# THE ACTION OF CHLORINE
AND ITS
DERIVATIVES ON LIGNIN

# THE ACTION OF CHLORINE AND ITS DERIVATIVES ON LIGNIN

By

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A thesis presented to the Faculty of
Graduate Studies and Research of McGill
University in partial fulfilment of the
requirements for the Degree of Doctor
of Philosophy.

McGill University,
Montreal. 1936.

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# ACKNOWLEDGMENTS

The writer wishes to express his gratitude to

Dr. Harold Hibbert

under whose direction this investigation was carried out, for his continued interest and support.

Acknowledgment is made to the Howard Smith Paper Mills for the award of a Fellowship, during the tenure of which this investigation was carried out, and to

Mr. G. H. Tomlinson.I.

Technical Director for the company who has been in constant touch with the problem.

Acknowledgment is also made to the United States Bureau of Standards and to

Dr. S.F.Acree

under whose guidance the writer became acquainted with the use of the Glass Electrode as a means of measuring hydrogen ion concentration.

# GENERAL INTRODUCTION

## Chemical Constituents of Plants; The Occurrence of Lignin.

The plant, by an unknown mechanism which involves the assimilation of Carbon Dioxide, Water and Energy (Sunlight) is able to transform these into both simple and complex compounds. The former embrace the simple carbohydrates, for example, mannose, glucose and galactose, while the latter consist of two classes of compounds, namely, the polysaccharides and lignin. Polysaccharides represent polymerized pentose or hexose anhydrides, for example, pentosans, cellulose and starch; while lignin which comprises about 30% of all woods is a substance of unknown composition.

## Chemistry of Plant Products.

The chemical constitution of the natural products, cellulose, pentosans and lignin which form the bulk of plant tissues has interested scientific investigators for several decades.

The chief difficulty in the investigation of this field lies in the permutoid character of the substances in question. As colloidal compounds, highly polymerized, and difficultly soluble in common reagents, their isolation, purification and stoichiometric reaction are matters of great difficulty. Much conflicting literature has in consequence arisen which is extremely difficult of evaluation.

## The Role of Cellulose in Industry.

Cellulose is of great importance industrially and its use as a raw material is continually increasing. It is essential to the Cotton, Paper, Rayon, Explosive and Lacquer industries, forming in all cases the basis of the finished product. Its isolation from whatever source, and in greatest purity, is a problem of prime importance.

## The Role of Lignin in Industry.

The commercial production of cellulose from plant products involves the removal of the other plant constituents, or encrustants, as they are sometimes called. This can be done either by kier boiling or by digester cooking. The former applies to the dilute caustic treatment of textile fibres while the latter takes the form of either an acid treatment ($NaHSO_3$ + $H_2SO_3$) for coniferous woods or an alkaline treatment ($NaOH$ or $NaOH$ + $Na_2S$) for both coniferous and deciduous woods.

Lignin is the encrustant most difficult of removal and the above treatments are usually followed by bleaching with chlorine and hypochlorite solutions, Lignin may therefore be regarded as a by-product in the cellulose industry whose commercial utilization offers much of interest.

## Object of the present Investigation.

As mentioned above, the final chemical treatment in the production of cellulose, either in the form of raw cotton, or of wood pulp, involves the use of bleaching agents. These are employed in such a manner as to bring about the removal of the lignin and other non-cellulosic materials with a minimum degradation of the cellulose. Since this removal is effected industrially by the use of chlorine and hypochlorite solutions it is necessary to have as clear an understanding as possible of the changes which take place when these reagents act upon cellulose and upon lignin. Such a study should lead to, a) better control of the bleaching process, b) higher yield of pure cellulose, and, c) a considerable reduction in chlorine consumption, as well as provide more definite information relating to the structure of lignin.

## Action of Chlorine and Hypochlorite solutions upon Cellulose.

The action of hypochlorite solutions upon cellulose results in the formation of Oxy-cellulose. Nastukoff (1) found that when cellulose, in the form of filter paper, was treated with hypochlorite solution a compound was formed containing more oxygen than the original cellulose. This compound was termed by him "Oxy-cellulose" and contained one more oxygen atom for every four to six $C_6H_{10}O_5$ groups than cellulose. Jecusco (2) also noted the oxidizing action of hypochlorite solutions upon cellulose.

The more recent researches of Birtwell, Clibbens and Ridge (3) who have studied the action of chlorine and hypochlorite upon cellulose in solutions of varying hydrogen ion concentration are especially valuable. The changes brought about in the cellulose were measured by the changes in the Methylene Blue absorption and in Copper number. Birtwell and co-workers found that the Methylene Blue absorption increased as the pH of the medium increased and reached a maximum at pH 10 - 12. The Copper number on the other hand decreased with increasing pH to a minimum at pH 10 - 12. The rate of change in both cases was most rapid in the neighborhood of pH 7. The authors concluded that the progressive changes in the properties of hypochlorite oxy-cellulose, accompanying changes in hydrogen-ion concentration, were probably due to the equilibrium changes in the hypochlorite solutions. The latter can be considered to contain three oxidizing agents - hypochlorous acid, hypochlorite ion, and free chlorine - but the ratio of the contents of these three varies with the hydrogen-ion concentration. Hypochlorite ion is, for practical purposes, the only oxidizing agent present in alkaline solutions, chlorine in acid solutions, and hypochlorous acid in the range of hydrogen ion concentration near the neutral point. The hypochlorite solutions of pH 4.6 - 2.7, which yield a maximum copper number, contain HOCl as the sole oxidizing agent. The fall in copper number which occurs in still more acid solution coincides with the rapidly increasing concentration of free chlorine. Solutions of pH 10 - 11 which yield a maximum methylene blue absorption contain only hypochlorite ion as the oxidixing agent.

Further information relating to the formation and properties of oxy-cellulose is to be found in the very complete bibliography on this subject by[7] Birtwell and co-workers.

## Action of Chlorine and Hypochlorite solutions upon Lignin.

The action of these reagents upon lignin has been investigated by several workers and, since their results are related to the present investigation the subject is made a separate section in the Historical Review.

Modern views on the mechanism of bleaching wood cellulose together with the more recent patents dealing with the bleaching process and the results of the present investigation are given in the chapter, "Bleaching of Wood Cellulose".

## HISTORICAL REVIEW

Since this thesis is concerned primarily with fundamental data relating to the bleaching of wood pulps, the previously established facts regarding the structure of lignin are of especial importance.

In view of the recent literature surveys on Lignin by Freudenberg (17) and especially by Phillips (4), no extensive review of lignin chemistry will be given. These authors point out quite clearly the marked lack of fundamental experimental data on which to base a sound knowledge of the structure of lignin.

Concerning the structure of lignin, apart from its elementary composition (carbon, hydrogen and oxygen), there is only relatively slight information. Definite evidence exists as to the presence of methoxyl and hydroxyl groups and at least one aromatic nucleus. The existence of methoxyl groups is shown by the formation of methyl iodide on treatment with HI. Lignin can be methylated and acetylated with ease, and the acetylated product hydrolysed with reproduction of the hydroxyl group. Apparently also, some of both the methoxyl and hydroxyl groups are attached to different types of carbon atoms. A yield of about 8% crystalline vanillin (5), obtained by alkaline treatment of ligno-sulphonic acid establishes the presence of the aromatic ring.

The present review will deal only with such aspects of the subject as are germane to the present study.

The properties of lignin, because of its amorphous, colloidal nature, vary greatly with the method of isolation used so that none of the known methods can be considered as ideal and no lignin preparation regarded as identical with that native in the plant.

The gradual co-ordination of dependable and reproducible data on the various preparations is, however, slowly leading to a final elucidation of the problem.

In the present investigation alkali lignin was chosen as starting material because,

(i) it most closely approches the residual lignin in alkaline pulps,

(ii) it is readily obtained in reproducible form, and,

(iii) it is readily soluble in many organic solvents and in aqueous solutions containing $OH^-$ ion.

The preparation and properties of alkali lignin, dating from the original work by Lange (7) to the present, have been exhaustively reviewed by Marshall in these laboratories (18). The more important of these investigations, and especially those of interest to the present problem are discussed in the following pages.

## Review of Alkali Lignin

### A Review of the more important investigations concerning the Isolation and Properties of Alkali Lignin.

Following the researches of the earlier investigators, Lange (7), Streeb (8), and Holmberg and Wintzell (10), a series of experiments was carried out by Beckmann, Liesche (11) and Lehmann in order to determine the most satisfactory conditions for the extraction of lignin. They treated different kinds of straw and wood with alkali under controlled conditions of temperature, pressure, time and concentration. Each succeeding extraction was made more drastic than the previous one. They found that most woods required several treatments with 1.5% NaOH solution at temperatures varying from 165°C to 180°C for several hours in order to obtain complete extraction. The amount of lignin from each extraction was determined by acidifying the liquor extract and weighing the precipitate.

The fractions isolated became darker in color as the extraction temperature was increased, the methoxyl content also increased and the solubility in organic solvents decreased. Doubling the alkali concentration practically doubled the yield under the same extraction conditions. Over a moderate range the alkali concentration had no effect on the properties of the extracted lignin.

In order to obtain a lignin isolated under the mildest possible conditions they treated winter rye straw with an aqueous alcohol (60%) solution of NaOH (2%) for 48 hours at room temperature. (Alcohol prevents the solution of Pentosans) The free alkali was then neutralized with HCl, the alcohol distilled off, and the lignin precipitated with acid. Three extractions gave a total lignin yield of 7% based on the weight of original material. The residual straw still contained 15% lignin (Willstätter HCl method) but was not investigated further.

The lignin isolated gave the following analysis;

| | | |
|---|---|---|
| Carbon - - - - - - | 62.1% | 63.0% |
| Hydrogen - - - - - | 5.4% | 5.8% |
| Methoxyl - - - - - | 14.3% | 15.8% |
| Calculated formula - - - | $C_{40}H_{44}O_{15}$ | |
| Mol. Wt. (Freezing point method in phenol) - | 756 - | 1056 |
| (Boiling point method in g. acetic acid) | 768 - | 891 |

The sodium salt contained somewhat more than two atoms of sodium.

Methylation established the presence of four hydroxyl groups so that the formula could be expanded to $C_{36}H_{28}O_7(OCH_3)_4(OH)_4$.

Mehta (12) has made a very thorough investigation in order to determine the conditions for the complete resolution of the ligno-cellulose in wood into its components by the use of aqueous alkaline solutions under pressure. The same conditions have been extended to the preparation and quantitative estimation of lignin. The hydrolysis of Lignocellulose with 5 - 10% NaOH only proceeded to 15 - 20% completion at ordinary pressures (100°C); at higher pressures this amount increased rapidly. Similarly when the pressure was kept constant and the strength of alkali varied the hydrolysis increased with the strength of the alkali up to a maximum, beyond which decomposition of the lignin took place. The exact conditions were established by carrying out a number of cooks using NaOH solutions varying from 1 - 15% concentration at 2.5 (139°C) and 3.0 (144°C) atmospheres pressure. The resulting alkaline extract was filtered, diluted to 250 cc. and a 50 cc. aliquot portion precipitated with concentrated HCl. The lignin was filtered off, washed free of chlorides and dissolved in 95% alcohol. The alcohol solution was filtered evaporated to dryness and the yield of lignin calculated from the weight of dry residue.

It was found that maximum extraction was obtained with a four percent solution of sodium hydroxide at either pressure. In a further series of experiments the alkali concentration was kept constant at 4% and the pressure varied from 1 - 16 atmospheres (100°C - 205°C).

The results showed that the extraction of lignin was practically complete at pressures above 10 atmospheres (185°C).

Cellulose remains practically unattacked at this temperature while at lower temperatures much longer periods were necessary for the complete extraction of the lignin.

Mehta also stated that no decomposition of the lignin had occurred during isolation since the product was not attacked by further treatment under the same conditions and could be quantitatively recovered. The lignin content of different woods by this method are lower than that given by either the Willstätter or Klason methods. Neither of these methods is regarded as being completely satisfactory however and Mehta contends that the determination of lignin content by alkaline extraction gives more accurate and reliable results.

The lignin prepared under these conditions is a light brown powder, insoluble in water, soluble in dilute alkalies, alcohol, acetone and acetic acid. It has practically no reducing power, gives no test for pentosans (phloroglucinol-HCl) melts without decomposition at 167°C-169°C and shows somewhat more pronounced acidic properties than phenol. Insoluble barium and calcium salts can be isolated by precipitation in high yield. These properties tend to indicate the homogeneous nature of Mehta's alkali lignin.

Powell and Whittaker (13)(14) conducted a more fundamental research on the structure of alkali lignin isolated from several different woods and from flax shives. The lignin products were obtained by digesting the chipped wood with aqueous 8 - 12% NaOH for 6 - 8 hours at 140 - 160°C. The filtered extract was treated with a slight excess of HCl and the precipitated lignin washed with dilute, hot HCl, centrifuged and dried. The yield from flax shives was about 21%.

The crude lignin contained about 0.9% pentosans which were removed by the precipitation of an acetone solution of the crude substance into hot 20% HCl. After several such treatments no test was obtained for pentosans (distillation with 12% HCl and precipitation of the furfuraldehyde with phloroglucinol-HCl). The final purification was carried out by dissolving the lignin in NaOH solution and fractionally precipitating with HCl. The four fractions isolated gave identical analyses. Since these agreed fairly well with those recorded by Dorée and Hall (15) for a ligno-sulphonic acid Powell and Whittaker concluded that their product was homogeneous.

The alkali lignin obtained was an amorphous, light-brown powder, insoluble in water, acetone and acetic acid but soluble in mixtures of acetone-water and acetic-acid-water. It showed acidic properties being soluble in dilute alkalies and formed insoluble salts with various metallic ions.

An acetyl derivative was prepared which was insoluble in cold NaOH indicating that the acidic properties of the lignin were due to phenolic hydroxyl groups. Moreover, as is typical of phenolic esters, the acetyl groups were readily hydrolysed with boiling water. A fully methylated derivative could not be prepared. A phenyl hydrazone and a nitro compound are also described. The work on halogenation will be discussed later.

From the results of their work on lignin products from six different types of wood Powell and Whittaker concluded that lignins from different natural sources represent derivatives of the same poly-hydroxy compound and differ only in the number of methoxyl groups which they contain. This hypothetical mother substance was termed by them "Lignol"; it contains nine hydroxyl groups and is represented by the empirical formula $C_{38}H_{30}O_4(OH)_9CHO(CO_2)_2$. Attempts to isolate this substance by treatment of lignin with HI were not successful.

The value of the researches of Dorée and Barton-Wright (16) are greatly enhanced by the fact that they used a carefully purified wood meal as their source of lignin. The spruce wood meal was extracted with a benzene-alcohol mixture, then with water and finally subjected to four successive treatments with a 5% NaOH solution for 36 hours at room temperature. (Friedrich and Diwald method for hemi-cellulose extraction. (27); The lignin was isolated by the method recommended by Mehta (12) namely; the wood meal was heated in an autoclave with a

4% NaOH solution for one hour at 8 atmospheres. The alkaline extract was filtered, the lignin precipitated by addition of HCl, washed by decantation and dissolved in 95% alcohol. The alcoholic solution was filtered and evaporated to dryness. The lignin was purified by dissolving the alcoholic residue in glacial acetic acid and precipitating into water. This process was repeated until the melting point of a sample became constant at 185-186°C. The product was then filtered, washed and dried at 60°C.

The lignin so obtained was a light brown powder, readily soluble in organic solvents and in aqueous solutions containing $OH^-$ ion. It could be quantitatively precipitated from the latter by the addition of acids.

From the analyses of the benzoyl, acetyl, and methoxyl derivatives Dorée and Barton-Wright concluded that alkali lignin contained two methoxyl groups and one hydroxyl group. The analysis of the pure product corresponded to the formula $C_{20}H_{20}O_6$. The molecular weight, determined in glacial acetic acid and in napthalene, showed that this formula represented the molecular building unit and the product was named by them "metalignin".

They also prepared an oxime corresponding to two carbonyl groups. One of these was assumed to be ketonic, the other aldehydic. The phenyl hydrazone could not be prepared.

On the basis of their results they suggested an expanded formula for "metalignin" viz. $C_{16}H_{12}O(OH)(OCH_3)_2(CHO)(CO)$.

Dorée and Barton-Wright also point out that when the various lignin formulae which have been proposed are reduced to a basic hydroxylic compound a remarkable similarity exists. It is suggested that "metalignin" is the unit from which the natural lignins are derived.

In these laboratories, Marshall (18), using the method described by Mehta, has prepared an alkali lignin which he separated into two fractions A and B. The methoxyl content of fraction B is about 1% lower than that of fraction A. A series of experiments (methylation, acetylation and preparation of phenol derivatives) was performed upon these two fractions and from the analytical data obtained conclusions were drawn as to the number and nature of the hydroxyl groups in alkali lignin; empirical formulae for both alkali lignin fractions and for their phenol derivatives were derived.

Such portions of the above research as are relevant to the present investigation are given below in detail.

After several preliminary investigations Marshall found that the most satisfactory extraction of lignin from wood was obtained when the conditions outlined by Mehta (12) were adhered to. A carefully purified wood meal was heated in a closed iron bomb for one hour at 172°C. The contents of the bomb (after cooling) were filtered and the lignin precipitated from the alkaline extract by the addition of HCl. After centrifuging and dialysing the lignin was sucked to a thick moist paste on a Büchner funnel and dissolved while still moist in dioxan.

N. B. Marshall notes in his preliminary experiments that the centrifuged, dialysed product was not completely soluble in dioxan and has given the methoxyl content of this material. He does not mention its presence however when Mehta's procedure is followed. Further reference will be made to this insoluble portion in the Experimental part.

The residual water was removed from the dioxan-lignin solution with anhydrous sodium sulphate. The dried solution, concentrated to approximately 10% alkali lignin was precipitated dropwise into well stirred ether.

By this method of purification, the crude alkali lignin was separated into two fractions; Fraction I, a dioxan-ether insoluble material, was designated as alkali lignin A; Fraction II, a dioxan-ether soluble substance named alkali lignin B. The separation into these two fractions was only complete after four or five successive precipitations of the crude product into ether.

Alkali lignin A had a methoxyl content of 15.0%. The fact that three separate wood meal extractions gave products of the same methoxy content after purification was considered to be good indication that the material was at least a homogeneous mixture if mot a true chemical compound.

The analysis of alkali lignin A is given as;

| | C % | H % | $OCH_3$ % |
|---|---|---|---|
| Calculated $C_{67}H_{71}O_{23}$ | 64.6 | 5.8 | 15.0 |
| Found | 64.5 | 5.6 | 14.9 |
| | 64.7 | 5.8 | 14.9 |
| | 64.7 | 5.7 | 14.9 |

The ether-dioxan soluble fraction was obtained by concentration of the combined ether solutions from the precipitation of alkali lignin A,and precipitated dropwise into well stirred 1:1 ether: petroleum ether. The product was redissolved in dioxan and precipitated into benzene. After several precipitations a product of constant methoxyl content was obtained.

The formula for alkali lignin B, calculated from the carbon and hydrogen analysis and transformed to the same oxygen basis as in the case of alkali lignin A is given as $C_{68}H_{67}O_{23}$, a difference of one carbon atom and four hydrogen atoms as compared with that of alkali lignin A. Such a small difference is well within the limits of experimental error considering the large size of the molecule.

However, Marshall found that his alkali lignin B had a methoxyl content of only 14.0% as compared with 14.9% required by the formula $C_{68}H_{67}O_{23}$ for six $OCH_3$ groups. He therefore assumes that alkali lignin B possesses but five $OCH_3$ groups in which case the formula for alkali lignin B becomes $C_{108}H_{107}O_{37}$ as the smallest unit containing simple whole number oxygen atoms. The analysis of alkali lignin B is given as,

| | | C % | H % | $OCH_3$ % |
|---|---|---|---|---|
| Calculated | $C_{68}H_{67}O_{23}$ | 65.2 | 5.4 | 14.9 |
| | $C_{108}H_{107}O_{37}$ | 64.9 | 5.4 | 14.0 |
| Found | | 65.0 | 5.4 | 14.1 |
| | | 65.0 | 5.5 | 14.0 |

In the present investigation these two lignin fractions were not obtained. The argument against the definite existence of two such compounds will be given later.

## Action of Halogens upon Lignin

### Review of previous Investigations concerning the Action of Halogens on Lignin.

It was early noted that chlorine and bromine, and their oxygenated derivatives reacted readily with lignin and a large amount of literature has accumulated on this subject. The various investigators have used lignin preparations isolated by several of the well known methods and have treated them with halogens under widely different conditions. In the present survey a classification as regards reaction medium is proposed as a suitable basis for the presentation of the views of the authors.

### 1. Action of $PCl_5$, $SbCl_5$, and $SOCl_2$ on Lignin

The action of these reagents upon lignin has contributed little knowledge as regards lignin structure. Paschke (19) using a straw lignin, isolated by means of aqueous sodium carbonate solution, found that $SOCl_2$ at room temperature gave a compound $C_{37}H_{42}S_3Cl_3O_{12}$.(12.1% Cl) which contained no methoxyl groups. When the reaction was carried out in a sealed tube at 100°C for one hour the compound $C_{36}H_{48}Cl_{11}O_{10}$. (38.2% Cl) was obtained. The derivative

$C_{38}H_{46}Cl_5O_{15}$ (19.2% Cl), was obtained by the action of two parts $PCl_5$ in tetrachloroethane upon lignin.

Tropsche (20) using $SbCl_5$ found that lignin dissolved on boiling and that perchloroethane and hexachlorbenzene could be isolated from the reaction products.

## 2. Action of Halogens upon Lignin in Carbon Tetrachloride.

Powell and Whittaker (14) treated an alkali lignin, isolated from flax shives, with both chlorine and bromine in dry $CCl_4$. In each case a product could be isolated containing 12 halogen atoms on the basis of the building unit shown below. HCl was given off during the reaction and they concluded that substitution of halogen as well as addition had occurred.

The analysis and formula of the alkali lignin used is given as,

| | | C % | H % | $OCH_3$% |
|---|---|---|---|---|
| Calc. | $C_{41}H_{26}O_7(OCH_3)_4(OH)_5$ | 64.4 | 5.1 | 14.8 |
| Found | | 63.9 | 5.8 | 14.9 |

The analysis and formula of the corresponding chloro-lignin is given as, $C_{40}H_{20}O_8Cl_{12}(OCH_3)_2$.

The halo-lignins, as isolated, were found to be unstable and six halogen atoms could be replaced by hydroxyl groups by boiling with NaOH solution. The presence of the latter was shown both by methylation and acetylation and they concluded therefore that the halogen atoms taken up could be classified as loosely and firmly bound.

