorption was approximately the same, regardless of pH level.

It can be concluded from the data presented in this section of the experimental work that carbon dioxide is formed during the peroxide bleaching
of groundwood. The carbon dioxide appears to result from the oxidation of organic materials in the system by alkaline oxygen and by alkaline peroxide. Absorption of oxygen during the bleach causes an error in the measurement of the rate of oxygen evolution, but this error is now shown to be adequately corrected for in the previous consideration of the kinetics of the bleaching reactions.

THE REACTION OF ISOLATED GROUNDWOOD COMPONENTS WITH ALKALINE PEROXIDE

Up to this point in the presentation of experimental data, only the reaction between groundwood and peroxide has been considered. The consumption of peroxide by groundwood has not been referred to any specific material in the groundwood. As mentioned previously (page 8), Jones carried out an extensive investigation of the mechanism of the peroxide bleaching of groundwood. He demonstrated that the major bleaching effect exerted by alkaline peroxide on groundwood is attributable to its reaction with the lignin. Jones also concluded from a series of experiments on groundwood which was treated so as to inactivate the lignin with respect to peroxide that lignin was responsible for about 40%, and holocellulose for about 60%, of the total peroxide consumption. This conclusion was based on data which did not take possible peroxide decomposition into consideration.

It seemed advisable to perform some experiments on the reaction of holocellulose with alkaline peroxide in the present investigation. The purpose of this experimentation was to provide further information on the peroxide consumption of individual groundwood constituents. In addition,
it was considered possible that a study of the kinetics of the reactions of individual groundwood components with alkaline peroxide might provide information on peroxide-groundwood reaction kinetics as well.

**ISOLATED HOLOCCELULOSE**

The first material which will be considered in this section is chlorite holocellulose. This material has been described on page 20. It should be understood that this holocellulose is not intended to represent groundwood with the lignin removed. It is a different material from whole groundwood in physical form as well as in chemical composition. However, the chemical constituents of isolated sprucewood holocellulose can be considered similar to those of spruce groundwood holocellulose *in situ*, although they are probably somewhat altered and more reactive in the isolated form. Previous discussions of the kinetics of peroxide bleaching have pointed out that the course of the total peroxide consumption reaction does not depend upon the groundwood in the system, except as the groundwood affects the decomposition reaction. Therefore the use of isolated holocellulose is justified in the present case by the fact that this investigation is designed to determine the effect of a holocellulosic material on the course of the peroxide consumption reactions rather than to determine the chemical effect of peroxide on holocellulose.

Experiments to determine the total peroxide consumption and the oxygen evolution during the reaction were carried out according to Method 1A, page 28, and Method 2A, page 34, respectively. The experiments with holocellulose were carried out in exactly the same way as the experiments with groundwood. The consistency of the reaction mixture was 5% by weight.
of oven-dry holocellulose. The experiments were made at pH level 11.0 without adjustment of the pH before the start of the experiment. It should be noted that the concentration of holocellulose in the reaction mixture is greater in these experiments than is the concentration of holocellulose in a groundwood slurry at 5% consistency because holocellulose comprises only about 70% of the total groundwood. This situation was deemed more desirable than using a lower concentration of isolated holocellulose to give the same holocellulose-to-bleach liquor ratio as prevails during groundwood bleaching.

The peroxide consumption curves for the experiments with isolated holocellulose are given in Figure 65. As before, the curve labeled (N) represents the peroxide which was consumed by reaction with the holocellulose, Curve (D) represents the peroxide which was decomposed to oxygen, as determined experimentally, and Curve (T) represents the experimentally determined total peroxide consumption.

An examination of the curves in Figure 65 shows that the holocellulose consumed an appreciable amount of peroxide. The fact that this holocellulose contained 1.5% of Klason lignin should be taken into consideration. There can be little doubt that at least a portion of the peroxide consumed by the holocellulose was due to reaction with the remaining lignin. It is not possible, of course, to determine how much of the peroxide consumption was due to each of the individual chemical constituents of holocellulose.

The similarity of the curves in Figure 65 to those in Figure 36, for peroxide consumption of groundwood at pH 11.0p with added sodium silicate,
should be noted. The significance of this similarity will be discussed presently.

**Kinetic Analysis**

The total peroxide consumption data were tested for conformity to the first-order relationship by plotting, on semilogarithmic paper, residual peroxide concentration against reaction time. This plot is shown in Figure 66, Curve (a). It is evident that a first-order relationship exists. The two points shown during the first 10 minutes of reaction time indicate that the initial reaction was slightly more rapid than that represented by Curve (a). Since these experiments were not carried out with preadjusted pH, a slight variation in the rate of the reaction is to be expected during the initial few minutes of the reaction period. Because the magnitude of the initial deviation from first order is not large, the reaction will be considered as entirely of the first order with a reaction-rate constant, $k_3$, of $0.011 \text{ min}^{-1}$, as determined from the slope of Curve (a). It is evident that the kinetic order of total peroxide consumption is the same, whether holocellulose or groundwood is being reacted with alkaline peroxide.

Kinetic analysis of the individual reactions was carried out with the same methods that were used previously (pages 89 and 95). The rate-concentration plots for the decomposition and holocellulose-peroxide reactions are shown in Figure 67. Fitting a straight line to the calculated rate-concentration points for each reaction would serve no purpose. Therefore the specific reaction rate for each of the reactions has been estimated by
FIGURE 66

Peroxide Consumption
pH 11.0

Holocellulose and Alpha-Cellulose

Residual peroxide, g./l. (as Na$_2$O$_2$)

Curve (a) Holocellulose
Curve (b) Pre-reacted holocellulose
Curve (c) Alpha-cellulose

Reaction time, min.
FIGURE 67

Variation of Reaction Rate with Concentration
pH 11.0
Holocellulose

(d') Decomposition reaction
(e') Peroxide-holocellulose reaction
assuming each reaction rate to be correct at a total peroxide concentration of approximately 0.8 g./l. peroxide. The dotted Curves (e') for the holocellulose-peroxide reaction, and (d') for the decomposition reaction, indicate the rate-concentration relationship in each case. The curves represent a value of 0.004 min.\(^{-1}\) for \(k_a\), and 0.007 min.\(^{-1}\) for \(k_e\).

It is evident that the plotted points follow these lines to a fair degree. It is safe to assume that the variation of the points for both reactions from their respective curves is due to absorption of the oxygen used in alkaline oxygen oxidation. It can be observed that the rate values for the two reactions, for total peroxide concentrations of less than 0.5 g./l., vary about the same amount from their respective curves, and that this variation is within the range that would be expected from oxygen absorption. The relatively high concentration of low-molecular weight carbohydrate materials which would be present in an alkaline suspension-solution of holocellulose makes it quite probable that alkaline oxygen oxidation would be as high or higher than with groundwood.

A feature of these experimental data which is informative is the fact that the total peroxide consumption reaction was much less rapid for the reaction with holocellulose than for the reaction with groundwood at the same pH level (Figure 22, page 107). Because the total peroxide consumption reaction is of the first order with respect to peroxide, it is evident that the concentration of the organic materials in the reaction mixture does not affect the kinetics of the system, as was also the case with groundwood (page 85). However, it could be expected that peroxide consumption with holocellulose in the system would proceed at the same rate as with groundwood in the system under a given set of experimental conditions.
The situation appears to be analogous to that occurring when sodium silicate is added to the bleach liquor. It was concluded that the addition of sodium silicate decreased the rate of total peroxide consumption by acting as an inhibitor for both of the hydroxyl-ion-catalysed reactions, decomposition and the peroxide-groundwood reaction. The stabilizing effect of groundwood on alkaline peroxide solutions has been mentioned frequently in previous discussions. It would appear that the concentration or effectiveness of those groundwood constituents which are the active stabilizers is much greater in the case of holocellulose than with groundwood itself. The above observation is quite probable since materials which are known to be good peroxide stabilizers, such as carbohydrates containing alcoholic (OH) groups, are more likely to be released in a reaction involving holocellulose than in one involving the less reactive groundwood. Stabilizers occurring naturally in the alkaline peroxide-holocellulose mixture appear to be only slightly less effective than 5% sodium silicate in inhibiting both the decomposition reaction and the reaction of peroxide with organic material under the experimental conditions used.

In regard to the reaction of alkaline peroxide with isolated holocellulose, it can be concluded that an appreciable amount of peroxide was consumed by the holocellulose components. It is quite likely that the residual lignin accounted for a large portion of the peroxide consumption.