It is to be noted that the methoxyl content of the chlorolignin, calculated from the above formula, is 5·1%, that of the original lignin being 14.9%. The introduction of 12 chlorine atoms does not entirely account for this loss of methoxyl although Powell and Whittaker make no mention of the fact.

Phillips (21) chlorinated a lignin isolated from corn cobs, according to the procedure used by Powell and Whittaker(14).

The lignin used was isolated by the method of Beckmann Liesche and Lehmann (11) and compared favourably in its reactions with the lignin isolated by them as well as with that used by Powell and Whittaker. The formula for the three preparations is given in Table A.

Table A

| Beckmann, Liesche and Lehmann (11) Lignin obtained from rye straw. | Phillips (21) Lignin obtained from corn cobs. | Powell and Whittaker Lignin obtained from flax shives. |
|---|---|---|
| $C_{40}H_{44}O_{15}$ | $C_{40}H_{44}O_{16}$ | $C_{45}H_{48}O_{16}$ |

Phillips concluded from his results that lignin from corn cobs contained three methoxyl groups and at least four hydroxyl groups for each building unit $C_{40}H_{44}O_{16}$. The methoxyl analysis was 12.0% $OCH_3$.

The chlorinated product corresponded to the formula $C_{40}H_{36}O_{16}Cl_{10}$(32.1% Cl). Since no methoxyl analysis is given for this product it is to be concluded that no loss occurred on chlorination. This follows from the fact that the number of carbon and oxygen atoms in the formula for chlorolignin is the same as that present in the original lignin formula.

Fuchs and Horn (22) investigated the action of bromine upon an acetylated spruce wood meal. Brominations were carried out at 100°C for 25 minutes in dry $CCl_4$. They found that a definite amount (6%) of bromine was taken up, two-thirds of which could be removed easily by shaking with sodium acetate solution (5%), the bromine content of the reacetylated, de-brominated compound (A) being 2%. The lignin isolated by hydrolysis, with methyl alcohol HCl, of the 6% bromine product contained 11% Br.

Re-bromination of (A) under the same conditions gave a product (B) containing 9% Br., three-fifths of which was readily removed by shaking with sodium acetate solution leaving a bromine content of the reacetylated twice de-brominated compound of 3.5%. The lignin, isolated by methanol HCl hydrolysis of the product from the second bromination contained 17.8% Br.

No reaction was obtained on further bromination of (B). The authors assumed that no reaction took place with the acetylated cellulose and concluded that the above reactions are indicative of a tetrahydro-benzene ring in lignin. In the first bromination they postulate the addition of three bromine atoms. One of these is substituted in the lignin molecule while two are added on to a double bond. The removal of these two latter as HBr with sodium acetate resulted in the formation of two double bonds. Upon re-bromination of this compound four bromine atoms were taken up, of which only three were readily removed with sodium acetate.

These reactions, and the fact that the bromine content is not increased on further bromination are taken as evidence for the existence of the tetra-hydro-benzene ring. A long open chain or a polymethylene ring would brominate further.

Recently, Harris, Sherrard and Mitchell (23) have published the results of an extended investigation into the properties of Maple and Spruce lignins, these being isolated by the 70% Sulphuric acid method. From a study of the methylated and acetylated derivatives these authors postulate a building-unit with a molecular weight of approximately 800 for Spruce lignin and containing a total of ten base hydroxyl groups. For Maple lignin a unit of 1800 is chosen containing a total of twenty base hydroxyl groups.

It was found that Maple lignin combined with less chlorine than Spruce lignin. The former on treatment with chlorine in $CCl_4$ gave a product analysing 8.7% OMe; 19.8% Cl.

Calculated on a basis of 1440 this corresponds to 4 methoxyl groups and 8 chlorine atoms. The product loses HCl readily on exposure to air leaving a compound with 4 methoxyl groups and 7 chlorine atoms per building unit. Treatment with 5% NaOH gave an alkali chloro-lignin containing 4 chlorine atoms and 4 methoxyl groups per unit together with an 8% yield of chloroform.

In the case of Spruce lignin, chlorination in dry $CCl_4$ gave a product analysing 6.1% OMe and 27.5% Cl, which is equivalent to 2 methoxyl groups and 8 chlorine atoms per unit molecular weight of 1030. The action of 5% NaOH on this product also yielded an alkali chloro-lignin containing 2 methoxyl groups and 4 chlorine atoms per unit together with chloroform.

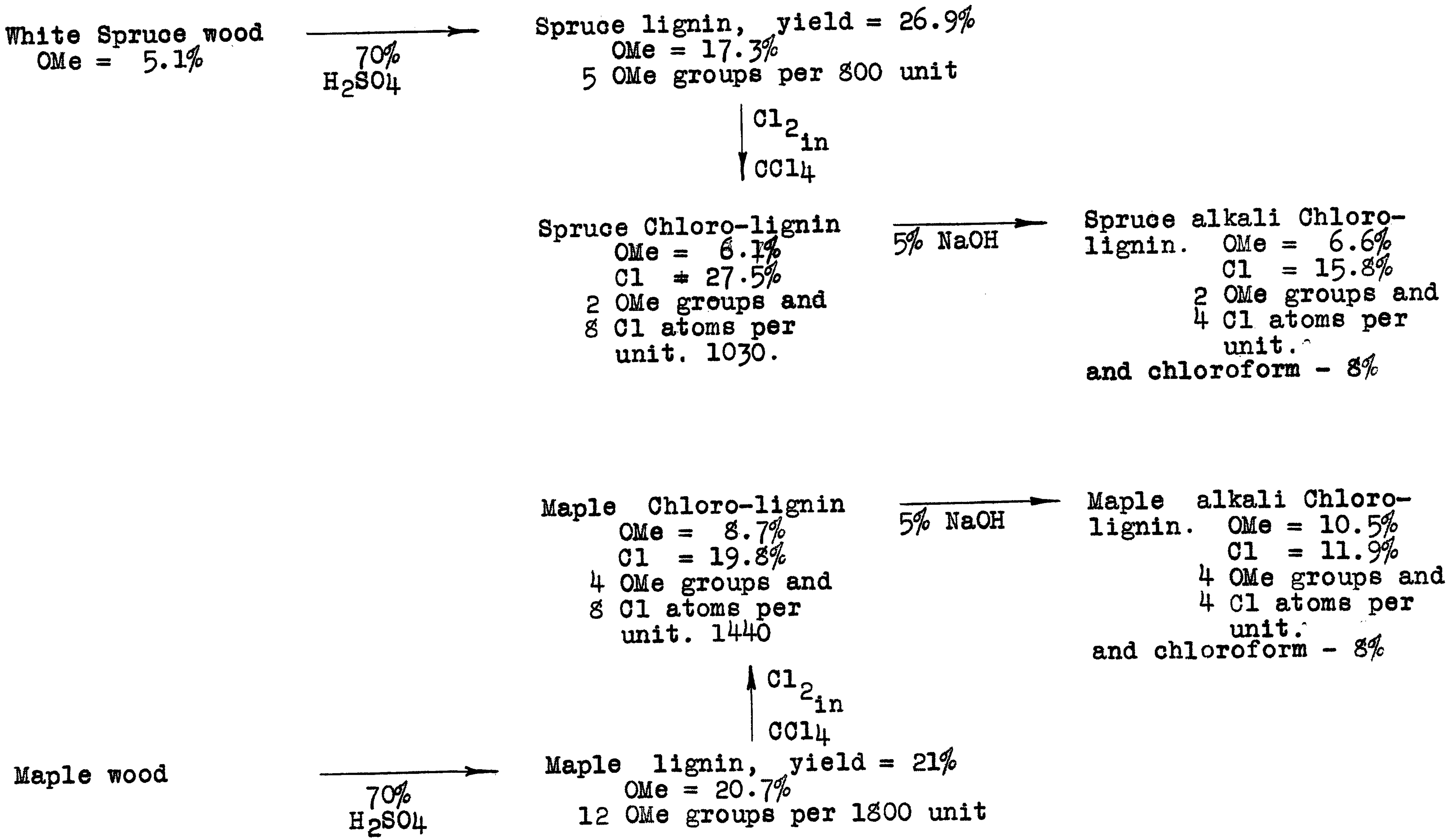
The yield of chloroform from both Maple and Spruce chloro-lignins led the authors to postulate the presence of the grouping $CH_3-\overset{|}{\underset{|}{C}}-OH$ in the original lignin. Since no chloroform is obtained from the methylated chloro-lignins on treatment with alkali the alternative grouping $CH_3-\overset{|}{C} = O$ is eliminated.

In this connection it is to be noted that Walde and Hixon (24) have recently reported the isolation of iodoform. They subjected a lignin, isolated by the action of ammonia upon oat hulls, to an alkaline iodine oxidization. Iodoform was isolated by treating an alkaline solution of the product with iodine and extracting the iodoform with ether. Carbon tetrabromide was obtained on alkaline bromine oxidation of the same lignin. The authors therefore conclude that a secondary alcohol group $CH_3CRHOH$ is probably present in the Lignin molecule.

Harris and co-workers also report that chlorine and bromine react in very much the same way upon Lignin. Both halogens bring about the removal of methoxyl groups, bromine being less reactive than chlorine in this respect. The loss of methoxyl is explained by the assumption of the presence of the grouping $-\underset{2}{\overset{|}{C}} = \underset{1}{\overset{|}{C}} - OCH_3$ . The addition of chlorine to this would result in the loss of methoxyl due to a building up of negative groups on carbon atom 1 giving rise to a ketone. Since all methoxyl groups cannot be removed a second type of methyl grouping is posultated, such as an aromatic ether or a tertiary carbon ether, not susceptible to oxidation.

The fact that chloro-lignin cannot be remethylated is taken as evidence for the loss of hydroxyl groups in the chlorination reaction. Since phenolic hydroxyl groups are resistant to the action of chlorine a third grouping, the enolic or ethylenic type, which could be easily methylated and destroyed by chlorine, is assumed. This assumption is also supported by the fact that the methylated compound reacts

A Summary of ~~the~~ the Chlorination Experiments performed by Harris, Sherrard and Mitchell(23).



White Spruce wood
OMe = 5.1%

Spruce lignin, yield = 26.9%
OMe = 17.3%
5 OMe groups per 800 unit

Spruce Chloro-lignin
OMe = 6.1%
Cl = 27.5%
2 OMe groups and
8 Cl atoms per
unit. 1030.

Spruce alkali Chloro-lignin. OMe = 6.6%
Cl = 15.8%
2 OMe groups and
4 Cl atoms per
unit.
and chloroform - 8%

Maple Chloro-lignin
OMe = 8.7%
Cl = 19.8%
4 OMe groups and
8 Cl atoms per
unit. 1440

Maple alkali Chloro-lignin. OMe = 10.5%
Cl = 11.9%
4 OMe groups and
4 Cl atoms per
unit.
and chloroform - 8%

Maple wood

Maple lignin, yield = 21%
OMe = 20.7%
12 OMe groups per 1800 unit

with more chlorine than the original lignin.

A summary of a few of the reactions carried out by Harris and co-workers is given, diagramatically, on pg. 26, and may be of assistance in understanding this rather complicated research.

## The Action of Halogens upon Lignin in dry $CH_3OH$, dry $CCl_4$ and in Hanus Reagent

Hibbert and Sankey (25) have attempted to determine the unsaturation existing in the lignin molecule by means of bromine addition. Various solvents were used as reaction media and several compounds, possibly related to lignin were investigated.

It was found for wood products that the amount of bromine absorbed after allowing for substitution reactions, was not only a funtion of time, concentration, and bromine solvent, but also varied markedly with the acidity of the medium. The authors cite as evidence in support of this fact, the conclusions of Williams and James (26), namely, that HBr acts as a catalyst for bromine addition to ethylenic compounds in non-hydroxylic solvents. The reaction mechanism involves a partial preliminary substitution, the HBr formed then catalysing the main reaction of addition to the double bond.

The more important analytical data was obtained with freshly prepared solutions of bromine in MeOH or $CCl_4$.

Allowance was made for the substitution taking place and Table B summarizes the results obtained with glycol lignin.

### Table B

### Bromination of glycol lignin

| | Br in MeOH | | Br in $CCl_4$ | | Hanus reagent | |
|---|---|---|---|---|---|---|
| | T hrs. | C = C | T hrs. | C = C | T hrs. | C = C |
| Glycol lignin M.W. = 400 | 24 | 1.14 | 24 | 0.91 | 24 | 1.20 |
| | 48 | 1.22 | 48 | 1.09 | 48 | 1.50 |
| | 48 | 1.18 | | | 71 | 1.50 |

Hibbert and Sankey concluded therefore that glycol lignin contains approximately one ethylenic linkage per Mol. Wt. of 400.

## 4. Action of Halogens upon Lignin in glacial acetic acid.

Friedrich and Diwald (27) used glacial acetic acid as a bromination medium. A lignin prepared by tha action of 1.17 sp. gr. HCl upon a de-resinified, hemi-cellulose extracted wood meal was used as starting material. Bromination of this compound was carried out in glacial acetic acid-bromine solution. the product was isolated after reaction periods of one minute, one hour and four hours, respectively; HCl was evolved during the course of the reaction.

The analysis of the products showed that bromine was rapidly taken up and that a loss of methoxyl groups had occurred. The authors concluded that 4, 5, and 6 bromine atoms were taken up in the periods specified. The only explanation offered for the loss of methoxyl was the assumption that $CH_3Br$ had been formed although this was not isolated.

The results of their experiments are given in Table C.

### Table C.

### Bromination of Lignin, (Friedrich and Diwald)

| | Time | Analyses | | | | Calculated |
|---|---|---|---|---|---|---|
| | | C % | H % | Br % | $OCH_3$ | % |
| Hydrochloric acid lignin.<br>$OCH_3$ = 20.96% | 1 min. | 45.2 | 4.3 | 29.6 | - | 4 Br = 30.2 |
| | 1 hr. | 38.7 | 3.4 | 36.6 | 6.7 | 5 Br = 35.1 |
| | 4 hrs. | 38.1 | 3.1 | 39.4 | - | 6 Br = 39.3 |

In a later communication Friedrich and Pelikan (28) made a more fundamental investigation into the halogenation of lignin. The bromination experiments were again carried out in glacial acetic acid to prevent oxidation. A lignin, prepared from a de-resinified spruce wood meal by the use of HCl and acetic acid, was used as a starting material.

The brominated products were precipitated by pouring the reaction mixture into water. The analysis of the isolated compounds showed that bromination was accompanied by loss of methoxyl, amounting to about 30 percent of the methoxyl originally present.

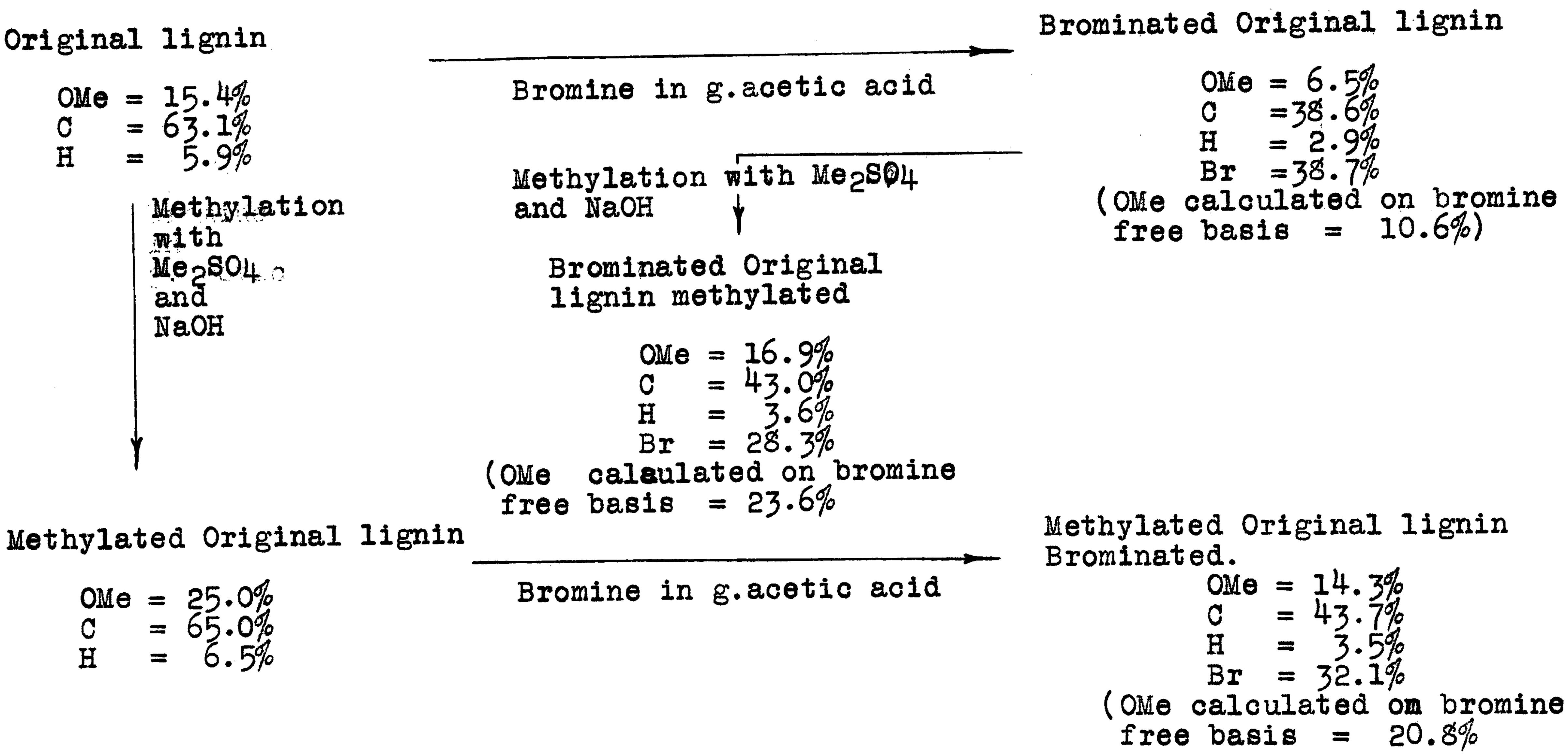
Similar experiments were carried out with the fully methylated lignin derivatives and bromination again resulted in a loss of approximately the same amount of methoxyl.

A series of experiments was performed in order to determine the mechanism of this reaction. The authors were unable to isolate $CH_3Br$, $CH_2Br_2$, $CHBr_3$ or any volatile carbon compound from the reaction nor did the examination of the fission products yield any substance of higher methoxyl content than that of the original starting material. It was therefore concluded that methoxyl had not been removed by reaction of the bromine with the lignin but that a molecular rearrangement, involving the formation of hydroxyl groups had occurred. As evidence in support of this theory they found that the brominated lignin could be methylated and the methoxyl content of the fully methylated derivative was only slightly lower than that of the fully methylated original lignin. (Methoxyl content calculated on a bromine free basis.)

Friedrich and Pelikan also found that the bromine atoms taken up by the lignin possessed different properties; one portion was firmly bound while the other was combined loosely with the lignin. The latter was readily removed either by methylation or by simply shaking with sodium hydroxide.

A summary of these bromination and methylation experiments is given, diagramatically, on pg. 31.

# A Summary of the Bromination Experiments performed by Friedrich and Pelikan (28)



Original lignin

OMe = 15.4%
C = 63.1%
H = 5.9%

Methylation with $Me_2SO_4$ and NaOH

Bromine in g.acetic acid

Brominated Original lignin

OMe = 6.5%
C = 38.6%
H = 2.9%
Br = 38.7%
(OMe calculated on bromine free basis = 10.6%)

Methylation with $Me_2SO_4$ and NaOH

Brominated Original lignin methylated

OMe = 16.9%
C = 43.0%
H = 3.6%
Br = 28.3%
(OMe calaulated on bromine free basis = 23.6%

Methylated Original lignin

OMe = 25.0%
C = 65.0%
H = 6.5%

Bromine in g.acetic acid

Methylated Original lignin Brominated.

OMe = 14.3%
C = 43.7%
H = 3.5%
Br = 32.1%
(OMe calculated om bromine free basis = 20.8%

## 5. Action of aqueous halogen, including hypohalous acid and the hypohalites upon Lignin.

The action of aqueous halogen upon lignin is necessarily of a complicated nature due to the equlibrium relationships existing in an aqueous solution of halogen, hypohalous acid, hypohalites and halates. An excellent review of the subject has been published quite recently by Opferman (29) and will be discussed later. Numerous investigators have largely overlooked these important equlibrium relationships in connection with the lignin problem and a correct interpretation of their results is therefore impossible.

The bleaching action of chlorine upon wood was first noted by Payen (30). Later, a quantitative method for cellulose determination was developed by Fremy and Terriel (31) through the observation that after treatment with chlorine the encrusting substances became soluble in alkali.

Cross and Bevan (32) while investigating the chemistry of bast fibers, isolated an alkali soluble lignin compound formed by the action of chlorine in aqueous solution. They stated that the same compound was always obtained under controlled conditions. Since the amount of HCl developed during the reaction was equal to one-half of the total chlorine used they concluded that the reaction was one of simple substitution. The formula of the lignin chloride was given as $C_{19}H_{18}O_9\ Cl_4$ (26.8% Cl) and its properties resembled those of a quinone.

Heuser and Sieber (33) in studying the action of chlorine upon spruce wood found that far more of the chlorine added was present after reaction as HCl than had entered the lignin molecule. The reaction was therefore thought to be mainly one of oxidation. The lignin chloride isolated gave on analysis C = 47.0%; H = 4.6%; Cl = 22.7%. It was not considered to be a uniform compound, nor to have a cyclic structure since it could not be reduced to a pyrogallol derivative as claimed by Cross and Bevan. Fusion with alkali gave only oxalic acid.

Jonas (34) found that treatment of Willstätter Lignin with chlorine under controlled conditions gave a reproducible lignin chloride as end product. He assumed that chlorination was accompanied by oxidation.

Hägglund (35) by chlorinating Willstätter Lignin at 0° for two days obtained a product containing 39.7 to 46.2% chlorine.