It can also be concluded that isolated holocellulose exerts a strong stabilizing effect on alkaline peroxide solutions. However, the mechanisms of the reactions in the holocellulose-peroxide system are essentially the same as in the groundwood-peroxide system.
PREREVERSED HOLOCELLULOSE

The results obtained by reacting isolated holocellulose with alkaline peroxide indicated that the residual lignin could have been responsible for part of the peroxide consumption. It was decided to carry out further experiments on holocellulosic materials which were more nearly lignin-free. It appeared that the material obtained after the reaction between peroxide and holocellulose was complete would be satisfactory for this purpose. This material, which will be referred to as preredacted holocellulose, was recovered at the end of the 180-minute reaction period between alkaline peroxide and the isolated holocellulose discussed previously. Recovery was accomplished by filtering the solids from the liquor, suspending the solids in distilled water and acidifying to pH 5.0, re-filtering, and washing the solids acid-free. A quantitative reaction (procedure on page 43) was carried out to duplicate, on a smaller scale, the conditions during the holocellulose-peroxide reaction. It was determined that 15.9% of the holocellulose had been removed during the first reaction of holocellulose with peroxide and subsequent recovery of the holocellulosic residue. It can be concluded that the material remaining after the reaction still contained a considerable portion of those carbohydrate materials which are contained in holocellulose, exclusive of alpha-cellulose. This conclusion is based on the fact that the original holocellulose represented about 70% of the wood substance, and the residue after reaction represented, therefore, about 59% of the wood substance, whereas the alpha-cellulose content of sprucewood is about 43%. It was assumed that the reaction of the holocellulose with alkaline peroxide, which combined oxidation with alkaline extraction, had removed the objectionable lignin residue.
The total peroxide consumption for preracted holocellulose was determined by Method 1A, page 28, and the oxygen evolution during the run was determined by Method 2A, page 34. These methods are the same as used with isolated holocellulose, at pH level 11.0 and 5% consistency.

The peroxide consumption curves for these experiments are shown in Figure 68. The nomenclature is the same as that used previously.

The rate of the various reactions is seen to be somewhat slower than with holocellulose. A semilogarithmic plot of residual peroxide for total peroxide consumption is shown as Curve (b) in Figure 66. In the case of preracted holocellulose the rate of total peroxide consumption is again first order, with a reaction-rate constant, \( k_t \), of 0.006 min.\(^{-1}\). This value can be compared with that of 0.011 min.\(^{-1}\) for holocellulose.

Examination of Curve (b) in Figure 68 shows that there is no change in the rate of the peroxide-holocellulose reaction after about the first 30 minutes of the reaction period. Obviously, this curve cannot represent a reaction which is first order with respect to the total peroxide concentration. It is reasonable to expect that the decomposition reaction would be of the first order because it has been so in every previous experiment. However, the total peroxide consumption reaction is clearly first order, as shown in Figure 66, Curve (b), which could not be the case if it resulted from the sum of the peroxide consumption of one first-order reaction and one reaction which was not first order. It must be concluded that the peroxide consumption indicated by Curve (b) in Figure 68 is due, for the most part, to the absorption of oxygen by the reaction mixture. A previous consideration (page 190) indicated that oxygen absorption took place
FIGURE 68

Peroxide Consumption

pH 11.0

Pre-reacted Holocellulose

(E)

(D)

(T)
at a uniform rate over the entire reaction period, and was of about the same magnitude, as is the case with the apparent peroxide consumption indicated by Curve (E).

If the apparent peroxide consumption shown by Curve (E), Figure 68, is due to oxygen absorption, it must be concluded that the reaction between prereacted holocellulose and alkaline peroxide, if any, was very slight, and that the decomposition reaction alone accounted for the first-order total peroxide consumption data.

A small-scale quantitative experiment, duplicating the conditions used for the data under discussion, showed that only 2.7% of the prereacted holocellulose was removed during its reaction with alkaline peroxide.

ALPHA-CELLULOSE

To complete the series of experiments on the reaction of alkaline peroxide with the isolated groundwood components, a sample of commercial alpha-cellulose was subjected to the reaction conditions which were used with the previous holocellulosic materials. The alpha-cellulose is described on page 20. The experimental methods used were Method 1A, page 28, for total peroxide consumption, and Method 2A, page 34, for oxygen evolution. The reaction was carried out at pH level 11.0 and 5% consistency.

The peroxide consumption data for alpha-cellulose showed that the course of total peroxide consumption, and peroxide consumption due to decomposition, were almost identical for the entire 180-minute reaction period. The two sets of data had a slightly different peroxide concentration at the
end of the bleaching period, indicating that no more than 0.03 g./l.
peroxide might have reacted with the alpha-cellulose.

The residual peroxide for the total peroxide consumption of 
alpha-cellulose is plotted, on semilogarithmic paper, against time in 
Figure 66, Curve (a). It can be concluded that this total peroxide con-
sumption reaction is first order with a rate constant of 0.001 min.⁻¹. 
This is the lowest value for \( k_a \) obtained in the present investigation. In 
the case at hand \( k_a \) is equivalent to \( k_d \) because only decomposition is taking 
place. It is evident that alpha-cellulose or the materials formed from it 
during reaction with alkaline peroxide are very good stabilizers for the 
decomposition reaction.