The researches of Freudenberg, Belz, and Niemann (36) were carried out in 10% HBr solution. A lignin, isolated from wood meal by alternate treatment with dilute $H_2SO_4$ and cupric ammonium hydroxide (Schweitzer's reagent) was treated with a solution of excess bromine in 10% HBr. (approximately pH = 1). In this acidic medium such bromine derivatives as hypobromous acid, hypobromites and bromates are not formed. Several aromatic substances considered as related to lignin were similarly treated. The residual bromine was determined by titration after the reaction. The products, after 2, 24, and 48 hours reaction respectively were analysed. The results of the investigation are given in Table I and are represented graphically in Fig. I

Table I

Bromination of lignin and related compounds. (Freudenberg and Co.(36)

| No. | Starting material 1 gm. | % OMe | time hrs | Br used |  | Product analysis |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Br |  | OMe |  |
|  |  |  |  | gms. | atoms | % | atoms | % | moles lost |
| 1 | Lignin | 16 | 2 | 0.88 | 2.12 | 24.0 | 0.78 | 9.4 | 0.24 |
| 2 | " | 16 | 24 | 1.06 | 2.57 | 29.8 | 1.01 | 8.6 | 0.25 |
| 3 | " | 16 | 48 | 1.36 | 3.3 | 32.3 | 1.13 | 8.5 | 0.23 |
| 4 | Methyl lignin | 32 | 2 | 0.45 | 1.19 | 16.5 | 0.53 | 25.0 | 0.16 |
| 5 | " | 32 | 24 | 0.73 | 1.93 | 23.7 | 0.82 | 23.0 | 0.16 |
| 6 | Dehydro-divanillin | 20.5 | 24 | 0 | 0 | 0 | 0 | 20.5 | 0 |
| 7 | Polymerized coniferyl alcohol | 17.2 | 2 | 1.44 | 3.24 | 33.0 | 1.05 | 8.0 | 0.32 |
| 8 |  | 17.2 | 24 | 1.90 | 4.28 | 40.8 | 1.48 | 4.2 | 0.61 |
| 9 | Br vanillic acid | 12.6 | 2 | 1.21 | 3.70 | 55.0 | 1.40 | 2.7 | 0.71 |
| 10 | " | 12.6 | 24 | 1.89 | 5.80 | 66.0 | 2.82 | 1.8 | 0.73 |
| 11 | Methyl cellulose | 34.8 | 20 | 0 | 0 | 0 | 0 | 32.0 | 0.21 |

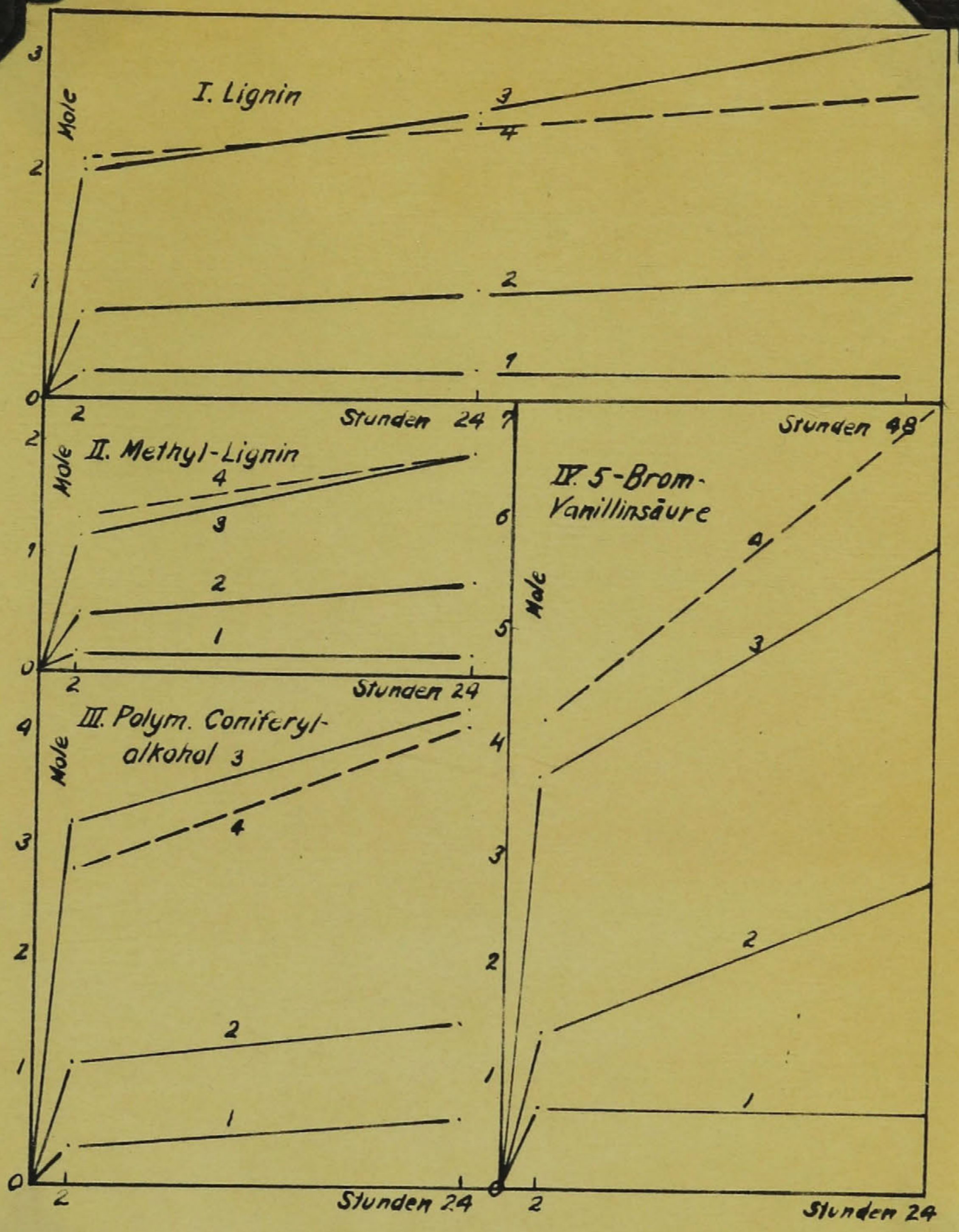


FIG. 1.

The following reaction mechanism is given: The main reaction is that of substitution: $RHH + Br_2 = RHBr + HBr$, which is slowly followed by a further substitution $RHBr + Br_2 = RBr_2 + HBr$. The amount of HBr thus formed, however, does not agree with the amount actually present as shown by curve 111 - 11. A secondary reaction is indicated leading to a loss of methoxyl and taking place simultaneously with the substitution reaction.

The reaction reaches equilibrium very shortly after the first reaction is finished. It was observed that the greater the methoxyl loss the greater was the difference between curves 11 and 111, so that either HBr or $CH_3Br$ was being formed. The presence of the latter could not be detected. If tribromphenol were being formed, the reaction, in this case, could not be distinguished from that of substitution while the formation of a quinone would lead to an increased bromine requirement and so raise the slope of curve 111. Freudenberg considers it probable that the loss of methoxyl is associated with that of quinone formation. Two bromine atoms would in this case be required for each methoxyl and the total bromine requirement of the lignin should be possible of evaluation, as indicated below:

After 2 hours reaction 0.24 moles of OMe were lost
0.78 moles of bromine were taken up per one mole of OMe originally present.

Bromine requirement = (2 x 0.24) + 2 x 0.78 = 2.02 moles.
Actual requirement = 2.12 moles.

The calculated bromine requirement is represented by the dotted line in Figure I... The agreement is very good for lignin, Methyl Lignin and polymerized Coniferyl alcohol. In the case of Brom-vanillic acid, where the methoxyl loss is greatest and secondary reactions come into play the agreement of the theoretical and actual values is not as good.

Harris, Sherrard and Mitchell (23) also chlorinated and brominated Spruce and Maple lignins in aqueous solutions. They found that Maple lignin took up about the same amount of chlorine from an aqueous as from a $CCl_4$ solution, but that the loss of methoxyl was considerably greater. In the reaction not only are methoxyls attached to ethylenic groups removed but also methoxyls attached to groupings which require oxidation as well as chlorination in order to split the ether linkage. Substitution reactions are assumed in this case and the reaction compared with the chlorination of ethyl ether in the presence of moisture. If these methoxyls were ethers of primary or secondary alcohols, chlorination in aqueous solution should give rise to carbonyl and carboxyl groups. Evidence of the presence of the latter was found.

Hibbert and Taylor (37) in these laboratories have investigated the action of hypochlorous acid upon wood meal and upon glycol lignin.

A study was first made of the action of HOCl upon glycol lignin and upon methylated glycol lignin with the view of determining the presence or absence of keto-methylene groups in the lignin molecule. The addition of HOCl to the unmethylated lignin should result in the formation of an unstable addition product which would lose HCl and form a ketone. In the case of the methylated lignin this addition compound should be stable. The amount of HOCl absorbed and of HCl formed was found to be a function of time. The amount of HCl formed in the reaction was less with a methylated lignin, but the amount of HOCl absorbed was decreased to about the same extent. The amount of HOCl absorbed without formation of HCl was therefore practically unaffected by methylation. The results seemed to indicate (assuming no hydrolysis of the keto-methylene compound) that HOCl absorption, resulting in chlorination, is a separate and independent reaction from that of the formation of HCl. It would seem that keto-methylene groups are either not present in lignin, or if present do not enolize to a sufficient extent to react rapdily with HOCl.

Hibbert, Maass and Taylor (38) in a previous communication have shown that the addition of HOCl to the ethylenic linkage is catalysed by undissociated HCl. In the case of lignin, however, the velocity of such a reaction could not be distinguished from that of the chlorination of a phenol or phenol ether since both velocity equations are dependent upon the chlorine concentration. The effect of alkali, as shown by Soper and Smith (39), provided a means of distinguishing between addition to an ethylenic bond and chlorination of a phenol nucleus. From the results of experiments carried out upon the action of HOCl on Glycol Lignin in alkaline media the authors were able to conclude that one nucleus of an aromatic type was present in 800 gm. of Lignin. This calculation was based upon the assumption that only one mole of HOCl per 800 gm. of Lignin is actually absorbed in chlorinating the phenol nucleus.

# Review of Properties of Hypochlorites

## Review of the Properties of aqueous Chlorine and Hypochlorite solutions.

A thorough understanding of the equlibrium relationships existing in aqueous solutions containing chlorine, hypochlorous acid, and hypochlorite ion is necessary before attempting any explanation of their action upon organic substances. In addition there are certain irreversible reactions occurring in these solutions which give rise to a loss of active chlorine and consequent reduction in the quantity of reactant available. A comprehensive survey of the physico-chemical relationships in this field has been recently published by Opfermann (58) and this is discussed, in part, in the following pages.

### a) Chlorine Water.

A yellowish-green liquid, possessing a strong odour, is formed when chlorine is dissolved in water. The maximum solubility occurs at 9 - 10°C and is explained by the formation of a sparingly soluble hydrate $Cl_2.8H_2O$. Hydrolysis of the chlorine also takes place according to the equation;

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO$$

and this, as shown, is reversible and obeys the mass law. A true definition of this equlibrium must therefore take into account the ions of the highly-dissociated HCl so that the reaction is better expressed as;

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HClO$$

According to Jakowkin (59) this hydrolysis is independent of the presence of light; it proceeds slowly and reaches equlibrium only after 48 hrs. at 25°C.

In the presence of light a secondary reaction occurs whereby the hypochlorous acid decomposes according to the equation;

$$HClO \longrightarrow HCl + O$$

The nascent oxygen acts upon the remaining hypochlorous acid forming chloric acid, so that the ultimate products are $HCl$ and $HClO_3$.

The hydrolysis reaction is endothermic, hypochlorous acid formation (together with that of HCl) being favoured by higher temperatures. The following Table ( II ), prepared by Jakowkin, shows the effect of increasing temperatures and indicates that the increase in hydrolysis is greatest between 35 - 40°C.

Table II

Variation of the Chlorine Hydrolysis Constant with Temperature.

| T°C | $K \times 10^4$ | T°C | $K \times 10^4$ | T°C | $K \times 10^4$ |
|---|---|---|---|---|---|
| 0 | 1.45 | 25 | 4.84 | 50 | 8.51 |
| 5 | 1.96 | 30 | 5.65 | 55 | 9.12 |
| 10 | 2.58 | 35 | 6.43 | 60 | 9.75 |
| 15 | 3.28 | 40 | 7.15 | 83.4 | 10.93 |
| 20 | 4.06 | 45 | 7.84 | | |

Increased dilution also increases the ratio of the hydrolysed to the total molecules present. Table III gives the results of determinations made at two different temperatures by Jakowkin.

### Table III

### Degree of Hydrolysis with increasing dilution at different temperatures.

V = dilution, expressed as the number of litres dissolving one mole of chlorine.
x = degree of hydrolysis.

| | | | | | |
|---|---|---|---|---|---|
| 0°C | V = | 16.2 | 23.47 | 43.43 | 99.0 |
| | x = | 0.309 | 0.381 | 0.518 | 0.732 |
| 25°C | V = | 11.74 | 23.38 | 43.22 | 91.84 |
| | x = | 0.345 | 0.500 | 0.666 | 0.845 |

The equilibrium, since it obeys the mass law, is of course shifted to the left by addenda capable of increasing the concentration of the hydrolysis products. The concentration of HClO is thus reduced by the addition of $Cl^-$ ion or of strong acids, and especially by HCl.

## b) Hypochlorous Acid.

Hypochlorous acid is known only in aqueous solution or in the form of its salts and esters. At elevated temperatures it is volatile with steam and can therefore be obtained as a pure aqueous solution by distillation of decomposed hypochlorites. (The distillation of the anhydride, $Cl_2O$, may occur actually, but in any event on condensation this would react with two moles of water regenerating the acid.)

The free acid is a very powerful oxidizing agent, stronger even than $HNO_3$ or $HClO_3$. According to many workers this oxidizing action depends upon its ready decomposition into hydrochloric acid and free oxygen,

$$HClO \longrightarrow HCl + O$$

The liberated oxygen reacts with organic or other oxidizable substances present, or is evolved as such.

Goldschmidt (60) considers that hypochlorous acid, besides undergoing electrolydic dissociation in aqueous solution, may also exist in equlibrium with its anhydride $Cl_2O$,

$$2\ HClO \rightleftharpoons Cl_2O + H_2O$$

This same phenomenon is shown by carbonic, sulphurous, and other weak acids and may explain the higher oxidizing power of free hypochlorous acid as compared with the hypochlorite ion. The latter should be more reactive because of its higher oxygen pressure (oxidation potential).

### c) Spontaneous decomposition of Hypochlorous Acid.

The spontaneous decomposition of hypochlorous acid gives rise to the liberation of oxygen and the formation of hydrochloric acid. Under the influence of the latter a reversal of the hydrolysis equilibrium occurs and free chlorine is formed.

$$HClO + HCl \rightleftharpoons H_2O + Cl_2$$

Equlibrium conditions must, however, be reached eventually unless chlorine is removed in some manner. This is actually the case, in that the chlorine reacts with further quantities of hypochlorous acid to give chloric acid and an additional amount of hydrochloric acid as shown in the following equation;

$$2\ Cl_2 + HClO + H_2O \longrightarrow HClO_3 + 4HCl$$

The HCl formed brings about a shift of the hydrolysis equlibrium still further to the left and the final products as in the case of the reaction promoted by sunlight, are HCl and $HClO_3$.

Similar decomposition reactions to those brought about by the presence of chlorine ions are presumably initiated by the strongly dissociated chlorides of the alkali and alkaline earth metals and may lead to the formation of chlorate and free chlorine;

$$NaCl + 6\ HClO \longrightarrow NaClO_3 + 3\ H_2O + 3\ Cl_2$$

The chlorine set free oxidizes further quantities of hypochlorous acid and is itself reduced to HCl. The stability of hypochlorous acid solutions is therefore decreased by the addition of chlorides.

### d) Electrolydic dissociation of Hypochlorous acid.

All acids in aqueous solution possess the property of dissociating into anions and positively charged hydrogen ions, the strength of the acid being directly proportional to the degree of electrolytic dissociation. In the case of hypochlorous acid, two types of dissociation must be distinguished, namely;

$$\text{(i)}\quad HClO \rightleftharpoons H^+ + ClO^-$$

$$\text{and (ii)}\quad HClO \rightleftharpoons OH^- + Cl^+$$

The latter is so slight as to have no measurable effect and can therefore be neglected. (Several authors maintain that the second dissociation cannot possibly occur since it requires a positive chlorine ion.)

The ionic dissociation into $H^+$ and $ClO^-$ is a reversible reaction which is decreased by the addition of acids or $ClO^-$ ion, and of course is subject to the law of mass action;

$$K = \frac{(H^+)(ClO^-)}{(HClO)}$$

The dissociation constant K has been repeatedly determined and a Table ( IV ) of the results of various investigators is given below;

Table IV

Dissociation Constants of Hypochlorous Acid

| T°C | $K \times 10^{-8}$ | Author |
|---|---|---|
| 17 | 3.7 | Sand (61) |
| 17 | 3.87 | Giordani (62) |
| 18 | 3.7 | Davidson (63) |
| 20 | 4 | Yorston (64) |
| 25 | 1.0 | Soper (65) |
| 25 | 4.4 | Abel (66) |
| 30 | 5.1 | Giordani (62) |
| 70 | 9.35 | Sand (61) |

The value $4.4 \times 10^{-8}$, calculated by Abel from Giordani's results appears to be the most accurate.

The constant K regulates the concentration of the interacting components and at a given temperature is applicable for all dilutions. The degree of dissociation however, increases with increasing dilution and is defined by the expression;

$$a = \text{degree of dissociation} = \frac{\text{amount dissociated}}{\text{total amount}}$$

For weak acids, such as HClO, this relationship is governed by Ostwald's dilution law;

$$\frac{a^2}{1 - a} = K \times V$$

where K = dissociation constant.
V = dilution in litres in which one mole is dissolved.

The degree of dissociation can therefore be calculated for any dilution. In N/10 solution HClO is only 0.03% dissociated as compared with oxalic acid, 50%; acetic acid 1.3%.

It is well known that in the neutralization of a mixture of acids the strongest is first neutralized, and then followed in turn by those progressively weaker. The solution becomes less acidic in character and the neutralization can be followed by measurement of the hydrogen-ion concentration. The term "acid exponent", defined as $pK = -\log K$, forms a bridge connecting hydrogen ion concentration and acidity and is a measure of the strength of the acid in question.

For hypochlorous acid pK = 7.4 as compared with 4.7 for acetic and 1.7 for sulphuric acids,

The hydrogen-ion concentration of a pure acid solution can be readily calculated from the acid exponent value by means of the Oeman equation;

$$pH = \frac{1}{2} pK - \frac{1}{2} \log c, \quad \text{where } c = \text{acid concentration}$$

In the case of hypochlorous acid,

$$\begin{aligned} pH &= 4.2 \text{ in } 0.1N \text{ solution} \\ &= 4.7 \text{ in } 0.01N \text{ solution.} \end{aligned}$$

e) Hydrolysis of Hypochlorites.

Like all salts of weak acids, the hypochlorites in aqueous solution undergo a partial hydrolysis into free acid and free base;

$$NaClO + H_2O \rightleftharpoons NaOH + HClO$$

Both alkali and hypochlorite can be regarded as completely dissociated in aqueous solution so that the equation can be written;

$$Na^+ + ClO^- + H_2O \rightleftharpoons Na^+ + OH^- + HClO$$

which can be simplified to;

$$ClO^- + H_2O \rightleftharpoons OH^- + HClO$$

as representing the exact expression for the hydrolysis of hypochlorites. Their solutions contain more $OH^-$ ions than water and therefore react alkaline. The addition of alkali increasing the OH concentration reduces the concentration of free HClO.

The hydrolysis equlibrium constant is given by the equation,

$$K_{hydr.} = \frac{(HClO)(OH^-)}{(ClO^-)}$$

The values obtained for K by different workers are shown in Table V.

Table V.

Hydrolysis Constant of Hypochlorites

| T°C | $K_{hydr.} \times 10^{-7}$ | Author |
|---|---|---|
| 25 | 2.7 | Abel (66) |
| 25 | 10.0 | Soper (65) |
| 30 | 3.3 | Giordani (62) |
| 30 | 11.2 | Giordani (62) |

The constant increases with temperature, the coefficient being 1.76 according to Abel, (66).

Increasing dilution also increases the hydrolysis as found by Michaelis (67), Table VI.

Table VI.

Hydrolysis of Hypochlorites with increasing Dilution.

| Normality | Degree of Hydrolysis |
|---|---|
| 1 | 0.001 |
| 0.1 | 0.0032 |
| 0.01 | 0.01 |
| 0.001 | 0.032 |

In consequence of this hydrolysis the solutions become less alkaline upon dilution as shown in Table VII by Michaelis (67); the results agree with those deduced from the Oeman equation,

$pH = 7 + \frac{1}{2}pK + \frac{1}{2}\log C$, where C = concentration.

Table VII.

pH values of Hypochlorite solutions with increasing dilution.

| Normality | pH |
|---|---|
| 1 | 11.0 |
| 0.1 | 10.5 |
| 0.01 | 10.0 |
| 0.001 | 9.5 |

### f) Equilibrium relationships existing in aqueous solutions of Hypochlorous acid, Hypochlorite ion, and free Chlorine.

The equilibrium relationships existing in aqueous solutions of chlorine and its oxygenated derivatives as the acidity of the medium is varied over the pH scale can now be discussed.

Davidson (63) and Yorston (64) have carried out potentiometric titrations of hypochlorous acid with the aid of the glass electrode and a reproduction of the curve representing the results of the former is shown below in Fig. II.

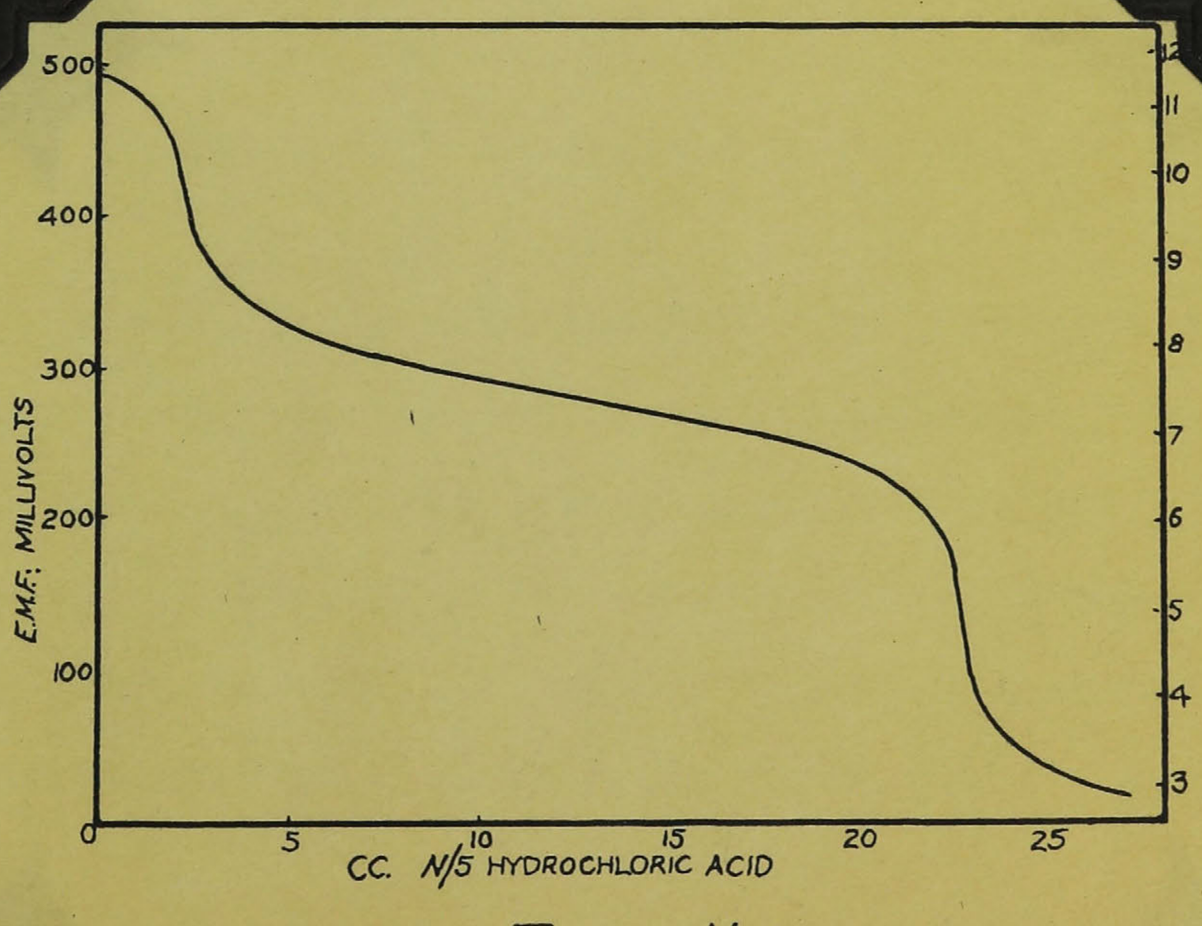


FIG. II.

The various equlibria discussed in the foregoing sections are clearly indicated. The free alkali, present in the upper portion of the curve, is gradually neutralized by the HCl titrated. The sudden drop at approximately pH 10 indicates complete neutralization of the alkali and the solution contains only the salts NaCl and NaOCl plus a small quantity of HClO due to the hydrolysis of NaClO. Further addition of HCl results in the formation of HClO (the weaker acid) from its sodium salt. Between pH 9 - 6 the acidity changes slowly, due to buffering action, and the pH of any desired point can be accurately calculated from the Oeman equation;

$$pH = pK + \log \frac{salt}{residual\ acid}$$

The rapid fall from pH 6 - 4 indicates the complete transformation of the hypochlorite into NaCl and HClO. Further addition of HCl, corresponding to the lower flat portion of the curve, causes the reversal of the chlorine hydrolysis equation with consequent production of free chlorine.

The hypochlorite solution thus has a fundamentally different composition according to its acidity. The relative composition of a hypochlorite solution which is 0.034 N with respect to available chlorine is given in the following Table by Bergqvist.(68). The dissociation constant of hypochlorous acid at 25°C as found by Sand (61), and

Jakowkin's (59) constant for chlorine water hydrolysis were used for the calculation.

Table VIII

Relative composition of a Hypochlorite solution at different pH values. T = 25°C.

| pH | $HClO:ClO^-$ | $Cl_2:HClO$ |
|---|---|---|
| 1 | $2.3 \times 10^6$ | 30 |
| 2 | $2.3 \times 10^5$ | 1 |
| 3 | $2.3 \times 10^4$ | 0.09 |
| 4 | $2.3 \times 10^3$ | 0.009 |
| 5 | $2.3 \times 10^2$ | 0.0009 |
| 6 | $2.3 \times 10$ | |
| 7 | 2.3 | |
| 8 | $2.3 \times 10^{-1}$ | |
| 9 | $2.3 \times 10^{-2}$ | |
| 10 | $2.3 \times 10^{-3}$ | |
| 11 | $2.3 \times 10^{-4}$ | |
| 12 | $2.3 \times 10^{-5}$ | |

## g) Strength of Hypochlorous acid solutions

The strength of hypochlorite solutions is usually determined by adding an aliquot portion to an acidified KI solution and titrating the liberated iodine with thiosulphate. The following reactions take place, (69);

$$HClO + 2\,KI + H_2SO_4 \longrightarrow K_2SO_4 + H_2O + HCl + I_2$$
$$Cl_2 + 2\,KI + H_2SO_4 \longrightarrow H_2SO_4 + 2KCl + I_2$$
$$2\,Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\,NaI$$

One mole of thiosulphate is required by the iodine liberated either from one mole of hypochlorous acid or one mole of chlorine. The available chlorine is the same in both cases although $HClO$ contains but one atom of chlorine while two atoms are present in the chlorine molecule.

The relative proportions of the three components present in the solution, namely; chlorine, hypochlorous acid, and hypochlorite ion, is defined by the hydrogen-ion concentration. They react in this ratio only when the pH of the reaction medium is controlled.

## h) Spontaneous decomposition of Hypochlorite solutions.

Hypochlorous acid is known to be an unstable substance. It is always present in hypochlorite solutions and since one of its decomposition products is a strong acid, namely HCl the existing equlibrium is disturbed. It is to be assumed that amounts of the hypochlorite are continually undergoing decomposition so that finally the whole quantity will have taken part in this change. The higher the concentration of HClO the more rapidly this change occurs.

In acid solutions the decomposition was found to be monomolecular with respect to the hypochlorite ion by Föerster and Jorre (70). The reaction velocity varies as the square of the HClO concentration, the latter remaining constant since it is continually re-formed from the hypochlorite ion. When all the hypochlorite has disappeared a second phase of the spontaneous decomposition takes place and the concentration of HClO decreases as the result of the formation of free chlorine and chlorate, thus;

$$Cl_2' + 6\ HClO \longrightarrow ClO_3^- + Cl_2 + 3\ H_2O$$

Acidification, addition of $CO_2$, or an increase in the temperature promotes the spontaneous decomposition since each tends to increase the HClO concentration.

The mechanism of the decomposition of hypochlorites in alkaline solution has not been satisfactorily explained. According to Föerster (70) this is a bimolecular reaction, the velocity of chlorate formation being proportional to the fourth power of the hypochlorous acid concentration. The stabilizing effect of free alkali is thus explained in that the hydrolysis of the sodium hypochlorite is depressed, thus decreasing the concentration of HClO. Kaufmann (72) has also carried out kinetic studies on the decomposition of hypochlorite solutions and also concludes that the reaction is bimolecular. However, he assumes that chlorate formation takes place through the intermediate stage of chlorite formation;

$$HClO + ClO^- \longrightarrow ClO_2^- + H^+ + Cl^-$$

Prutton and Maron (71) investigated the decomposition of hypobromite solutions between pH 6.4 - 7.8 and concluded that the rate of decomposition is a third order reaction with respect to the hypobromite concentration and first order with respect to the hydroxyl ion concentration.

## Review of the Development of the Glass Electrode

The present investigation has been made possible by the recent development of the glass electrode as a dependable piece of apparatus for the determination of Hydrogen-ion concentration. The author, although not concerned in this research with the further development of the electrode except perhaps for the design of certain supplementary apparatus and equipment, considers that a brief review of the discovery and development of the electrode should be included in this introduction.

The original discovery, by Cremer (40) in 1906, that a thin glass membrane could give rise to potentials that were a function of the Hydrogen-ion concentration of an aqueous solution in which it dips, has been exhaustively investigated. The shape of the glass membrane as used by Haber and Klemensiewicz (41) has been found to be the most satisfactory although other types have been proposed by Mrs. Kerridge (42), MacInnes and Dole (43), MacInnes and Belcher (44).

Investigations have been carried out by MacInnes and Dole (45) to determine the most satisfactory glass composition. Kahler and DeEds (46) have investigated the various characteristics of several types of glass. The most suitable glass for the construction of the electrodes has the composition,

$SiO_2$ = 72%, $Na_2O$ = 22%, CaO = 6%. (This is the composition of 015 Corning glass).

The theoretical basis underlying the function of the glass electrode has been the subject of much discussion, the various investigators developing their own interpretations. These theories may be roughly divided into groups: (a) The phase boundary theories of Haber (41), Gross and Halpern (47), and Hughes (48); (b) The ion adsorption or "ion exchange" theories of Horovitz (49), Schiller (50) and Lengyel (51); (c) The membrane or diffusion potential theories of Cremer (40), Michaelis (52) and Quittner (53); (d) The thermodynamical considerations of Dole (54), and (e) the glass reservoir of constant hydrogen-ion activity by MacInnes and Belcher (55).

The operation of the electrode is relatively simple. In contact with a reference electrode of known e.m.f. it dips into a solution of unknown hydrogen-ion concentration. The latter is connected through a liquid junction to a second reference electrode. The potential set up across the two reference electrodes is equal to the sum of that of each reference electrode, plus the asymmetric potential of the glass, and plus the glass potential due to the unknown hydrogen-ion concentration. The potential of the two reference electrodes is known, the asymmetry potential varies slowly and can be accounted for, so that the potential of the glass can be determined. It has been found that the variation of the glass potential with hydrogen-ion concentration follows the regular gas law equation as used for the hydrogen electrode so that the pH of the unknown solution is given by the expression $pH = \frac{E}{0.0591}$, where E = net potential, and 0.0591 = the gas law constant.

The dependability of the glass electrode has been investigated by Kahler and DeEds (46), Buchbock (56), Dole (54), Sokolov and Passinski (57). The electrode functions quite satisfactorily and obeys the gas law equation over the range pH = 1 to 10.5. Above pH = 10.5 it is still dependable for hydrogen-ion concentration if used in a solution of known metallic ion concentration, $Na^+$, $K^+$, $Li^+$, etc. and previously calibrated therefore. Horovitz has investigated this phase and concludes that in very low hydrogen-ion concentration the electrode functions for any positive ion.

The glass electrode serves as a very convenient apparatus for the measurement of hydrogen-ion concentration between the limits pH = 1 and 10.5. Its accuracy, provided it has been standardized in buffer solutions, is limited only by the accuracy with which these buffers have been standardized. It functions not only in colored and turbid solutions, but also in oxidizing, reducing, and in very weakly buffered solutions where other electrodes either function poorly or fail entirely. The electrode is however very fragile (glass approximately 1 micron thick). Because of its very high resistance (2 - 100 megohms) the currents set up are extremely minute and difficult of reproducible measurement. The recent construction of guarded potentiometers used with sensitive galvanometers, or, of well shielded vacuum tube circuits when inexpensive galvanometers may be used, have largely overcome these difficulties. MacInnes and others mentioned above have also used with success the Compton Electrometer as a current indicator.

## DISCUSSION OF RESULTS

### 1. Purification and Properties of Alkali Lignin.

The isolation of lignin from woody products, by any of the known methods, is open to the criticism that the lignin probably undergoes structural changes in the process due to its remarkable sensitivity to chemical reagents. Admitting this criticism to be correct it would seem that the first consideration in any method of isolation must be that of reproducibility of the product obtained. Lignin products, isolated by the different methods can then be compared with each other, and, in the final elucidation of the problem the changes brought about by isolation can be determined. In the absence of suitable methods for purification, and because the usual physical methods, for example, melting-point and molecular weight, cannot be employed, the only criterion of purity is reproducibility of methoxyl, carbon and hydrogen analysis, and to a less extent the determination of hydroxyl groups by methylation or acetylation.

The properties of alkali lignin have been previously investigated by several workers and their results have been discussed in another chapter. It is apparent that while certain general physical properties, such as solubility, melting-point etc., are in fair agreement, the values for methoxyl, carbon and hydrogen show marked differences. This lack of agreement is undoubtedly due to,

a) the different methods used for the isolation of the lignin, and,

b) the different methods used for the purification of the crude product.

In the present investigation a previously standardized method was used for the isolation of the lignin and a new procedure, based upon fundamental fractionation principles, was developed for the purification of the crude product.

## a) Isolation of Alkali Lignin.

The method proposed by Mehta (12) and re-investigated by Marshall in these laboratories (18) was chosen as the most satisfactory procedure for the isolation of alkali lignin. In this process, finely ground spruce wood, previously extracted with benzene-alcohol in order to remove resins etc., followed by 5% NaOH solution to remove hemi-celluloses and pentosans, was heated with a normal sodium hydroxide solution for one hour at 172°C. The mixture was then filtered and the alkaline extract neutralized with HCl whereby the crude lignin was precipitated. The latter was freed from the mother liquor by centrifuging, filtering and washing, and then dissolved as a moist precipitate in dioxan, the solution being freed from moisture by successive distillation with absolute dioxan,Table X.

A sample of the crude product, isolated from the dioxan solution by slowly dropping the latter into stirred ether, separating and washing the precipitate, gave on analysis 13.74% $OCH_3$, c.f. Table XII A. The analysis recorded by Marshall for his crude product was 13.48% $OCH_3$.

b) Purification of Alkali Lignin.

The use of anhydrous solvents and precipitants for the purification of alkali lignin was first introduced by Marshall. This worker separated alkali lignin into two fractions (A) and (B) by dropping a dioxan solution of the crude lignin into excess of well-stirred, anhydrous ether and separating the precipitate from the resulting mixture. Several treatments were necessary to separate completely the dioxan-ether insoluble fraction (A) from the soluble fraction (B). The two fractions gave slightly different analyses (Table XVI) and were assumed to represent individual homogeneous compounds. Marshall also noted in connection with this method of purification that a small quantity (C) of the (A) fraction remained as a residue when the product was dissolved in dioxan prior to further purification. The present investigation has shown that this substance (C) is an impurity which cannot be completely removed from the (A) fraction by the above purification procedure.

A new method of purification, using the same solvent, (dioxan) and precipitant, (ether) based on fundamental fractionation principles was developed in the present research. The experimental details are described later and the results, given in Tables XI, XII A, XII B, are represented graphically in Fig. V. Ether is slowly dropped into a dioxan solution of the crude lignin whereupon a precipitate forms which, when isolated, is found to be insoluble in dioxan; the small quantity of lignin precipitated simultaneously is removed by washing the precipitate with fresh solvent. By slowly increasing the ratio of ether to dioxan and separating the precipitate formed, the impurity is completely separated from the solution. The former amounts to 15 - 20% of the purified alkali lignin and is completely precipitated in ether-dioxan solution 40:60, while in the same mixture only 20% of the alkali lignin is precipitated, Fig. V. After removal of the impurity (C) the fractions of purified alkali lignin, precipitated in any given ether-dioxan mixture, give identical methoxyl analyses, Table XII A, and may be assumed to arise from one and the same homogeneous substance possessing a graded solubility in dioxan-ether mixtures.

It may be argued that a sufficient number of precipitations such as were performed by Marshall would lead to a complete removal of this impurity (C). However, since alkali lignin possesses a graded solubility in dioxan-ether mixtures, purification by this method must stop after the removal of the fraction soluble in the dioxan-ether solution of the specific ratio employed. The presence of the impurity (C) in Marshall's alkali lignin, fraction (A), probably explains the slightly lower methoxyl content (14.9) obtained by him as compared with that of the author's purified material (15.2%).

The properties of the purified alkali lignin are similar to those recorded by Marshall, Dorée and Barton-Wright and others. The lignin is an amorphous, buff-colored powder, readily soluble in aqueous solutions containing $OH^-$ ion, in dioxan, glacial acetic acid and ethyl alcohol, and insoluble in aqueous acids, ether, chloroform and petroleum base solvents.

Purified alkali lignin, as isolated, is not permanently stable in alkaline solution but slowly decomposes, resulting in a decrease in yield and in methoxyl, carbon and hydrogen values, and consequently (by difference) an increase in oxygen content. This decomposition probably takes place as a result of a slow oxidation, a change which would seem to justify the conclusion that the alkali lignin products reported in the literature and including that prepared by the author, represent to a small extent, partially oxidized lignins. The data is given in Tables XIII and XIV. This conclusion is further supported by the fact that the equivalent carbon to hydrogen ratio calculated for the various analyses reported for alkali lignin is usually a constant within the limits of experimental error. The mechanism of this oxidation is at present unknown although the data obtained in the present investigation indicate that loss of methoxyl accompanies the oxidation.

The analysis of purified alkali lignin and a comparison with that found by other investigators is shown in Table IX. On the basis of Marshall's conclusions that alkali lignin contains six methoxyl groups it is possible to calculate an empirical formula as given below. It is possible that a repetition of his work using the authors' purified product might lead to a simplification of same.

Table IX

Analysis of Alkali Lignin

| Lignin. | Formula | C % | H % | $OCH_3$% | Equiv. ratio C/H | Author |
|---|---|---|---|---|---|---|
| Straw | $C_{40}H_{44}O_{15}$ | 62.1<br>63.0 | 5.4<br>5.3 | 14.3<br>15.8 | 13.7<br>12.9 | Beckmann and co. (11) |
| Flax shive | $C_{45}H_{48}O_{16}$ | 64.0 | 5.7 | 14.7 | 13.4 | Powell and Whittaker (13) |
| Spruce wood | $C_{20}H_{20}O_6$ | 67.4 | 5.6 | 17.4 | 14.3 | Doree and (16) Barton-Wright |
| Corn cob | $C_{40}H_{44}O_{16}$ | 62.8 | 5.7 | 12.0 | 13.1 | Phillips (21) |
| Spruce wood | $C_{67}H_{71}O_{23}$<br>$C_{108}H_{107}O_{37}$ | 64.7<br>65.0 | 5.7<br>5.4 | 14.9<br>14.0 | 13.5<br>14.3 | Marshall (18)<br>Marshall (18) |
| Spruce wood | $C_{67}H_{70}O_{21}$ | 66.1 | 5.8 | 15.2 | 13.6 | White |
| Lignin after 3 months - in alkaline solution |  | 64.7 | 5.6 | 14.8 | 13.7 | White |

It has been observed, generally, that alkali lignin is soluble in aqueous solutions containing $OH^-$ ion but no statement is made regarding the alkali concentration necessary for solubility. In the present research the behaviour of alkali lignin in solutions of different hydrogen-ion concentration was investigated quantitatively and the pH value at which alkali lignin flocculates determined. This information, in its quantitative aspect, is of considerable importance in the practical application of the results to the bleaching of pulp.

The dark=brown to black-colored solution of alkali lignin changes slowly to a light reddish color on the gradual addition of acid, the resulting increase in hydrogen-ion concentration finally causing the lignin to precipitate. The details are given in the Experimental Part (5) and the results (Tables XXVIII, XXIX) are represented graphically in Figs. XVII and XVIII, respectively.

The change in color takes place over a considerable range of hydrogen-ion concentration, namely, pH 10 - 5, and is probably due to the formation of the less highly-colored, or colorless, undissociated form of the lignin, R-OH, from its colored, dissociated sodium salt $R-O^- + Na^+$. A further increase in the hydrogen-ion concentration to pH 4.2 causes the undissociated lignin to flocculate and precipitate from the solution. It is evident therefore that while alkali lignin is soluble in aqueous solutions containing $Na^+$ ion having a pH greater than 4.2 it will be precipitated in more acid media (pH lower than 4.2).

## 2. Action of Chlorine and its Derivatives upon Lignin.

The action of chlorine, hypochlorous acid and hypochlorites upon lignin was investigated by treating an aqueous solution of a purified alkali lignin with solutions of "available chlorine" in media of different hydrogen-ion concentration. The equlibrium relationships of chlorine, hypochlorous acid and hypochlorite ion in aqueous solution were discussed in a previous chapter and it was shown that a solution of "available chlorine" possesses a fundamentally different composition depending upon its hydrogen-ion concentration. In alkaline solution hypochlorite ion functions as the oxidizing agent, in presence of acid it is molecular chlorine, while in the neighborhood of the neutral point hypochlorous acid is, for practical purposes, the only oxidizing agent present. Previous investigators have largely overlooked these important facts and have conducted their experiments without regard to the constancy in the pH value of the reacting solution. Freudenberg (36) however, whose work has been discussed, recognized that uncontrolled mixtures of bromine, hypobromous acid and hypobromite ion would lead to results that could not be interpreted and so performed his experiments in a ten percent HBr solution (approximately pH = 1). In this acid solution the concentration of hypobromous acid and hypobromite ion can be neglected but the important effect of the acidity of the medium was overlooked in his discussion of the results relating to the mechanism of the reaction.

The details of the experimental methods and apparatus used in the present investigation are discussed in the Experimental Part and a brief description only of the procedure follows:

A known quantity of alkali lignin in a solution of pre-determined hydrogen-ion concentration was treated with an aqueous solution containing a known quantity of "available chlorine". The hydrogen-ion concentration of the reacting mixture was measured potentiometrically with the glass electrode and was maintained constant by continually neutralizing the hydrochloric acid formed in the reaction with N/5 NaOH solution. The reaction was allowed to proceed to equlibrium, the latter being indicated by no further change in the hydrogen-ion concentration.

A separate series of experiments showed that the reaction of"available chlorine" solutions with lignin at pH = 6 was extremely rapid and reached eighty percent completion in 30 minutes, Table XXVII, Fig. XVI. A period of 4 - 5 days was therefore assumed to be ample for complete reaction in the main series of experiments.

The lignin reaction product was precipitated from the solution with HCl and isolated by a procedure similar to that used for the isolation of alkali lignin. Since the present investigation was concerned only with the changes brought about by the action of chlorine and its derivatives upon lignin the acid-soluble products of the reaction were not investigated and are to form the basis of a future investigation.

Several experiments were performed at a specified pH using the same quantity of lignin and varying the amount of " available chlorine" used. The course of the reaction was followed by comparing the methoxyl and halogen analysis of the resulting product with the amount of "available chlorine" consumed in the experiment.

Various series of experiments were conducted in this manner at pH 2, 4, 5, 6, 7, 8, 10, and the results combined to show the co-related changes effected in the original lignin by increasing amounts of "available chlorine" at any hydrogen-ion concentration over the pH scale from 2 - 10.

The results obtained are given in Tables XVII to XXIV and are represented graphically for the reaction at pH 2, 4, 6, 8, and 10, in Figs. XI toXV. A graphical representation is not given for the reaction at pH = 5 and 7 since the results only supplement those obtained at pH = 4, 6, and 8.

## a) Discussion of the action of " available chlorine" solutions upon alkali lignin based on the graphical representations of the results obtained. Figs. XI to XV.

A consideration of the results obtained, and of their graphical representations, clearly indicates the course of the reaction of "available chlorine" solutions with alkali lignin. A decrease in the methoxyl content and an increase in the chlorine content of the products isolated, varying with the amount of "available chlorine" entering into reaction is seen to take place over the pH range 2 - 10. Furthermore, these changes are brought about with the consumption of considerably less reactant in acid as compared with alkaline solutions.