The experiments on the reaction of alkaline peroxide with isolated 
groundwood components show that each of the materials exerted a pronounced 
stabilizing effect on the decomposition reaction. In the case of isolated 
holocellulose, the peroxide-holocellulose reaction was also inhibited. It 
was indicated that one or more of the carbohydrate materials in groundwood 
is responsible for the stabilizing effect of whole groundwood.

It was demonstrated that alkaline peroxide reacts very slowly, 
if at all, with alpha-cellulose and with a material containing higher-
molecular weight carbohydrates (representing holocellulose less about 17% 
of the hemicelluloses). Isolated holocellulose showed an active reaction 
with alkaline peroxide. However, this reaction could be due to residual 
lignin in the holocellulose. It can be concluded that the reaction of alkaline 
peroxide with the higher-molecular weight carbohydrates does not contribute 
in any significant amount to the total peroxide consumption during groundwood 
bleaching.
DISCUSSION

The experimental data presented for this investigation represent primarily a study of the kinetics of alkaline peroxide bleaching of spruce groundwood in relation to the individual reactions which contribute to peroxide consumption during the bleaching period. The color changes resulting from the bleaching process have been studied in detail, and the relation between groundwood bleaching reaction kinetics and these color changes has been established. The present discussion is intended to integrate the various phases of the investigation, and to consider the commercial peroxide bleaching process in the light of the information now available. The results of the experimental work apply, most directly, to bleaching under the conditions used in this investigation, i.e., low consistency (5%), a temperature of 35°C., 2% peroxide (as sodium peroxide), based on the weight of oven-dry groundwood, and a liquor prepared of c.p. chemicals without added stabilizers. However, the conclusions reached in this work are of a general nature and, with proper consideration, may be applied to all alkaline peroxide bleaching conditions.

The kinetic analysis of the bleaching reactions is based on an oxygen balance for the bleaching system. To establish such a balance it is necessary to measure any oxygen which might be formed from peroxide decomposing during the bleaching period. Preliminary experiments established the fact that oxygen, and only oxygen, is evolved from the bleaching system, and that the rate of this oxygen evolution could be determined satisfactorily with the experimental equipment used. It was found that oxygen is evolved from the bleaching system under all the experimental conditions used in this investiga-
tion. It was also established that some of the oxygen which is formed during the bleaching period is subsequently absorbed in the peroxide-groundwood mixture and is consumed in a non-bleaching oxidation reaction which proceeds simultaneously with peroxide oxidation. An evaluation of the amount and rate of oxygen consumption by this alkaline oxygen oxidation showed that such oxygen consumption could be adequately compensated for in measurements of the rate of oxygen evolution and in the establishment of an oxygen balance.

Other experimentation showed that groundwood and groundwood extracts have a decided effect on the rate of decomposition of alkaline peroxide solutions to oxygen. Groundwood and groundwood extracts act to stabilize alkaline peroxide solutions which are initially unstable. In the case of alkaline peroxide solutions which are stabilized with sodium silicate, magnesium sulfate, or both, decomposition is accelerated by the presence of groundwood. Experiments on the reaction of alkaline peroxide with isolated carbohydrate groundwood components indicate that it is these materials which are responsible for the stabilizing action of groundwood and groundwood extract on alkaline peroxide. There is some indication that the groundwood stabilizing effect increases with the pH of the peroxide solution.

Previous studies on the variables of the peroxide bleaching process have indicated that one of the most critical is alkalinity of the bleach liquor. From information on the chemistry of alkaline peroxide solutions, presented in the introduction to this work, it appears that the reason for the importance of pH in bleaching must be the fact that it controls the com-
position of the bleach liquor in free hydrogen peroxide and hydro-
peroxide ion. It is evident that changes in pH during the bleaching
period would complicate a kinetic analysis of the bleaching reactions.
Therefore most of the bleaching experiments in this investigation were
carried out at a controlled pH level. It was found that the hydroxyl-ion
concentration is extremely important in determining the course of the
reactions which take place in the process of bleaching. The effect of
pH was evaluated fully by making experiments at pH levels from 9.0 to 12.5.
Facts obtained in all phases of this investigation were carefully considered
and used to develop the theory of peroxide bleaching kinetics which is
presented below.