In alkaline solutions, pH = 10,(Fig. XV) where hypochlorite ion is, for practical purposes, the only active agent present, the reaction becomes increasingly difficult so that finally a large increase in the amount of "available chlorine" used is required to produce even a small change in the methoxyl content of the isolated product. The introduction of chlorine into the lignin molecule has in the meantime reached a constant value at 2.6 - 2.8%. The latter result would seem to show,

a) the structure of the isolated product has not undergone drastic change other than is occasioned by the loss of methoxyl, and,

b) the increased quantities of reactant added are in some measure being utilized in interaction with the reaction products resulting from the loss of methoxyl.

The latter conclusion cannot, however, be entirely correct because the yield of product isolated continually decreases, indicating that the increased consumption of reactant is due to the formation of acid-soluble products from the lignin and its probable interaction with same.

In less alkaline solutions, pH = 8, (Fig. XIV.), the active agents are hypochlorous acid and hypochlorite ion and a larger proportion of the reactant added is consumed in the de-methylation and chlorination reactions as compared with the reaction in media of pH 10. The reaction also proceeds farther than with the latter and there is less tendency for the amount of chlorine introduced to reach any constant value.

The reaction in media of pH = 6, (Fig. XIII), appears to be somewhat irregular in that the amount of "available chlorine" required both for the removal of methoxyl groups and the introduction of chlorine atoms passes through a minimum. The composition of the reactant is constant, being represented largely by hypochlorous acid, so that any explanation of the above noted minimum must be sought in the properties of the lignin itself. If, on the basis of Marshall's (18) conclusions alkali lignin contains six methoxyl groups, it is of interest to mention that the point of inflection in the methoxyl curve, (Fig. XIII), may actually represent the removal of two labile methoxyl groups and the initiation of a reaction involving the loss of similar but less labile groups. A similar, but only a very slight break can also be observed in the methoxyl curve both at pH 8 and pH 10. (Figs. XIV and XV).

At all stages of the reaction at pH 6 the decrease in methoxyl is closely paralleled by a corresponding increase in chlorine content of the product and both tend toward final constant values at 6 and 9% respectively. The above speculation regarding the loss of methoxyl groups can now be extended to include the removal of the two additional less stable groups and leads to the conclusion that the remaining pair must be of a more stable type, for example, as might be attached to an aromatic ring.

The composition of the reactant in solutions of pH 4 is still largely represented by hypochlorous acid although molecular chlorine begins to appear in consequence of a reversal of the chlorine hydrolysis equation,

$$Cl_2 + H_2O \rightleftharpoons HClO + H^+ + Cl^-$$

A considerable reduction is noted in the amount of reactant required to produce a given decrease in methoxyl, or increase in chlorine content as compared with the reaction at pH 6. In pH 4 solutions (Fig. XII) the reaction follows a regular course, no distinct break can be detected in either curve and the relationship is consistent as far as investigated.

With "available chlorine" solutions of pH 2 (Fig. XI) the maximum effect is found as regards methoxyl removal and chlorine introduction. The change in methoxyl and chlorine content of the isolated product follows the consumption of reactant in a regular manner and in the case of the former tends toward a constant value at approximately 4.5%. The introduction of chlorine however continues to take place with increasing consumption of reactant and this, of necessity, causes a further reduction in the methoxyl content of the isolated product in proportion to the amount of chlorine introduced into the molecule.

It is to be noted that no definite end-point product possessing colloidal properties similar to those of alkali lignin can be isolated from any reaction mixture over the entire pH scale from 2 - 10. A loss in yield, probably due to a secondary reaction taking place simultaneously with the de-methylation and chlorination reactions described above, would finally result in the formation of completely acid-soluble products. The structures of the latter probably bear little resemblance to the original lignin structure and were not investigated.

The effect of an increase in the concentration of chloride ion upon the reaction, in consequence of a reversal of the chlorine hydrolysis equation,

$$Cl_2 + H_2O \rightleftharpoons HClO + H^+ + Cl^-$$

was investigated briefly at pH 3.5. The results given in Table XVIII tend to show that the increased concentration of molecular chlorine, brought about by the addition of chloride ion, increases the amount of de-methylation and chlorination when equivalent quantities of reactant are added. However, the results are almost within the limit of experimental error when duplicate experiments are performed and sufficient data were not obtained to permit of drawing definite conclusions.

### b) Relationship between the de-methylation and chlorination reactions which result when alkali lignin is treated with "available chlorine" solutions.

The relationship between the amount of methoxyl lost by, and the amount of chlorine introduced into, the lignin molecule by the action of "available chlorine" solutions at various hydrogen-ion concentrations is represented graphically in Fig. III as a function of the reactant consumed. The equivalent ratio, $\frac{\text{methoxyl lost}}{\text{chlorine introduced}}$, was calculated in the following manner;

$$\frac{\%\text{Cl}}{35.5} \times \frac{1000}{100} = \text{milliequivalents of chlorine introduced per gm. lignin.} \qquad (1)$$

$$\frac{\%\text{OCH}_3}{} \times \frac{100}{100 - \%\text{Cl}} = \%\ \text{OCH}_3 \text{ on chlorine free basis} \qquad (\text{II})$$

$$15.20 = \%\ \text{OCH}_3 \text{ of original lignin} \qquad (\text{III})$$

$$(\text{III}) - (\text{II}) = \%\ \text{OCH}_3 \text{ lost in the reaction} \qquad (\text{IV})$$

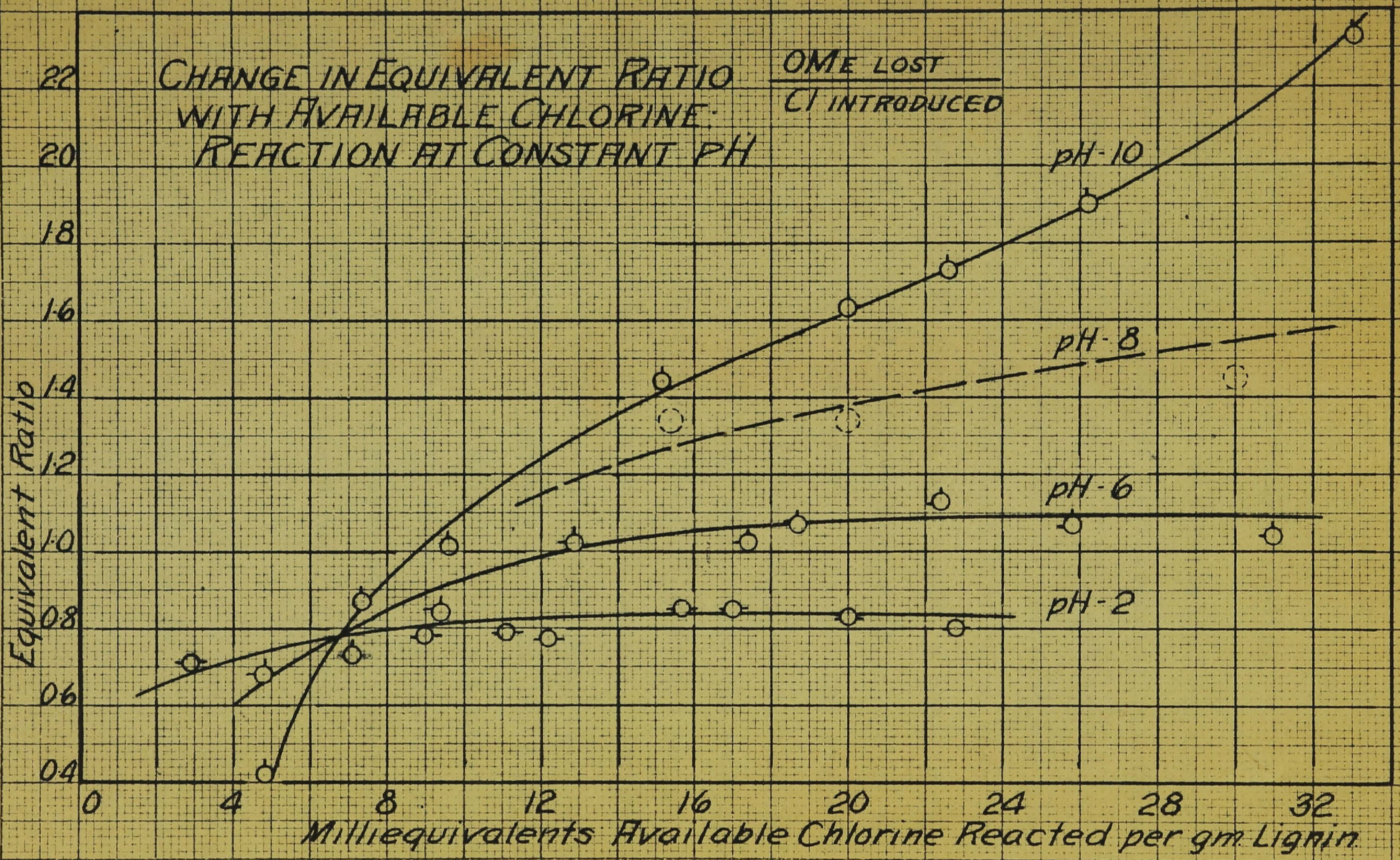

CHANGE IN EQUIVALENT RATIO
WITH AVAILABLE CHLORINE:
REACTION AT CONSTANT PH
OMe LOST
Cl INTRODUCED
pH-10
pH-8
pH-6
pH-2
Equivalent Ratio
22
20
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0
4
8
12
16
20
24
28
32
Milliequivalents Available Chlorine Reacted per gm Lignin

FIG. III.

$$\frac{(IV)}{31.0} \times \frac{1000}{100} = \text{milliequivalents } OCH_3 \text{ lost in the reaction per gm. of lignin.} \qquad (V)$$

$$\frac{(V)}{(I)} = \text{equivalent ratio.}$$

Reference to Fig. III shows that no constancy in the equivalent ratio is obtained as increasing amounts of reactant are used in solutions of pH 10. The equivalent ratio (less than unity when small quantities of reactant are used) increases through unity to a considerably higher value when relatively large quantities of reactant are added to the lignin.

At pH 6 however a marked degree of constancy in the equivalent ratio is observable. The initial stage of the reaction results in the introduction of more chlorine than corresponds to de-methylation, but, after the consumption of approximately 16 milliequivalents of reactant per gm. of lignin, the equivalent ratio reaches unity. Further reaction brought about by the addition of larger quantities of reactant results in the removal of methoxyl and the introduction of chlorine at a practically constant ratio slightly greater than unity. The reaction at pH 5, where the composition of the reactant is almost entirely represented by hypochlorous acid approximates still more closely the 1:1 ratio of "methoxyl lost" to "chlorine introduced".

In solutions of pH 2 the equivalent ratio never attains the value of unity. The amount of chlorine introduced into the molecule is always considerably in excess of the quantity of methoxyl lost. It is to be assumed therefore, that in addition to the de-methylation and simultaneous chlorination, some secondary reaction, probably involving substitution of chlorine in the lignin molecule is taking place. The equivalent ratio in these media (pH = 2) appears to pass through a poorly defined maximum, and, taken in conjunction with the results graphed in Fig. XI leads to the conclusion that further chlorination takes place after the loss of methoxyl has ceased.

The results of experiments performed at pH 4, 5, 7, and 8, supplement the data presented in Fig. III; the change in equivalent ratio for the reaction at pH 8 is indicated by a dotted line.

A significant feature of all curves represented in Fig III is the indication that the initial stage of all reactions involves the introduction of chlorine prior to the loss of methoxyl.

### c) Effect of variation in the pH of the reaction medium upon the quantity of "available chlorine" consumed.

A consideration of the experimental results obtained when lignin is treated with "available chlorine" solutions shows that the quantity of reactant required to produce,

a) an equivalent decrease in the methoxyl content of the lignin, and,

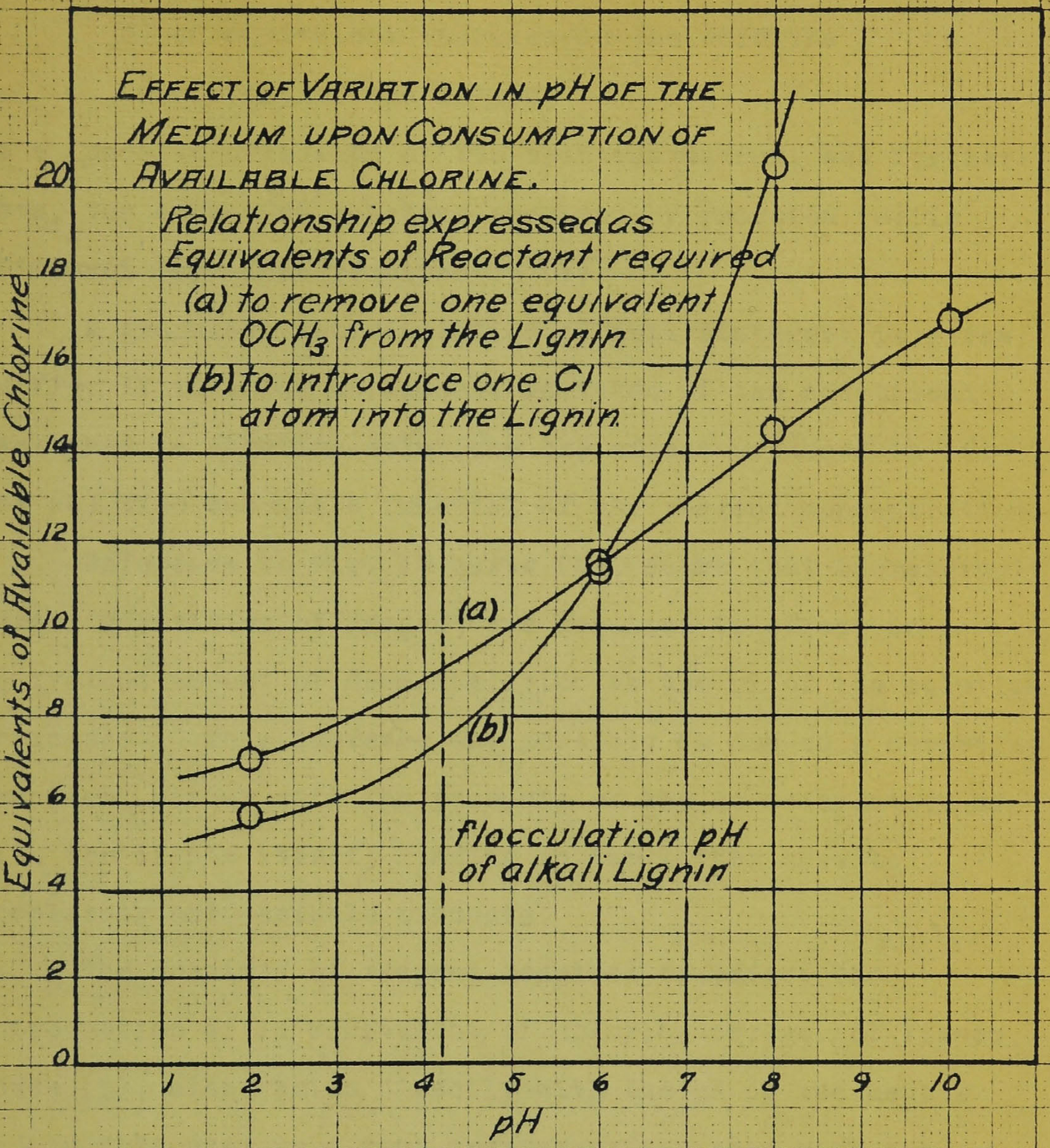

EFFECT OF VARIATION IN pH OF THE
MEDIUM UPON CONSUMPTION OF
AVAILABLE CHLORINE.
Relationship expressed as
Equivalents of Reactant required
(a) to remove one equivalent
OCH3 from the Lignin
(b) to introduce one Cl
atom into the Lignin.
(a)
(b)
flocculation pH
of alkali Lignin
Equivalents of Available Chlorine
0
2
4
6
8
10
12
14
16
18
20
1
2
3
4
5
6
7
8
9
10
pH

FIG. IV.

b) an equivalent increase in the chlorine content of the lignin,

is a function of the pH of the readtion medium, and furthermore, the amount of reactant required by reaction (a) is different from that required by (b).

A graphical representation of this statement is givem in Fig. IV in which no account is taken of the additional fact that in alkaline solutions the effect produced in (a) and (b) also becomes a function of the reagent concentration.

Reference to Fig. IV curve (a), shows that increasingly larger quantities of reagent are required to effect an equivalent amount of de-methylation as the pH of the solution increases. This increase may possibly be due to a competing reaction, either with the products of the de-methylation or with the lignin itself, leading in the latter case to completely acid-soluble products.

The quantity of reagent required to effect the introduction of an equivalent of chlorine per gm. of lignin, curve (b), also varies directly with the pH of the medium and in this case to a much greater extent than with the de-methylation reaction, (curve a). The increased difficulty of chlorination may be due to,

a) removal of molecular chlorine from the reaction medium through a reversal of the chlorine hydrolysis equation, consequent upon increasing pH,

$$Cl_2 + H_2O \rightleftharpoons HClO + H^+ + Cl^-$$

b) removal of hypochlorous acid by the formation of sodium hypochlorite,

$$HClO + NaOH \rightleftharpoons NaClO + H_2O$$

c) removal of the introduced chlorine atoms in the alkaline reaction medium.

(the significance of (b) will be discussed later)

Fig. IV. can be considered therefore as supplementary to Fig. III in that it explains the changes in the equivalent ratio as the pH of the medium varies.

## 3. Methylation of the products obtained after interaction of "available chlorine" solutions with lignin.

The results of previous investigators are not in agreement regarding the possibility of methylation of the products resulting from the action of "available chlorine" solutions upon lignin.

Harris, Sherrard and Mitchell (23), whose work was discussed previously (pg. 26), treated Klason lignin (70% $H_2SO_4$ method) with a solution of chlorine in carbon tetrachloride and found that the resulting product could not be methylated with dimethyl sulphate and alkali. They concluded that the reaction of lignin with chlorine had resulted in the loss of hydroxyl groups.

Friedrich and Pelikan (28) on the other hand treated a lignin (isolated from wood meal by the action of HCl in glacial acetic acid) with bromine in the same solvent and found that the reaction product could be methylated with dimethyl sulphate,(Pg. 31). These investigators obtained a methoxyl content for the fully methylated derivative, calculated on a bromine free basis, only slightly below that for the fully methylated original lignin.

In the present investigation the results of Friedrich and Pelikan have been partially confirmed. The reaction products obtained from two separate experiments using definite amounts of "available chlorine" at pH 10 were methylated with dimethyl sulphate and alkali and the methoxyl contents of the resulting fully methylated derivatives compared with that of fully methylated alkali lignin, methylated under the same conditions. The results of this study are given in Table XXV. The <u>increase</u> in methoxyl content upon methylation of the products, isolated, after the reaction with "available chlorine" approaches that obtained by methylation of the original lignin, amounting in one case to 89% and in the second to 88%.

The following conclusions appear to be well founded;

a) The structure of the reaction product from the inter-action of "available chlorine" with lignin at pH10 cannot be markedly different from that of the original lignin.(except for methoxyl groups lost)

b) The removal of methoxyl groups cannot give rise to the formation of hydroxyl groups or any structure susceptible to methylation with dimethyl sulphate in alkaline solution.

These experimental results are in disagreement with the reaction mechanism proposed by Friedrich and Pelikan to account for the loss of methoxyl arising from the action of bromine on lignin which they assume as due to a molecular rearrangement resulting in the formation of hydroxyl groups.

It was further noted in the above methylation studies that while alkali lignin and the product from Exp. No. 22 * became alkali insoluble upon methylation, the methylated product from Exp. No. 26 ** was alkali soluble. From the results of other investigators it would appear that alkali lignin contains a phenolic hydroxyl group, thus giving rise to its alkali solubility and accounting for the insoluble character of the fully methylated derivative. Since the fully methylated derivative (dimethyl sulphate and alkali) of the reaction product from Exp. No. 26 was alkali soluble the action of "available chlorine"solution had, in this case, probably given rise to a sufficient number of carboxyl groups to maintain alkali solubility of the methylated derivative. The details of the methylation studies are given in the Experimental Part (5) and the results in Table XXV.

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* Exp. No. 22 - 14.2 milliequivalents "available chlorine"used. Product - 12.3% $OCH_3$, 3.3% Cl.

**Exp. No. 26 - 29.8 milliequivalents "available chlorine"used. Product - 10.0% $OCH_3$, 2.7% Cl.

## 4. Dehalogenation of the products resulting from the action of "available chlorine" solutions upon lignin.

It has been stated that the halogen atoms introduced into the lignin molecule by the action of chlorine can be classified as,

a) atoms which are loosely bound and capable of ready removal, and,

b) atoms which are firmly bound to the lignin molecule.

(22)(23)(14)(28).

In the present investigation no such rigid classification of introduced chlorine atoms was indicated.

It was found, however, that the chlorine atoms could be removed from the chloro-lignins by treatment with zinc dust and alkali at 100°C, the extent of dehalogenation being a function of the time of reaction.

The results are given in Table XXVI and indicate that presumably no serious degradation of the lignin takes place on dehalogenation since the methoxyl content of the starting material and that of the product, calculated on a chlorine free basis, remains practically constant.

# THEORETICAL DISCUSSION

## 1. Action of "available chlorine" solutions upon Lignin.

A complete discussion of the action of "available chlorine" solutions on lignin must take into consideration the following factors;

a) Composition of the reactant and the specific character, or otherwise, of its active components.

b) The unknown but admittedly complex structure of lignin.

The composition of aqueous solutions of "available chlorine" depends upon the hydrogen-ion concentration and is dicussed in a previous chapter. In alkaline solution the active agent is hypochlorite ion; in acid media molecular chlorine is present, and in the range of acidity bordering upon the neutral point hypochlorous acid exists, for practical purposes, as the only active agent. The available literature concerning the reactions of these compounds in aqueous solution indicates a lack of specificity in reactions with the majority of organic compounds, especially those containing hydroxyl groups and ethylenic linkages; the mechanism of the reaction by means of which the halo-hydrins and di-halides are formed from such relatively simple substances as ethylene and related compounds is still a matter of uncertainty.

The experimental results, presented in another chapter show that the action of "available chlorine" solutions upon lignin results in a decrease in the methoxyl content of the latter, and, although not the only reaction taking place, can be regarded as a process of de-methylation in which the basic structure of the lignin molecule is left unchanged.

A de-methylation of this type, brought about by the action of aqueous "available"chlorine" solutions on compounds of known structure has not been previously observed*. It is known, however that the alkoxy groups of the stable aromatic and aliphatic ethers are only attacked by chlorine under drastic conditions involving a pronounced change in the entire molecular structure. On the other hand, the glucosidic and enolic ethers are known to be considerably less stable in character, both being readily hydrolysed in acidic media but stable in alkaline solution.

In the present investigation it was found that the de-methylation reaction was attended by one of chlorination, so that an enolic type of ether grouping would seem to be the

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*In this connection Jacobsen (6) found that ethyl ether is attacked by hypochlorous acid, the first change being a replacement of the hydrogen atoms in one ethyl group by chlorine. Harris and co-workers (23) have used this fact to explain the results obtained by them on the action of aqueous chlorine solutions upon lignin.

most probable. A survey of the literature on representative compounds containing this grouping, for example, beta methoxy crotonic acid, /methoxy tetra-hydro benzene, 3 methoxy kojic acid, 3 methoxy, $5,7,3',4'$ tetra hydroxy flavinol (quercetin), failed to reveal any information relating to the removal of the enolic ether group by either halogens or hypochlorites

In spite of this lack of positive information, a demethylation by such agents both in aqueous and anhydrous media has been reported by various workers in connection with studies on the lignin problem. The results obtained in the present investigation undoubtedly show that;

a) Aqueous solutions of "available chlorine" act upon lignin with resulting decrease in methoxyl content, Tables XVII - XXIV, Figs. XI - XV.

b) Chlorination of the lignin occurs with aqueous "available chlorine" solutions, Tables XVII-XXIV Figs. XI - XV.

c) Reactions a) and b) are intimately related and the extent to which each proceeds is a function of the hydrogen-ion concentration of the medium in which the reaction occurs, Fig. III.

d) Large quantities of HCl are formed in the reaction since NaOH solution must be continually added to the mixture to maintain constant pH, (Experimental Part 3).

e) The structure of the de-methylated and chlorinated lignin at pH 10 must closely resemble that of the original lignin; This conclusion is based not only on the fact that the chlorine analysis of the products isolated from the reaction at pH 10 is constant after the initial stages, Table XXIV A, Fig. XV, but also on the increase in methoxyl content upon methylation of the products, being about ninety percent of the increase obtained when alkali lignin is methylated, Table XXV.

f) The isolated reaction product is more acidic in character than the original lignin since it is only precipitated in much more strongly acid media and because the fully methylated derivative is alkali soluble, Table XXV. and Experimental Part 5.

The results obtained by previous investigators can now be discussed in the light of the conclusions drawn under a) to f) inclusive.

Freudenberg, Belz and Niemann (36) treated lignin (isolated by alternate treatment of wood with Schweitzer's reagent and dilute $H_2SO_4$) with bromine in ten percent HBr solution and found that a loss of methoxyl occurred. They concluded that the reaction was mainly one of substitution and that the loss of methoxyl was associated with quinone formation, (Pg. 33). Their conclusions, however, assume the presence of molecular chlorine as the active agent and this is only present in very minute quantities in media of pH 6 and above. Since the loss of methoxyl also occurs in solutions of pH 10 the validity of the assumed mechanism appears uncertain. In strongly acid solutions molecular chlorine can be considered as the active agent and substitution in the lignin molecule probably occurs. The present investigation has shown that the equivalent ratio of methoxyl lost, to chlorine introduced, is always less than unity in such media, indicating that more chlorine has been introduced into the lignin than is represented by the amount of methoxyl removed.

Harris? Sherrard and Mitchell (23) treated Klason lignin (70% $H_2SO_4$ method) with chlorine both in aqueous and anhydrous solutions,(Pg. 26). The results of their experiments in the former could not be interpreted by them on any basis other than the assumption that chlorine reacts with the hydrogen atoms of the alkoxy group as reported by Jacobsen (6) in the case of diethyl ether. Their work in anhydrous media led them to conclude that the enolic type of methoxyl grouping is present in lignin and that the addition of chlorine to the ethylenic linkage is followed by a loss of methoxyl, thus giving rise to ketone formation. These authors were unable to methylate the reaction products and also concluded that a loss of hydroxyl groups had occurred in the reaction.

The loss of methoxyl by the action of bromine in glacial acetic acid upon lignin (isolated from spruce wood by use of HCl and acetic acid), observed by Friedrich and Diwald (27), was later investigated by Friedrich and Pelikan (28). An exhaustive examination of the products of the reaction failed to reveal the presence of $CH_3Br$ or related compounds and they therefore concluded that a molecular rearrangement had taken place resulting in the formation of hydroxyl groups. As evidence in favour of this assumption they found the brominated product could be methylated and the methoxyl content of the fully methylated derivative, calculated on a bromine free basis, was only slightly less than that of the fully methylated original lignin.

It seems well established, therefore, that a loss of methoxyl groups occurs when lignin is treated with aqueous solutions of chlorine and its derivatives, or with halogens in anhydrous media. As a reasonable, working hypothesis it may be assumed that methoxyl groups of the enolic type are present in the lignin molecule and that their removal is brought about by a primary addition of chlorine or hypochlorous acid (Fig. III) to the ethylenic linkage, followed by subsequent elimination of methoxyl.

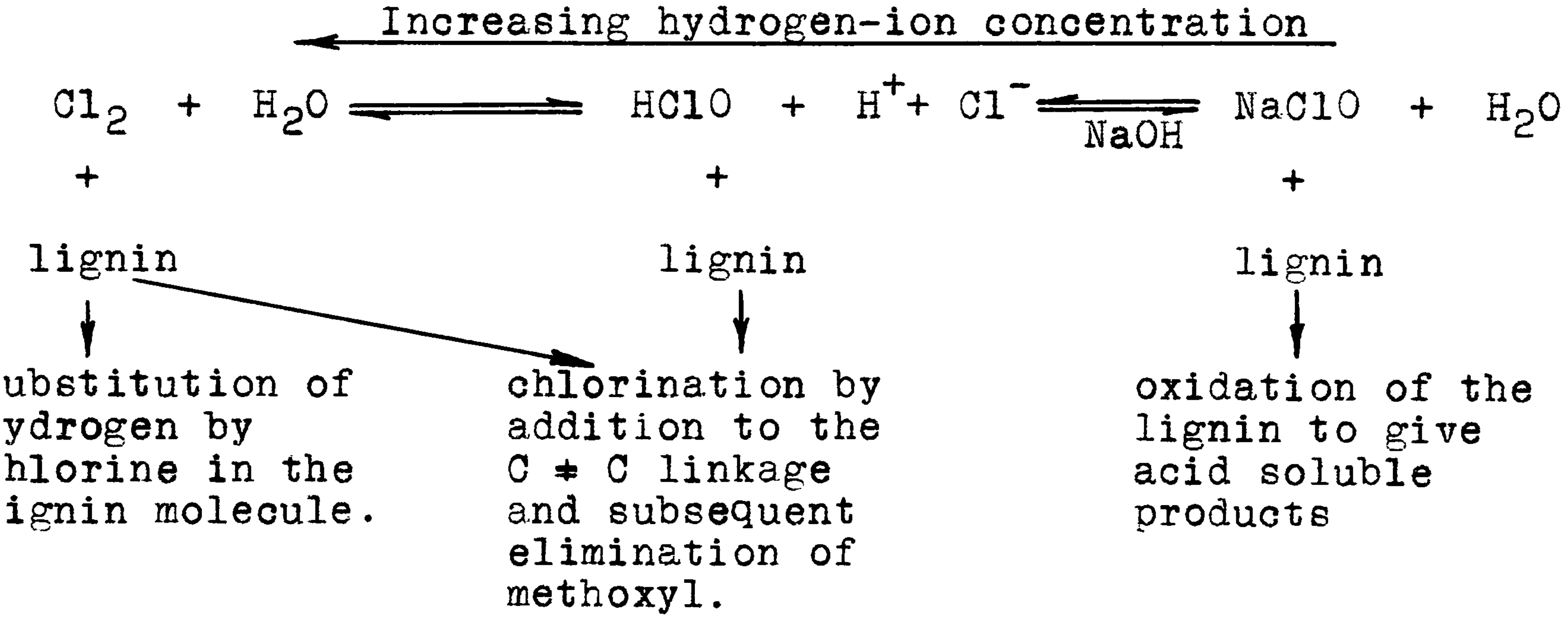
Since the reaction proceeds in media which contain only minute quantities of chlorine a choice of reactant must be made as between chlorine and hypochlorous acid, the main component of "available chlorine" solutions at pH 6. That such minute quantities of chlorine as are present in solutions of this hydrogen-ion concentration could give rise to the rapid chlorination of the lignin which occurs, appears to be very doubtful. The alternative assumption, that chlorination is effected by hypochlorous acid, is also open to the criticism that addition of OH' and Cl' as such to the ethylenic linkage involves the assumption of a positively charged chlorine atom, a theory not generally accepted. It is known, however, that chlorination actually occurs in solutions pH 6 - 10, and it can only be concluded that hypochlorous acid must play some role in the reaction as assumed by Read and co-workers, (9).

In connection with their investigation into the mechanism of formation of di-halides and halo-hydrins they assume that a partition reaction probably occurs and that the resulting ratio of di-halide to halo-hydrin is determined by the relative velocities of the two reactions;

$$\begin{array}{ccc} Cl_2 \quad + \quad H_2O & \rightleftharpoons & HClO \quad + \quad H^+ \quad + \quad Cl^- \\ + & & + \\ \text{ethylene} & & \text{ethylene} \\ \downarrow & & \downarrow \\ \text{ethylene di-chloride} & & \text{ethylene chloro-hydrin} \end{array}$$

Read and co-workers found that the experimental conditions giving the largest yields of chloro-hydrin were also those favouring the highest concentration of hypochlorous acid as compared with chlorine.

This type of reaction may also be applicable to the action of "available chlorine" solutions on lignin;



## Course of the reaction.

In acidic media the molecular chlorine present reacts to bring about both chlorination and de-methylation of the lignin by addition, and also effects the substitution of hydrogen by chlorine. These reactions are indicated by the fact that the equivalent ratio of methoxyl lost, to chlorine introduced is always less than unity in such solutions (pH less than approximately 4), Fig. III. In less acidic media, pH 4 - 6, where the "available chlorine" solution is largely composed of hypochlorous acid, the substitution reaction is suppressed and the equivalent ratio approximates unity, Fig. III. As the reaction medium becomes more alkaline, pH 6 - 10, the concentration of hypochlorous acid decreases while that of the hypochlorite ion increases, the latter reacting to bring about an extensive oxidation of the lignin to acid-soluble products. The increasing difficulty of chlorination in alkaline solution, Fig. IV, is also to be partially accounted for by the removal of the chlorine atoms in the alkaline solution following the elimination of methoxyl.

It would lead too far to enter into a thorough discussion of the evidence for and against the possibility of hypohalous acid addition to the ethylenic linkage. The question has received the attention of numerous investigators over a period of years and has not yet been satisfactorily settled. Bartlett (74), who has made the most recent contribution in this field states; "although we regard the positive halogen ions as a fiction, it is not to be ignored that free hydrogen ions in solution are also a fiction (79), and it may develop for purposes of classification, that positive halogen ions may be just as useful a fiction as free protons".

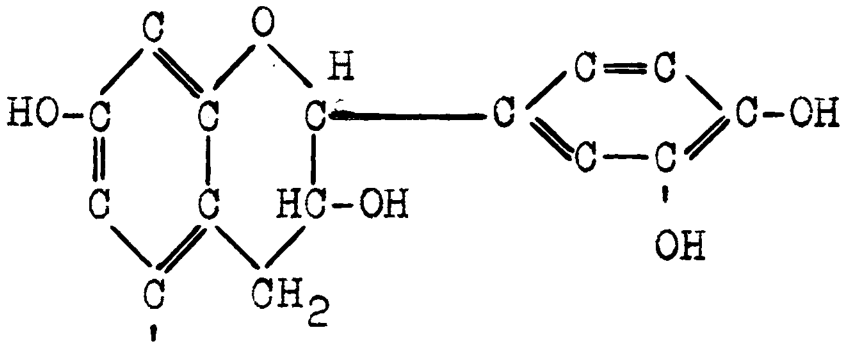
### 2. Nature of the methoxyl groups which are left unattacked by the action of "available chlorine" solutions upon lignin.

The results of the present investigation have shown that the methoxyl groups in lignin are of two different types, namely, two-thirds are removable by the action of "available chlorine" solutions, while the remaining one-third are resistant to the action of this reagent. The latter presumably are attached to an aromatic ring, or rings, the presence of this nucleus in the lignin molecule having been shown recently by Hibbert and Tomlinson (5).

## 3. The Natural Tannins: Possible relationship of Tannins to Lignin.

In conclusion, a brief discussion will be given of the natural tannins and of their possible relationship to lignin. This class of compounds, especially the phlobatannins* show a marked resemblance, both in general physical properties and in certain qualitative chemical reactions to lignin.

The phlobatannins are related to the natural plant pigments of the benzo-pyran type, their nearest analogues being the flavans. The only known naturally occurring member of the flavan group is catechin (A) the structure of which was established by Freudenberg (82).



(A)

Catechin itself is not a tannin but resembles the

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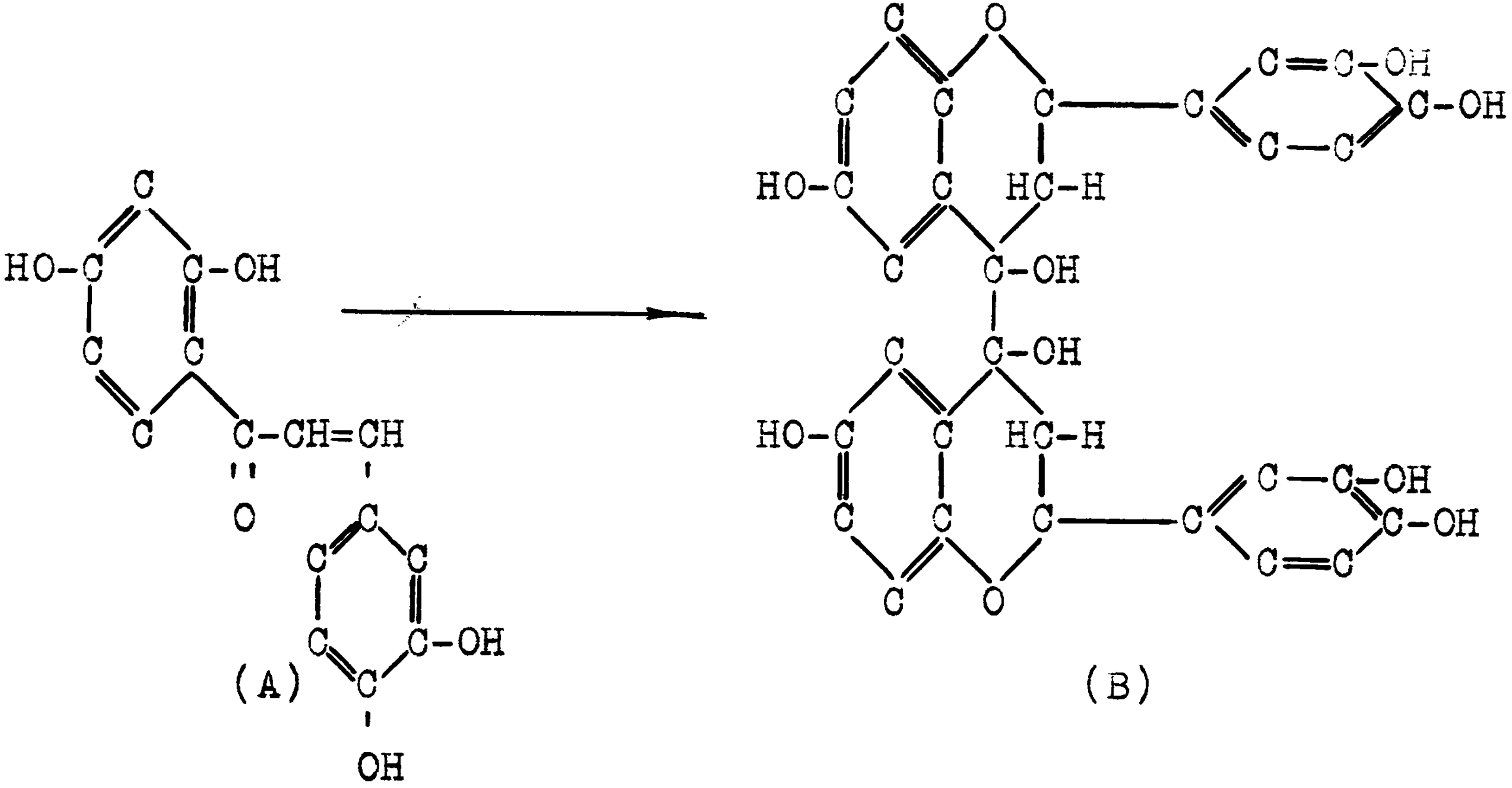
* The phlobatannins are classed as those natural tannins which on boiling with dilute mineral acids are slowly and completely converted into red or brown, amorphous insoluble substances named phlobaphenes.

phlobatannins in some respects and Freudenberg has expressed the view that each phlobatannin is a polymer of that particular 3 hydroxypolyhydroxyflavan yielding fission products corresponding to those given by the tannin.

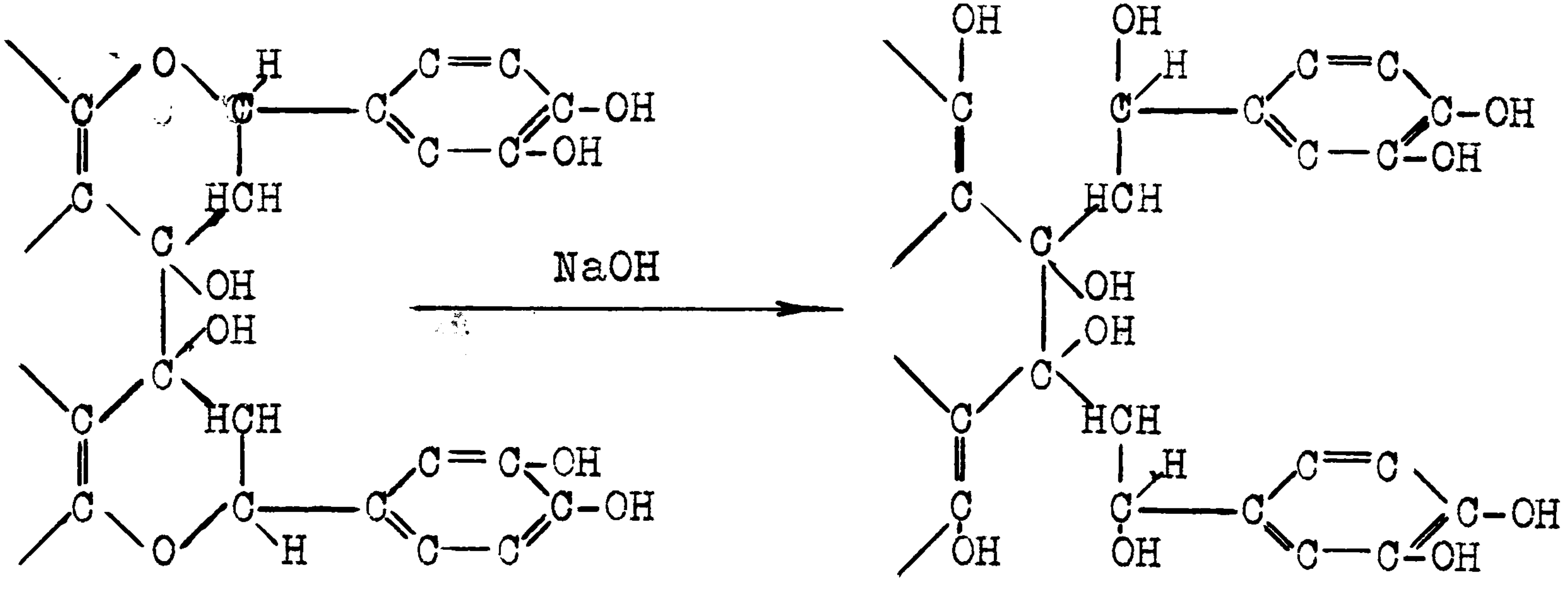
The failure to identify positively the phlobatannins with the 3 hydroxypolyhydroxyflavans led Russell (83) to assume that in the phlobatannin structure the pyranoid hydroxyl might be in the 4 rather than in the 3 position. Attempts to synthesize such derivatives by a simultaneous reduction and ring closure of 2,4,3', 4', tetra-hydroxy chalcone (A) resulted in the formation of bis(7,3', 4', tri-hydroxy)flavpinacol (B).



This amorphous reduction product (B) was quantitatively indistinguishable from typical natural phlobatannins and Russell on the basis of several such syntheses concluded that all phlobatannins are built up on the same general plan and differ from each other only with respect to the number and position of their hydroxyl groups. It is possible that part of the lignin molecule may have a structure related in some way to the groupings present in the phlobatannins.

Powell and Whittaker (14) from their work on alkali lignin concluded that ligninsfrom different sources are derived from the same polyhydroxy compound, termed by them "lignol", and that they differ only with respect to the number of hydroxyl groups present in the molecule.

Alkali lignin cannot have a flavpinacol structure, however, since the pyrone ring is unstable in alkaline solution. If lignin is in any way related to the phlobatannins alkali lignin (or a portion of it) would have the configuration shown by (C)



(B) (C)

## BLEACHING OF WOOD CELLULOSE

The commercial methods for the production of wood celluloses can be divided into two main classes, namely, the acid and alkaline processes in which acid bisulphites and alkalies respectively are employed. The crude product, obtained by either process, still contains varying proportions of the encrustants originally present in the wood, namely, hemi-celluloses, pentosans, and lignin, and their removal involves the use of bleaching agents.

The latter, in general, are strong oxidizing agents and consequently must be employed in such a manner that, in the process of purification, no degradation of the cellulose occurs. Industrially, the end-point of the bleaching process is reached when a further removal of the remaining encrusting impurities is simultaneously attended by chemical changes in the cellulose.

The bleaching agents in common use are limited almost entirely to aqueous solutions of chlorine, hypochlorous acid and its salts, sodium and calcium hypochlorites and much effort has been devoted to ascertaining the most efficient method of using these reagents in order to obtain the purest cellulose by the use of a minimum consumption of "available chlorine".

It was assumed initially, based on previous experience in the bleaching of textile fibers, that hypochlorite solutions could also be used as bleaching agents for wood cellulose. In the case of "sulphite pulps" calcium hypochlorite was found to give very satisfactory results but its use for the bleaching of "kraft" and "soda" pulps was not attended by any great measure of success, probably in consequence of the large amounts of reagent required to produce a pure white color.