In an alkaline peroxide solution the composition of the bleach
liquor is determined by the equation

$$\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{OOH}^- + \text{H}_2\text{O}$$  \hspace{1cm} (1)

It can be seen that the concentration of free hydrogen peroxide ($\text{H}_2\text{O}_2$)
and hydroperoxide ion (OOH\(^-\)) depends on the concentration of hydroxyl ion
in solution, other conditions remaining constant. The proportions of each
of the constituents in the bleach liquor can be calculated for most of the
conditions which might be used in peroxide bleaching. The constants which
are necessary to such a calculation are available in the literature, and
their use has been demonstrated in this investigation. A complete discussion
of this equilibrium and the factors involved in the calculations is given
on page 9 et seq.
Extensive data were obtained on the rate of peroxide consumption during bleaching. These data indicated that, with experimental conditions chosen to inhibit abnormal peroxide decomposition, the rate of total peroxide consumption is of the first order with respect to peroxide for the entire reaction period and at pH levels from 9.0 to 12.0. Other investigators have shown that the rate of the bleaching reaction doubles for a reaction-temperature increase of 10°C, indicating that a chemical reaction controls the bleaching rate rather than diffusion or adsorption. The fact that the total peroxide consumption reaction is of the first order infers that the organic material which reacts with peroxide is in large excess and thus can be considered to be at constant concentration in so far as bleaching kinetics are concerned. It was demonstrated that total peroxide consumption is due to two reactions, the decomposition of peroxide to oxygen and the reaction between alkaline peroxide and groundwood. The rate of total peroxide consumption is defined by Equation (10).

\[
\frac{dn_{\text{total}}}{dt} = k_t n_{\text{total}}
\]  

(10)

The rate of total peroxide consumption is represented by the specific reaction-rate constant, \(k_t\). The value of \(k_t\) for the experimental conditions used increases from 0.004 min\(^{-1}\) at pH 9.0 to 0.029 min\(^{-1}\) at pH 12.0. The values of \(k_t\) may be interpreted as the fraction of remaining peroxide which is being consumed per minute of reaction time. It can be concluded that pH has a large effect on the rate of total peroxide consumption.

Determinations of the rate of oxygen evolution showed that this rate is also of the first order with respect to total peroxide consumption and can be expressed by Equation (7).
\[ \frac{dc_{\text{total}}}{dt} = k_d c_{\text{total}} \]  

(7)

The value of \( k_d \), the decomposition rate constant, varies between 0.009 \( \text{min}^{-1} \) to 0.011 \( \text{min}^{-1} \) over a pH range of 10.5 to 12.0. These values of \( k_d \) can be compared with values of 0.017 \( \text{min}^{-1} \) at pH 10.5 (initial) to 0.080 \( \text{min}^{-1} \) at pH 12.0 (initial) for experiments where no groundwood was present in the alkaline peroxide solution. The comparison demonstrates the effectiveness of groundwood in stabilizing bleach liquor which does not contain other stabilizers.

By deduction, it is apparent that the reaction between peroxide and groundwood must be first order with respect to total peroxide consumption, because the sum of the rates of peroxide consumption by the first-order decomposition reaction and by the peroxide-groundwood reaction must give the rate of total peroxide consumption, which was determined to be of the first order. Calculations of the rate of the reaction between peroxide and groundwood showed that this reaction conforms to first-order Equation (8).

\[ \frac{dc_{\text{total}}}{dt} = k_s c_{\text{total}} \]  

(8)

The value of the specific reaction-rate constant, \( k_s \), for the reaction between peroxide and groundwood increases from 0.010 at pH 10.5 to 0.019 at pH 12.0.

The first-order reaction-rate equations given above indicate that decomposition and the peroxide-groundwood reaction are of the first order with respect to total peroxide concentration. This total concentration includes both free hydrogen peroxide and hydroperoxide ion. It is not reasonable to suppose that both of these constituents take part in both reactions.
Experiments on the decomposition of alkaline peroxide without the presence of groundwood show that the decomposition reaction depends on the concentration of free hydrogen peroxide in solution. Therefore Equation (7) can be written:

\[
\frac{da_{H_2O_2}}{dt} = k_a a_{H_2O_2}
\]  

(6)

without changing the dependence of the rate of decomposition on the total peroxide concentration, because the concentration of free hydrogen peroxide is proportional to the concentration of total peroxide at a given pH level. It follows that the rate of free hydrogen peroxide consumption is proportional to the rate of total peroxide consumption due to decomposition.

Experiments with a high initial hydroperoxide-ion concentration indicated that this ion is responsible for the bleaching action of alkaline peroxide liquor. As above, first-order Equation (8) for the reaction of peroxide with groundwood can be written:

\[
\frac{da_{COH^-}}{dt} = k_{a} a_{COH^-}
\]

without changing the experimentally determined kinetic relationship.

As stated above, the rate of decomposition appears to depend on the concentration of free hydrogen peroxide, and the rate of the groundwood-peroxide reaction appears to depend on the concentration of hydroperoxide ion. However, it is most important to note that both free hydrogen peroxide and hydroperoxide-ion concentrations are proportional to the total peroxide concentration at all times during a reaction at a controlled pH level. Regardless of the rate at which either free hydrogen peroxide or hydroperoxide
ion is consumed, the equilibrium concentration of the two constituents is maintained by constant and instantaneous interchange of free hydrogen peroxide and hydroperoxide ion according to Equation (1). If this interchange were not taking place, the rate of total peroxide consumption, in antithesis to the experimental data, would not be of the first order. The point brought out by the facts emphasized above is that the relation between the amount (and rate) of decomposition and the amount (and rate) of the peroxide-groundwood reaction does not depend on the respective concentrations of free hydrogen peroxide and hydroperoxide ion, but depends entirely on the specific reaction-rate constants for the individual reactions.

As mentioned before, the specific reaction rate for total peroxide consumption increases markedly with an increase in pH level. The decomposition reaction, however, has about the same value of specific reaction rate at pH 10.5 to 12.0, when bleaching conditions are designed to eliminate abnormal decomposition. In this same pH range the specific reaction rate for the peroxide-groundwood reaction is almost doubled. It can be concluded that the increase in the rate of total peroxide consumption with increase in pH level is due, in large measure, to the increase in groundwood-peroxide reaction rate. Therefore it is evident that pH is an important factor in establishing the rate of the bleaching reaction. If the rate of bleaching is more rapid than the rate of decomposition, a larger portion of the total available peroxide will be used in bleaching. The ratio of the rate of decomposition to the rate of the peroxide-groundwood reaction decreases regularly with an increase in pH over the range 10.5 to 12.0; thus more bleaching should be obtained at a higher pH level.
The rate of the decomposition reaction was found to be appreciably higher in certain experiments where the bleaching procedure was such that the stabilizing effect of groundwood was not fully utilized at the start of the experiment. However, the rate of the peroxide-groundwood reaction was approximately the same as with well-stabilized experiments. This fact indicates that there is no interdependence between decomposition rate and peroxide-groundwood reaction rate.

As mentioned previously, the specific reaction rate of the peroxide-groundwood reaction increases with an increase in pH over the pH range 10.5 to 12.0, for which the constant was most accurately determined. The relation between pH and $k_o$ is almost linear over this range. It must be concluded that the reaction between hydroperoxide ion and groundwood is catalysed by hydroxyl ions since there is no other apparent reason for the dependence of $k_o$ on pH level. The fact that the specific reaction rate for the peroxide-groundwood reaction is decreased by the addition of materials which inhibit the hydroxyl-ion-catalysed decomposition reaction is an indication that bleaching is also hydroxyl-ion catalysed.

Information on the color changes which take place during bleaching was obtained in conjunction with the experiments designed for kinetic analysis of the bleaching reactions. These color change data consist of the development of C.I. brightness during the bleaching period and the spectral reflectance change over the same period, as determined on the CMRS. The study of color change showed that there is a reaction between groundwood and sodium hydroxide which results in the formation of a colored compound during the bleaching period, simultaneously with the increase in reflectance brought about by the oxidizing action of alkaline peroxide. The groundwood-
alkali reaction causes the color of groundwood to shift toward yellow as the bleaching reaction progresses, and causes reversion of brightness in some cases. In general terms it can be stated that it is the balance between bleaching and the shift toward a yellow color that determines the effectiveness of the peroxide which is consumed in reaction with groundwood. According to the kinetic analysis of bleaching, as the pH is increased the rate and amount of the bleaching reaction increases. This fact is reflected by the data on brightness development during bleaching. The shift of groundwood color toward yellow also increases with an increase in pH and, if the pH level is too high, this color shift will cancel the brightness increase which is due to the bleaching reaction. The effect of the groundwood-alkali reaction is more pronounced toward the end of the bleaching period, apparently because the presence of appreciable peroxide in the bleaching solution inhibits the reaction between groundwood and sodium hydroxide. The most effective bleaching under the conditions used in this investigation (2% peroxide, controlled pH level, c.p. liquor) was obtained at pH 11.0. At this pH level the peroxide-groundwood reaction was fast enough in relation to the decomposition reaction to give appreciable bleaching in the first one third of the bleaching period. On the other hand, the pH level was not high enough to produce excessive color shift and the accompanying brightness reversion. It should be pointed out that the bleaching reaction, as measured by brightness increase, appears to stop during the reaction period in some cases. The spectral reflectance curves, however, show that the reaction of peroxide with groundwood continues to increase reflectance in some portion of the spectrum as long as appreciable peroxide is present in the bleach liquor.
The influence of sodium silicate on the peroxide bleaching reactions has been considered at pH level 11.0. The results of this study show that sodium silicate will inhibit both the decomposition and peroxide-groundwood reaction without changing the reaction mechanisms involved in the bleaching process. The decreased rate of the peroxide-groundwood reaction resulted in a diminished rate of brightness increase. The addition of silicate to the bleach liquor had no other apparent effect on pulp color.