Investigations on a practical scale showed that by the use of aqueous chlorine solutions as a pre-treatment stage there resulted a better color and less degradation of the cellulose, and a considerable saving in the quantity of active agent required in the bleaching process. Practically all bleaching operations in current use for alkaline pulps employ a two stage process, the soluble products from the first or acid stage being removed by filtration prior to the addition of the alkaline hypochlorite solution. The commonly accepted view-point accounting for the greater success of the two-stage process is that chlorination of the lignin in acid solution results in the formation of alkali-soluble chloro-lignins, while in the second or alkaline stage the difficultly bleachable, small residue of lignin and coloring matter is removed by oxidation. These explanations have been deduced largely from empirical observations and a large number of practical experiments performed upon unbleached pulps and cannot, therefore, be expected to give any insight into the mechanism of the chemical reactions involved.

A recent invention by Tomlinson (84) is indicative of the progress made in the development of a satisfactory bleaching process for alkaline pulps. This inventor found that clean, strong cellulose could be made from various wood pulps, including those classed as hard bleaching pulps, without impairing the strength or other desirable characteristics of the cellulose fibers. The pulps are treated successively with aqueous chlorine in the partially hydrolysed state, then with hypochlorous acid in the absence of HCl, and finally with calcium hypochlorite in alkaline solution. In some cases, as with difficultly bleachable pulps, a fourth stage is used and involves the treatment of the pulp from the third stage, after washing, with a fresh quantity of alkaline bleach solution.

The process, with the exception of the fourth stage is continuous and is so regulated that the bleached cellulose, or product for the fourth stage, can be filtered continuously from the exhausted bleach liquors. The invention claims to provide a rapid economical process for removing lignin and other coloring matter from wood pulp.

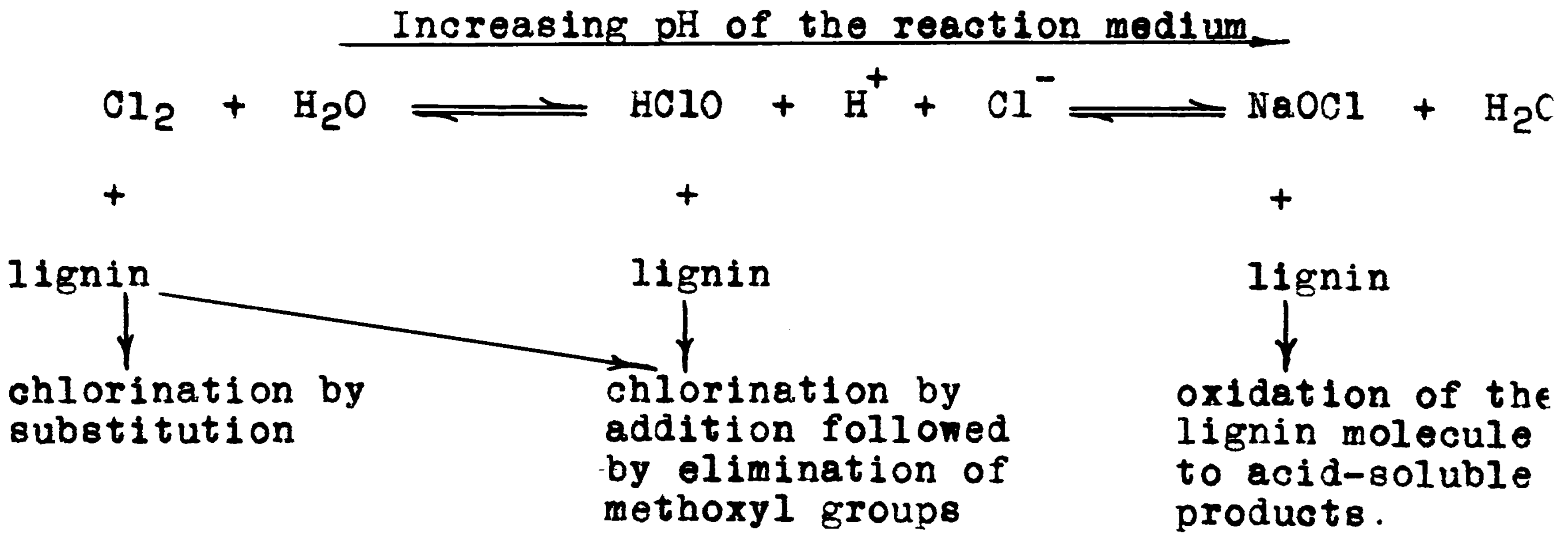
A still more recent invention by Opfermann and Feldtmann (85), relating to the manufacture of highly purified "kraft" pulps (alkaline process) deals in particular with the control of acidity and alkalinity of the bleaching solution. These inventors find that the use of aqueous chlorine solutions in the acid pre-treatment stage, especially for hard bleaching pulps, causes a reduction in the viscosity and tensile strength of the final bleached product. This behaviour of the pulp is attributed to the fact that chlorination proceeds slowly due to the formation of insoluble chlorinated lignin products and the excessive amount of free chlorine, present in the bath for a prolonged period of time reacts with the cellulose. According to O. and F.'s invention the time of chlorination can be considerably reduced, without damaging the fibers, by operating in such a manner that in the same proportion as chlorine enters into reaction, the chlorinated products formed are dissolved by the continuous addition of a suitable amount of alkali such that the pH value of the bath is maintained between pH 6 and pH 9, preferably between pH 7.5 and 8.5. A saving of chlorine can be effected by removing the dissolved chlorinated products by simultaneously adding water and removing the mother liquor.

The cellulose so obtained is claimed to be suitable,not only for the preparation of special papers but also for chemical processes such as, the manufacture of viscose and cellulose acetate silks. The process, furthermore, has the advantage that such refined celluloses still retain their high viscosities in solvents (cuprammonium etc.) and can be transformed into exceptionally white products of lower viscosity by subjecting them to a suitable, more vigorous type of bleaching.

The present investigation was undertaken in order to obtain fundamental data relating to the bleaching of alkaline pulps. The action of chlorine and its derivatives upon the main substance being removed in the bleaching process namely, the lignin, was studied under conditions of constant hydrogen-ion concentration. The investigation was then extended to cover the pH range from pH 2 to pH 10, and a further research conducted relating to the solubility of lignin in aqueous solutions. The results obtained, together with graphical representations and discussion, have been presented in other sections, see "Discussion of Results", "Theoretical Discussion", "Experimental Part"(IV).

In brief, it was found that a number of different reactions occur when lignin is treated with aqueous solutions of "available chlorine", and that the participation of any individual reaction is governed by the pH of the reaction medium, Fig. III. In acid solutions, pH 2 - 4, chlorination both by substitution and addition occurs, the latter leading to a loss of methoxyl groups, Figs. III, XI, XII. In less acidic media, pH 5 - 6, the chlorination by substitution is suppressed, and the reaction is mainly one of/a primary addition, either of chlorine or hypochlorous acid to an enol ether, followed by the elimination of methoxyl groups, Fig. III, XIII. As the reacting solution is made alkaline, the addition reaction becomes increasingly difficult and large quantities of the reagent are consumed in an oxidation of the lignin to acid-soluble products in consequence of the increasing concentration of hypochlorite ion in the solution, Fig. III, XIV, XV.

The variations in the different types of reaction taking place (substitution, addition, oxidation) as the controlled pH of the medium is varied are represented graphically in Fig. III and can be shown schematically in the following manner;



$$Cl_2 + H_2O \rightleftharpoons HClO + H^+ + Cl^- \rightleftharpoons NaOCl + H_2O$$

The consumption of "available chlorine" was found to be a function of the pH of the reaction medium as is shown in Fig. IV. The least quantity of reactant is consumed in acid solution, and this increases slowly as the pH of the medium is increased to pH 4 - 6. Further increase in the pH of the solution then results in the consumption of large quantities of reagent required to promote chlorination and de-methylation. It would therefore appear that bleaching operations when conducted in the most acidic medium "practically" available would correspond with a minimum consumption of chlorine. This conclusion is not justifiable, however, because the chloro-lignins formed are insoluble in the acid solution and therefore cannot be removed, and also because the undesired chlorine substitution reaction is taking place simultaneously.

The relationship between alkali lignin solubility and hydrogen-ion concentration was determined photometrically and potentiometrically and a graphical representation of the results is given in Figs. XVII, XVIII. It was found that alkali lignin flocculates in media having a lower pH than 4.2 and is thus precipitated from solution. Bleaching operations cannot therefore be conducted satisfactorily in media more acidic than pH 4.2 because the insoluble, colored, chlorinated products formed adhere to the cellulose fibers. In alkaline solutions, pH 7 - 10, on the other hand, large quantities of the bleaching agent are consumed in oxidation reactions involving both lignin and cellulose. In solutions of pH 5-6 however, the lignin is chlorinated and de-methylated in the same equivalent ratio while the hydrogen-ion concentration is sufficiently low to maintain solubility of the chloro-lignins. In this range of acidity the rapid rise in the consumption of

"available chlorine" is just commencing and the conclusion seems justified that bleaching operations conducted in media of pH 5 - 6 should therefore result in maximum solution of the lignin accompanied by minimum consumption of chlorine.
The effect upon the cellulose by bleaching under these conditions can be ascertained from the previously discussed researches of Birtwell, Clibbens and Ridge (3).

The possible saving in chlorine that can be effected by conducting bleaching operations in media of pH 5 - 6 can be seen by comparing the chlorine consumption shown in the following calculation with that actually found in practice.

Calculation;

Assuming on the basis of the results obtained,that two-thirds of the methoxyl groups present in lignin are removed in the reaction with "available chlorine", and that a pulp containing 4% lignin is to be bleached, the following data indicate the possible saving in chlorine consumption based on suitably pH controlled bleaching operations.

lignin per ton of pulp = 80 lbs.

methoxyl content of lignin = 15.2 %

methoxyl removed in bleaching = 10.2 %

methoxyl removed in bleaching one ton of pulp = 8.15 lbs.

= 0.262 equivalents.

equivalents of "available chlorine" required to remove one equivalent of methoxyl at pH 5 - 6, Fig. IV (a), (b). = 10 to 11

equivalents of "available chlorine" required per ton of pulp = 2.6 to 2.9

chlorine required per ton of pulp = 93 to 102 lbs.

In comparison with this figure the consumption of chlorine in the usual two-stage process varies between about 110 and 150 lbs. chlorine per ton depending upon the characteristics of the unbleached pulp and the degree of whiteness desired in the product.

# EXPERIMENTAL PART

## PART I. ISOLATION AND PURIFICATION OF ALKALI LIGNIN.

In the present investigation, dealing with the action of chlorine and its derivatives upon lignin, an alkali lignin prepared from carefully purified wood meal was used as starting material. The actual composition of alkali lignin is unknown as can be seen by reference to the literature dealing with its preparation and analysis. However, by careful control of experimental conditions (time, temperature alkali concentration, etc.) a reproducible, apparently homogeneous and easily handled product can be obtained. The experimental procedure for isolating alkali lignin developed originally by Mehta (12), used later by Dorée and Barton-Wright (16) and improved by Marshall (18) in these laboratories was adopted in the present research. A complete, schematic flowsheet for both the isolation and the purification of alkali lignin has been included, pgs. 106, 108.

### 1. Isolation of Alkali Lignin.

#### a) Preparation of the Spruce wood.

The wood used for the preparation of the lignin was obtained from a section of the trunk of a mature white spruce log. The sapwood, cut into 4 inch square blocks, was ground upon a lathe to a fine flour (20 mesh). This operation is readily carried out by slowly forcing a sharp cutting tool across the grain of the wood while the block is rotated at high speed. The screened wood flour was dried in a vacuum oven at 50 - 60°C.

### b) Removal of Resins, Fats and Waxes from the wood flour.

The resins, fats and waxes, amounting to 2 - 3 %, present in spruce wood were removed from the wood flour by extraction for 36 hrs. in a large Soxhlet apparatus with benzene - alcohol (1 : 1). The excess solvent was removed by filtration on a Büchner funnel and the de-resinified spruce wood flour dried first in the open air and finally in the vacuum oven at 50 - 60°C.

### c) Removal of Hemi-celluloses and Pentosans.

The hemi-celluloses and pentosans were removed by stirring the de-resinified spruce wood flour with four successive portions of 5% caustic soda solution, (method of Friedrich and Diwald (27). Each extraction was carried out for 36 hrs. at room temperature under an atmosphere of nitrogen to prevent oxidation. The liquor to wood flour ratio was 10:1. The alkaline extract was removed by filtration and the residual wood flour washed with fresh 5% NaOH solution. After the fourth extraction and filtration the wood flour was washed successively with water, dilute acetic acid, and finally with alcohol. The product was dried, first in the open air and finally in the vacuum oven at 50° -60°C.

### d) Extraction and Isolation of Alkali Lignin.

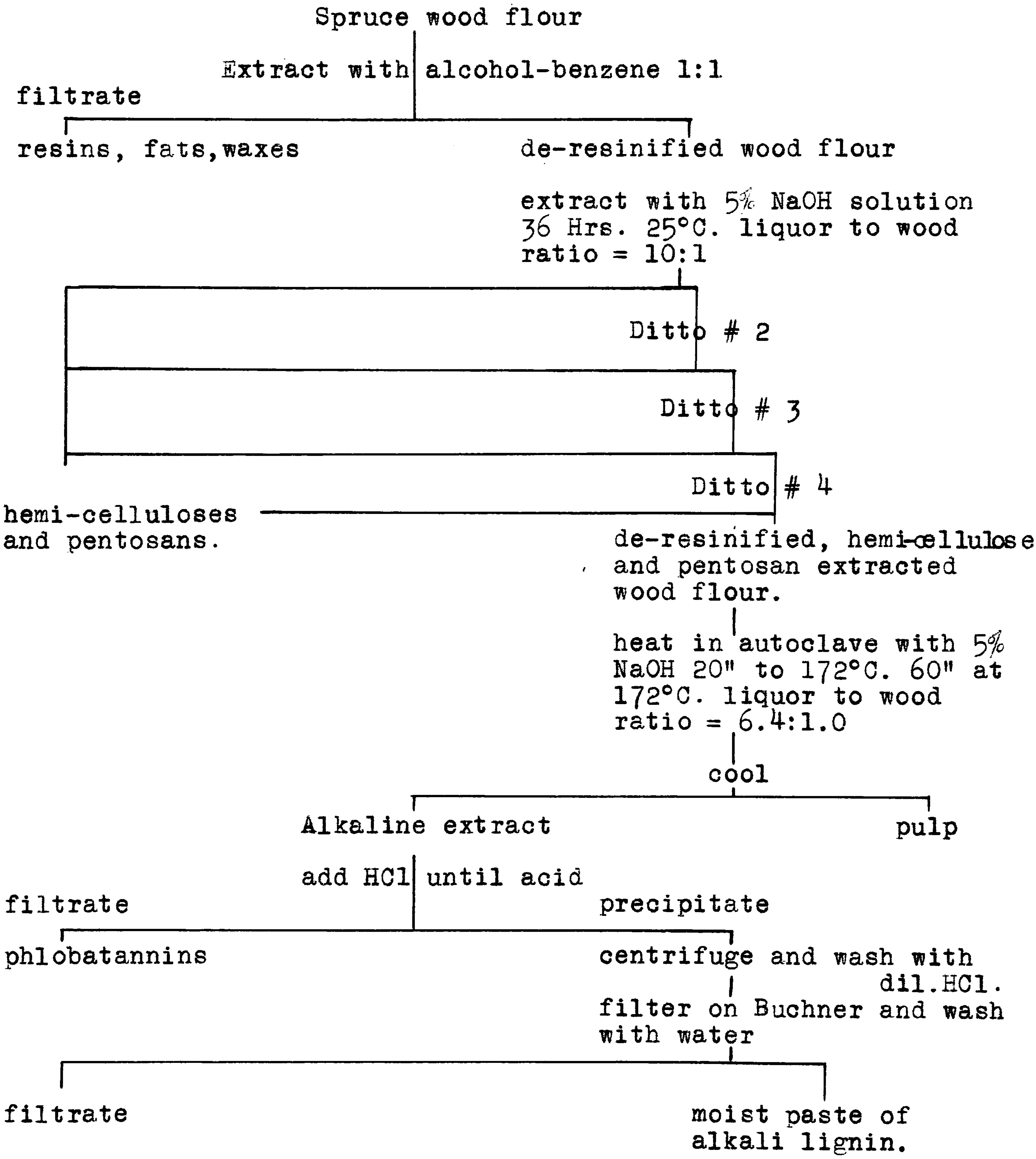
The alkali lignin was obtained by treatment of the above extracted wood flour with alkali according to the method proposed by Mehta (12). The wood flour was placed in a small rotary autoclave with a 4% NaOH solution, the liquor to wood ratio being 6.4 : 1.0.by weight. Nitrogen was bubbled through for several minutes to expel the air. The autoclave was then sealed, set in rotation, and the temperature (measured in a thermometer-well located in the autoclave wall) raised to exactly 172°C in twenty minutes and maintained there for one hour. The autoclave was then cooled rapidly by a stream of ice-water and opened. The reaction-product was filtered, the alkaline liquor being dropped into ice-water and then neutralized with HCl. The precipitated alkali lignin was centrifuged free from the mother liquor, washed with dilute HCl (0.01N), reduced to a moist paste by suction on a Büchner funnel and washed well with distilled water.

The crude alkali lignin thus obtained was dissolved in absolute dioxan and the water present removed by vacuum distillation with successive portions of dry solvent.

The methoxyl analysis of a sample obtained by precipitation into well stirred ether, washing and drying is given in Table XII A.

## Table X

## Isolation of Alkali Lignin.



Spruce wood flour
Extract with alcohol-benzene 1:1
filtrate
resins, fats, waxes
de-resinified wood flour
extract with 5% NaOH solution 36 Hrs. 25°C. liquor to wood ratio = 10:1
Ditto # 2
Ditto # 3
Ditto # 4
hemi-celluloses and pentosans.
de-resinified, hemi-cellulose and pentosan extracted wood flour.
heat in autoclave with 5% NaOH 20" to 172°C. 60" at 172°C. liquor to wood ratio = 6.4:1.0
cool
Alkaline extract
pulp
add HCl until acid
filtrate
precipitate
phlobatannins
centrifuge and wash with dil. HCl.
filter on Buchner and wash with water
filtrate
moist paste of alkali lignin.

## 2. Purification of Alkali Lignin.

The crude alkali lignin was found to be contaminated with a substance, soluble in dioxan-lignin solution but insoluble in dioxan or ether after isolation. The alkali lignin itself is soluble in dioxan and insoluble in ether. It was freed from the impurity by fractional precipitation with ether from its dioxan solution advantage being taken of the different solubility ratio of the impurity and of alkali lignin in dioxan-ether mixtures.

### Method.

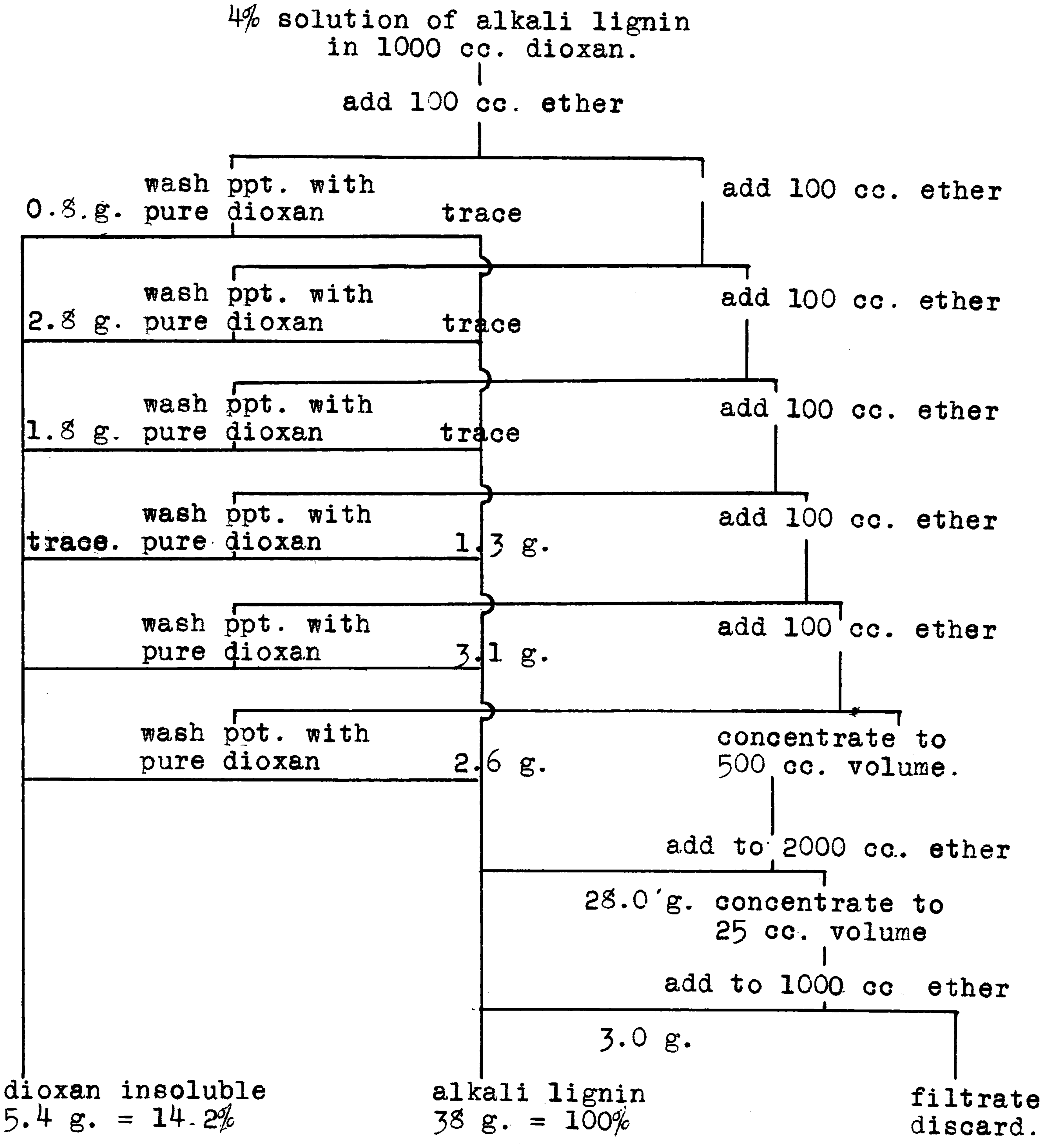
A litre solution containing approximately 4% of crude alkali lignin was vigorously stirred and 100 cc. of anhydrous ether added in a fine stream. The mixture was filtered and a further 100 cc. of ether added to the filtrate. The process was repeated six times giving six precipitates and one filtrate (A) containing ether and dioxan in the ratio 38:62.