Experiments which were carried out with isolated carbohydrate groundwood components indicated that there is little or no reaction between the higher-molecular weight carbohydrates and alkaline peroxide. However, the bleach liquor appears to react with some of the more alkaline-soluble hemicelluloses. Hemicellulose in contact with an alkaline peroxide solution showed a decided inhibitive effect on both the decomposition and hemicellulose-peroxide reactions.

It is interesting to consider the course of a commercial-type peroxide bleach in the light of the information on bleaching reaction kinetics which has been presented in this investigation. Bleaching variables and the rate of peroxide consumption during commercial alkaline peroxide bleaching have been considered by several investigators (1, 2, 3), and their publications can be used as references. The experiments in this investigation made without pH control (page 65) are similar in character to commercial bleaches.

Peroxide consumption in commercial bleaching is characterized by a rapid initial rate of indeterminate order. From the data presented in this investigation it is evident that this reaction is first order for any given instantaneous pH value and peroxide concentration. However, because the pH decreases continuously during a commercial bleach, it follows that the specific
rate of the peroxide-groundwood reaction must also decrease, producing a reaction of indeterminate order and decreasing rate. It must also be considered that the bleach is initiated by the addition of an alkaline peroxide solution of a higher pH than that desired for the peroxide-groundwood mixture. The stock bleach liquor contains, therefore, a high concentration of hydroperoxide ions which are rapidly consumed in the short period during which equilibrium is established. Stobo and Russell (2) have noted that the peroxide consumption reaction becomes first order after the completion of the so-called rapid initial reaction. Their data show that the bleaching solution was fairly well buffered, with the pH approximately constant by the time the peroxide consumption became first order. These authors assumed that only decomposition was taking place during the first-order reaction. However, their data confirm the facts, as shown in this investigation, that the peroxide-groundwood reaction continues throughout the bleaching period and is of the first order at a given pH level, because they obtained further brightness increase during the period of the first-order reaction.

From the standpoint of color change, the advantage of bleaching without controlling the pH is quite apparent. The bleach can be started at a relatively high pH level to take advantage of a high reaction rate between peroxide and groundwood at a time when the concentration of peroxide is appreciable, and consequently brightness reversion due to alkali is not objectionably large. As the bleach continues, peroxide is consumed, and the pH decreases to a buffered value. At this lower pH level further peroxide can be consumed in bleaching without the excessive brightness reversion which would have resulted if the entire bleach had been carried out at the initial
pH level. Thus, by proper selection of the initial pH, it is possible to obtain the maximum brightness for a given amount of peroxide consumption. Another factor to be considered is that the ratio of peroxide decomposed to peroxide used in bleaching will be greater as the pH decreases. Therefore the buffered pH level reached during the bleaching period could be too low to obtain the most effective bleaching from the peroxide remaining in the bleach liquor at this point.

A fact which has been noted frequently in connection with the commercial peroxide process is that maximum brightness increase is obtained in a specific, narrow initial pH range. The data on color change presented in this work show that the phenomenon of an optimum pH for maximum brightness increase arises from a balance of the increased brightness obtained by more and faster peroxide consumption with increasing values of initial pH, against brightness reversion, which also increases with an increase in the pH of the system.

It can be concluded from the preceding discussion that the present study of peroxide bleaching provides a better basis for the consideration of the chemistry of peroxide bleaching than was hitherto available. It is suggested that the procedures followed in this investigation could be applied to individual bleaching problems. The equipment necessary for obtaining comparative oxygen evolution and peroxide consumption data is neither complicated nor expensive. Oxygen evolution and peroxide consumption data, obtained for a series of pH levels and simulating the desired conditions as nearly as possible, can be more easily evaluated than data obtained from a series of bleaches made by the usual commercial procedure. The disadvantage
of the procedure followed in this investigation is that it is difficult to apply at high consistencies.

The results obtained in the present study of the kinetics of peroxide bleaching indicate that further investigation could be carried out to advantage. It has been pointed out that the peroxide-groundwood reaction appears to be catalysed by hydroxyl ion. A study of this catalytic reaction, especially with respect to materials which might promote or inhibit the catalysis, would seem to constitute a good starting point for further investigation.
CONCLUSIONS

Several conclusions can be drawn from the experimental results of the present investigation. In general these conclusions can be considered to apply to low-consistency peroxide bleaching. However, it should be borne in mind that these conclusions are based on data obtained under experimental conditions which differ somewhat from those used in commercial peroxide bleaching.

1. Gaseous oxygen is evolved during peroxide bleaching as the result of the decomposition of alkaline peroxide. The amount of decomposition can be varied by changing the bleaching conditions. Even with the use of stabilized bleach liquors a significant amount of peroxide decomposition takes place.

2. The presence of groundwood pulp inhibits the decomposition of unstable alkaline peroxide solutions (the c.p. liquor used in this investigation). However, alkaline peroxide solutions which contain sodium silicate and magnesium sulfate as stabilizers decompose more readily in the presence of groundwood than when groundwood is not present.

3. Under specific experimental conditions, including a controlled pH level, the rate of total peroxide consumption is kinetically of the first order. Of the two reactions which make up the total peroxide consumption, the decomposition reaction is first order with respect to the free hydrogen peroxide concentration of the bleach liquor, and the peroxide-groundwood reaction (the bleaching reaction) is first order with respect to the hydroperoxide-ion concentration of the bleach liquor. The decomposition and
peroxide-groundwood reactions are also of the first order with respect to the total peroxide concentration because the concentrations of hydrogen peroxide and hydroperoxide ion are directly proportional to the total peroxide concentration at a given pH level. The above conclusion has been demonstrated to apply from pH 10.5 to 12.0, and probably applies from pH 9.0 to 12.0.

4. The rate of total peroxide consumption increases with an increase in pH from 9.0 to 12.0, due, in large part, to an increase in the rate of the peroxide-groundwood reaction. The rate increase of the peroxide-groundwood reaction is practically linear with a pH increase from 10.5 to 12.0. The dependence of the rate of the peroxide-groundwood reaction on pH level indicates that it is hydroxyl-ion catalysed. The rate of peroxide decomposition also increases with increasing pH, but this effect is minimized by the stabilizing action of groundwood pulp (with c.p. liquor). The decomposition rate constant is not proportional to the hydroxyl-ion concentration.

5. The amount of peroxide which is consumed in reaction with groundwood depends upon the relation between the rates of the decomposition and the peroxide-groundwood reactions.

6. O.E. brightness development during bleaching is dependent on the rate and amount of the peroxide-groundwood reaction if the alkaline reversion effect is not considered.

7. The color of groundwood pulp may shift toward yellow as bleaching progresses, because of a reaction between sodium hydroxide and groundwood.
The color shift is more pronounced at higher pH levels (11.5-12.5).

8. The reaction between peroxide and groundwood produces an increase in reflectance in some portion of the spectrum in almost all cases. However, because of alkaline reversion, this reflectance increase is not always a G.E. brightness increase.

9. Alkaline reversion is minimized by allowing the pH to follow its natural course during bleaching.

10. The addition of sodium silicate to c.p. bleach liquor decreases the rate of both decomposition and the peroxide-groundwood reaction (as compared with the rates obtained with c.p. liquor) without an apparent change in the mechanism of these reactions, and without producing abnormal effects on the brightness and color of the pulp.

11. Carbon dioxide is formed during the peroxide bleaching of groundwood. The reaction of molecular oxygen in alkaline solution with the organic materials in the bleaching system is responsible for at least part of the carbon dioxide formed; alkaline peroxide oxidation may also be partially responsible. The amount of carbon dioxide formed during bleaching is not enough to produce the pH drop which is observed in the commercial process (for the most part, the pH drop is probably due to the saponification of the acetyl groups in groundwood).

12. The reaction of alkaline peroxide with hemicelluloses may be responsible for part of the peroxide consumed by the peroxide-groundwood reaction. The reaction of peroxide with carbohydrates which are less reactive than hemicellulose appears to be negligible under the experimental conditions used in this investigation.
LITERATURE CITED