Each of the six precipitates was then washed by shaking with absolute dioxan, filtered, dried and weighed. The total yield of dioxan-insoluble material was 5.4 gms. The washings from each of the precipitates were concentrated to small volume, precipitated into ether, and the precipitate washed, dried, weighed and in some cases analysed for methoxyl.

The filtrate (A) was concentrated to 500 cc. volume and slowly dropped into 2000 cc. of well stirred anhydrous

## Table XI

### Purification of Alkali Lignin by Fractional precipitation.



## Table XII A

### Purification of Alkali Lignin by Fractional Precipitation.

| Precipitation | | Fractionation<br>ether cc. | dioxan cc. | insol. gms. | sol. gms. | mgm. subs. | Analysis<br>cc.N/20 thio. | % OMe |
|---|---|---|---|---|---|---|---|---|
| ether added | | 0 | 1000 | - | - | 23.34 | 12.55 | 13.74' |
| to dioxan | 1 | 100 | " | 0.8 | - | | | |
| solution. | 2 | 100 | " | 2.8 | - | 25.98 | 10.85 | 10.67 |
| | 3 | 100 | " | 1.8 | - | | | |
| | 4 | 100 | " | - | 1.3 | 24.63 | 14.50 | 15.28 |
| | 5 | 100 | " | - | 3.1 | 26.10 | 15.51 | 15.20 |
| | 6 | 100 | " | - | 2.6 | 16.45 | 9.60 | 15.06 |
| dioxan added | 7 | 2000 | 500 | - | 28.0 | 15.91 | 9.30 | 15.15 |
| to ether | 8 | 1000 | 25 | - | 3.0 | 25.36 | 14.75 | 15.15 |

' crude alkali lignin

Average % OMe of alkali lignin fractions - 15.17

## Table XII B

### Purification of Alkali Lignin by Fractional Precipitation

| ether cc. | dioxan cc. | % ether | % dioxan | Insol. gms. | %Insol. | Sol. gms. | %Sol. |
|---|---|---|---|---|---|---|---|
| 0 | 1000 | 0 | 100 | 0 | 0 | 0 | 0 |
| 100 | " | 9 | 91 | 0.8 | 2.1 | - | - |
| 200 | " | 17 | 83 | 3.6 | 9.5 | - | - |
| 300 | " | 23 | 77 | 5.4 | 14.2 | - | - |
| 400 | " | 28 | 72 | 5.4 | 14.2 | 1.3 | 3.2 |
| 500 | " | 33 | 67 | 5.4 | 14.2 | 4.4 | 11.5 |
| 600 | " | 38 | 62 | 5.4 | 14.2 | 7.0 | 18.5 |
| 2000 | 500 | 80 | 20 | 5.4 | 14.2 | 35.0 | 92.0 |
| 1000 | 25 | 97.6 | 2.4 | 5.4 | 14.2 | 38.0 | 100.0 |

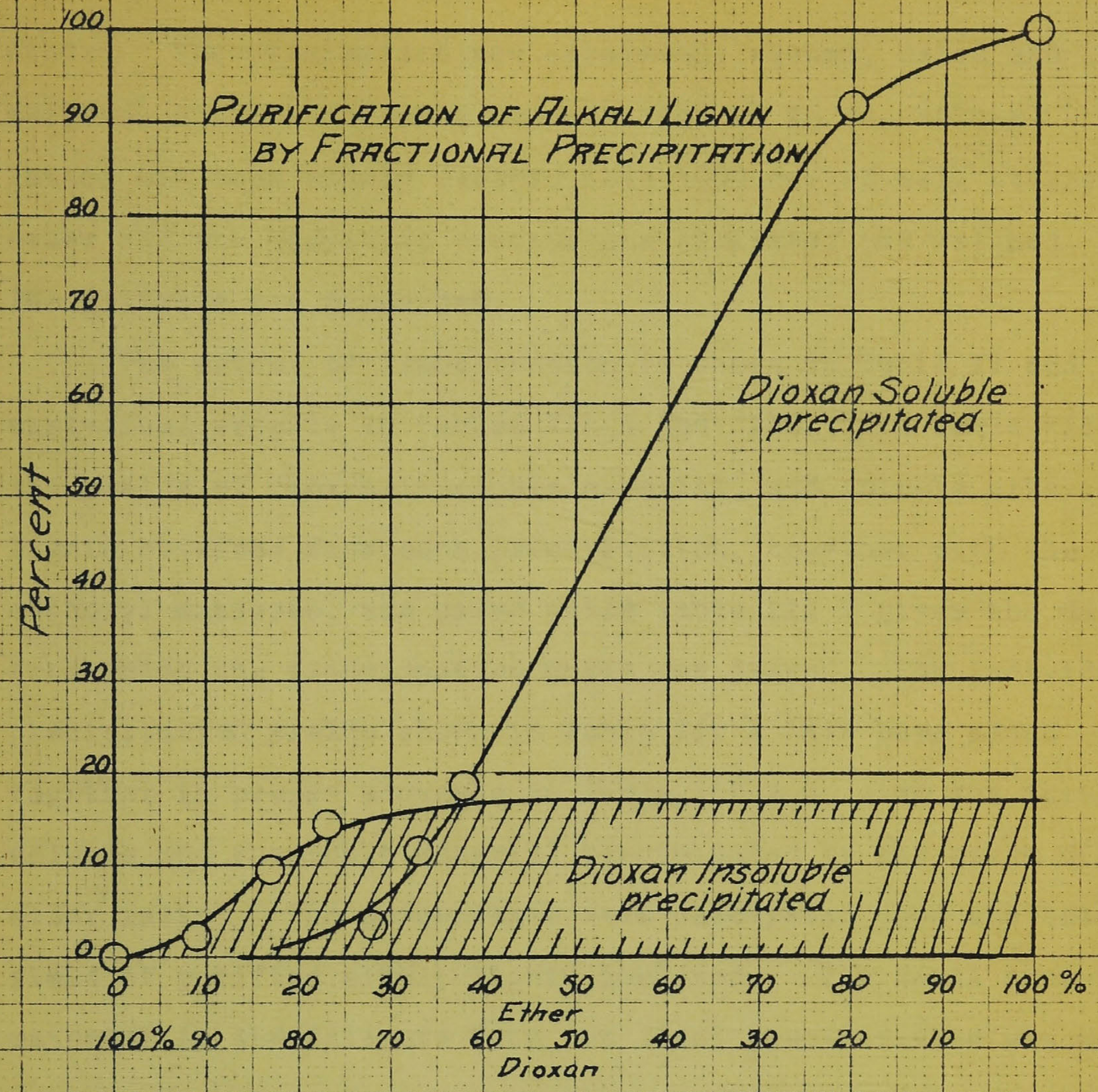

PURIFICATION OF ALKALI LIGNIN
BY FRACTIONAL PRECIPITATION
Percent
100
90
80
70
60
50
40
30
20
10
0
Dioxan Soluble
precipitated
Dioxan Insoluble
precipitated
0
10
20
30
40
50
60
70
80
90
100 %
Ether
100%
90
80
70
60
50
40
30
20
10
0
Dioxan

FIG. V.

ether. The precipitate was separated, washed, dried and weighed, and the filtrate concentrated to 25 cc. volume. The latter was then slowly dropped into 1000 cc. of well stirred ether and the resulting precipitate separated and weighed. The filtrate was discarded.

The method of fractionation is shown in Table XI and the analytical results in Tables XII A and XIIB. In Table XII A the yields of dioxan-insoluble material, and soluble alkali lignin obtained from each precipitation, together with the methoxyl analyses, are given while Table XII B gives the data from which the fractionation curve was drawn. The individual precipitation yields shown in Table XII A have been added together in proper sequence in Table XII B to give the total soluble and insoluble material precipitated by any given dioxan-ether ratio. The percentages were calculated upon the total yield of purified alkali lignin isolated. The small amount of material in the filtrate from the final precipitation was neglected.

## 3. Preparation of Standard solutions of alkali lignin

The action of chlorine and its derivatives upon alkali lignin was studied by adding known quantities of available chlorine solutions to known quantities of alkali lignin. Standard solutions of the lignin were prepared, from which volumes containing known weights of alkali lignin could be pipetted out for experiment.

The dioxan-soluble fractions obtained by the fractionation and purification of the crude product, (cf. pg. 108), were mixed together, weighed, and dissolved in 0.2 N NaOH. The volume was adjusted by adding distilled water to give a standard solution containing approximately 1.3% of alkali lignin. The amount of 0.2 N NaOH solution used was such that the standard solution was approximately 0.01 N in NaOH.

The exact amount of alkali lignin (by weight) contained in a solution was determined in the following manner: An aliquot portion by weight was diluted with distilled water and the lignin precipitated with dilute HCl. The precipitate was centrifuged, washed free of $Na^+$ ion, filtered on to a tared asbestos Gooch crucible, dried at 100°C and weighed. Ignition of the residue and re-weighing showed that no ash was present in the lignin. The percentage of lignin present in the standard solution was calculated from the weight of sample taken and the weight of dry residue.

The NaOH concentration of the solution was not of importance since the reacting solution was adjusted with acid to a pre-determined hydrogen-ion concentration before the addition of the available chlorine solution.

It was found that these alkaline solutions of alkali lignin were not stable over long periods of time. The decomposition taking place in a typical case is shown in the following Table (XIII).

## Table XIII

### Decomposition of Alkali Lignin in Alkaline solution

| Lignin solution | Lignin Analysis %C | %H | %OMe |
|---|---|---|---|
| Freshly prepared | 66.1 | 5.8 | 15.2 |
| After 3 months | 64.7 | 5.6 | 14.8 |

During the course of the work several standard solutions were therefore prepared from purified alkali lignin which had been kept in dioxan solution. The standardization results for these solutions is given in Table XIV.

## Table XIV.

### Standard solutions of Alkali Lignin

| Solution No. | Standardization Sample gms. | Lignin gms. | conc. % | Sample for Experiment gms. |
|---|---|---|---|---|
| 1 | 10.6 | 0.266 | 2.50 | 0.63 |
| 2 | 10.6 | 0.266 | 2.50 | 0.63 |
| 3 | 10.6 | 0.138 | 1.30 | 0.65 |
| 4 | 10.6 | 0.140 | 1.32 | 0.66 |
| 5 | 10.6 | 0.133 | 1.25 | 0.63 |

## 4. Analysis of Alkali Lignin.

The various alkali lignin fractions obtained in the fractionation and purification of the crude product showed essentially the same methoxyl content. They were therefore assumed to be fractions of the same homogeneous compound which displays a graded solubility in dioxan-ether mixtures. The analysis of a sample of alkali lignin, precipitated from a dioxan solution of the several purified fractions, and isolated in the usual manner, (cf. pg.136) is given in the following Table XV.

### Table XV

### Analysis of Alkali Lignin

| Analysis | Subs. | $CO_2$. | $H_2O$ | % C | % H | Subs | cc. Thio. N/20 | % OMe |
|---|---|---|---|---|---|---|---|---|
| No. 1 | 0.2407 | 0.5843 | 0.1266 | 66.1 | 5.83 | 19.28 | 11.34 | 15.20 |
| No. 2 | 0.2355 | 0.5709 | 0.1226 | 66.1 | 5.78 | 25.65 | 15.00 | 15.15 |

The average analyses of Alkali Lignin recorded by Marshall (18) are shown in Table XVI.

### Table XVI

### Analysis of Alkali Lignin according to Marshall (18)

| Product | % C | % H | % OMe |
|---|---|---|---|
| Alkali Lignin A | 64.75 | 5.71 | 15.00 |
| Alkali Lignin B | 65.02 | 5.43 | 14.00 |

## PART II. APPARATUS AND ITS OPERATION

### 1. The Constant Temperature Cabinet

The measurement of hydrogen-ion concentration is greatly simplified when the temperature is maintained at some constant value, for the following reasons;

(i) The saturated calomel half-cell, a recognized working standard, can be used with confidence.

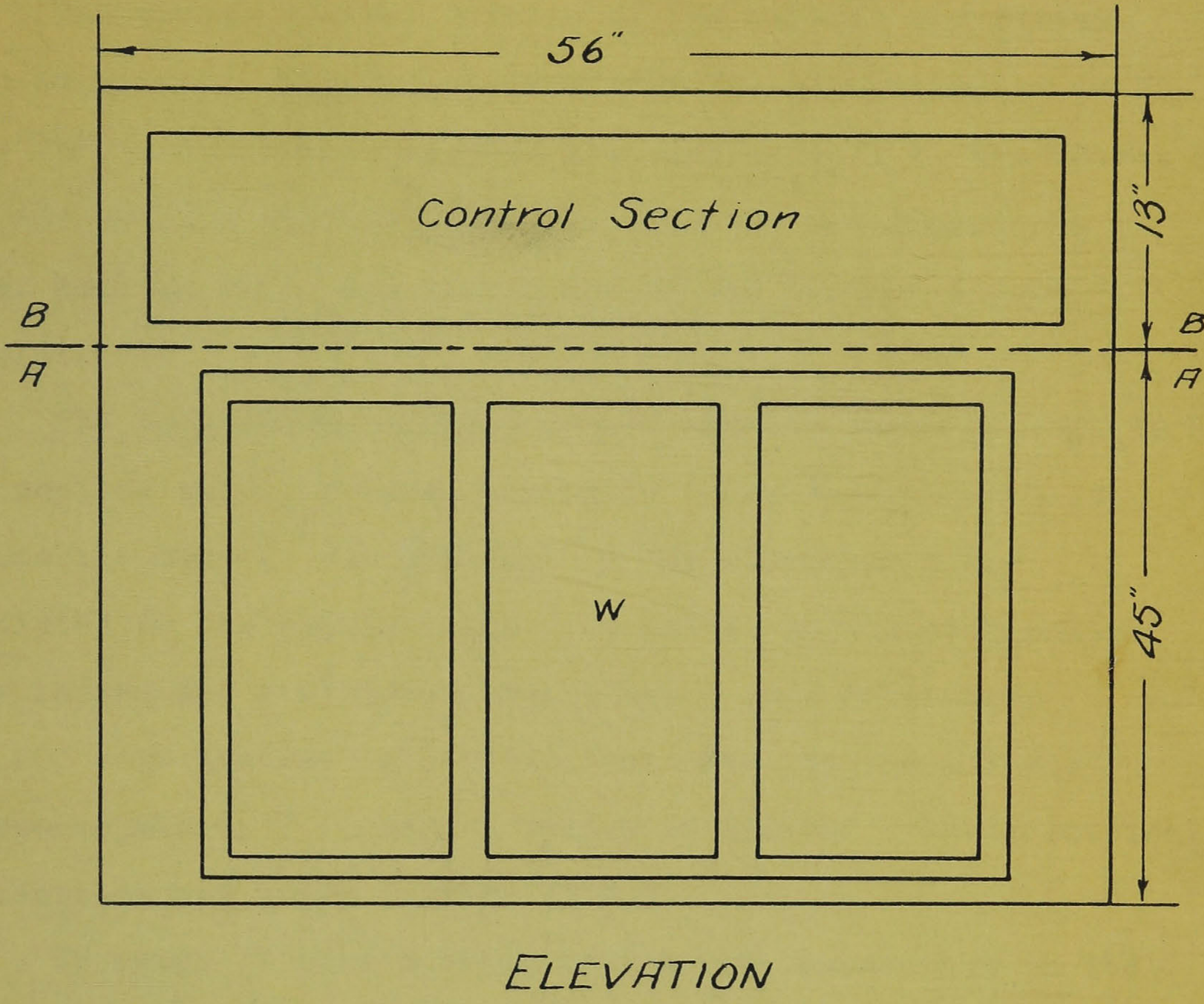
(ii) The uncertainty as to the existence of a temperature equlibrium in the various half-cells used is avoided.

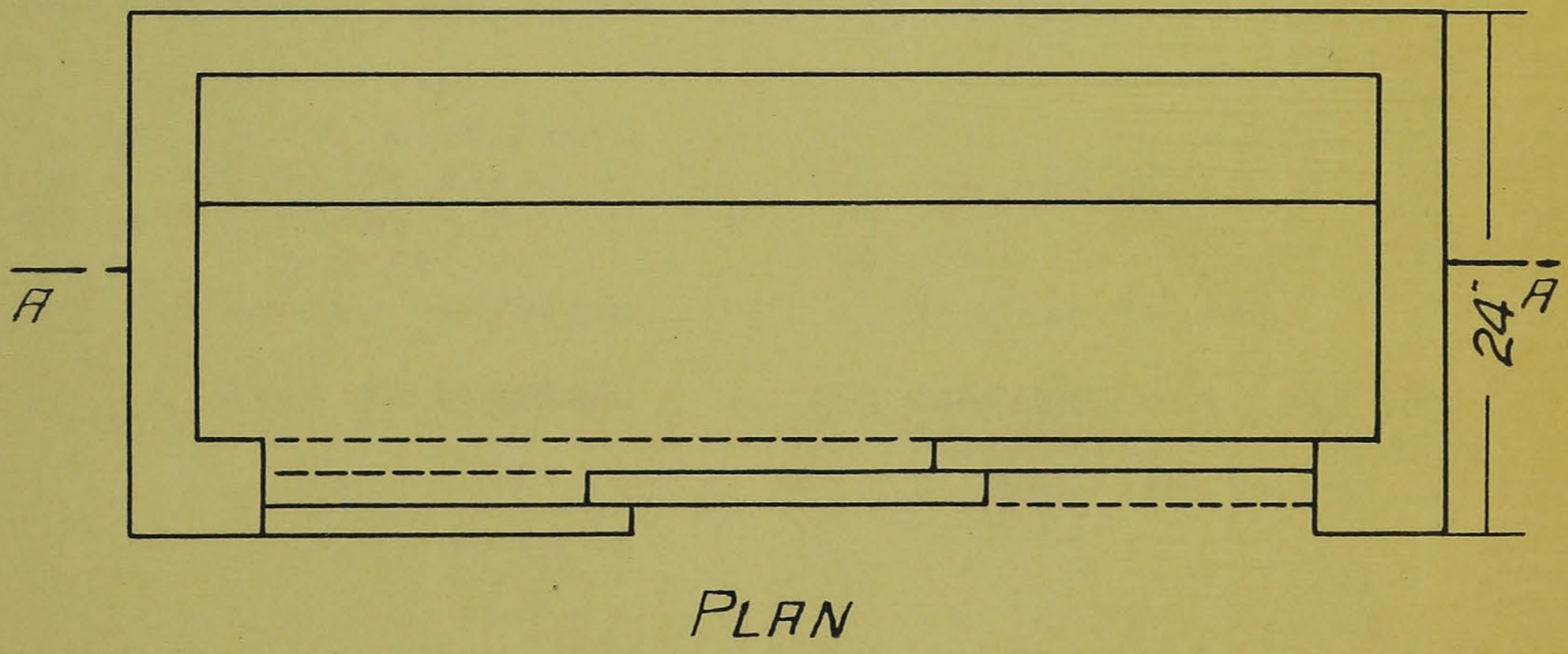
(iii) The necessity for using temperature coefficient corrections for the half-cells is avoided.

In the present investigation all reactions of available chlorine solutions with lignin were carried out at 25°C in the constant temperature apparatus described below.

The cabinet, Fig.VIA, was constructed of wood and lined with beaver-board so that an air space was left between the lining and outer wall. It was built in two parts, namely; an upper section for temperature control apparatus, and a lower section for experimental work. The top could be easily removed, giving access to the upper section.

The lower section was a chamber 17 in. x 52 in. x 33 in. fitted with a shelf at the rear and connected to the upper section through the vents V, V', Fig. VIB. Access to the chamber was made through three sliding doors W which had double glass windows.





CONSTANT TEMPERATURE CABINET.

FIG. VI-A.

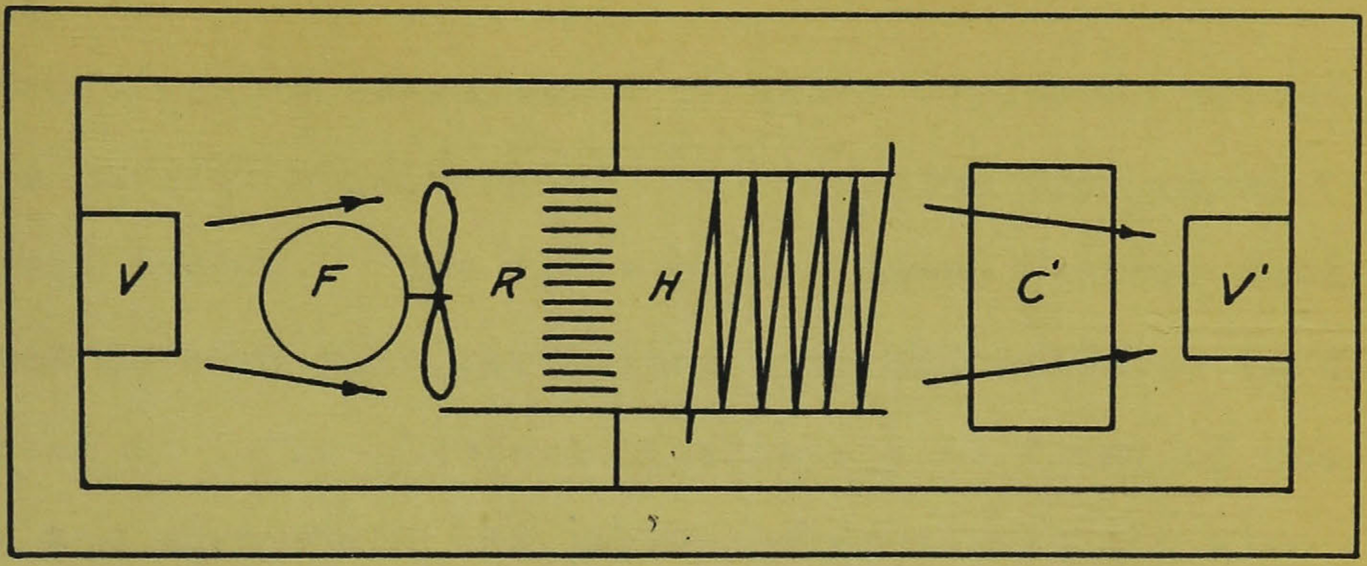
The upper, control section of the cabinet was fitted with an electric fan which circulated the air, entering at V from the lower chamber, across the cooling coil R, the heater H and the calcium chloride tray C'. The air re-entered the lower section at V' and passed across the toluene thermo-regulator T.

The temperature control system used is shown in Fig. VI B. The cooling water, flowing through a 10in. x 10 in. x 4 in. automobile heater, was measured in the flowmeter M and regulated by the needle valve C connected to the city main. Only infrequent settings of the valve C were necessary. The 200 watt heating coil H was controlled by the toluene thermo-regulator T through a system of relays. The electrical connections are shown in Fig. VI C.

By means of this control system the temperature in the lower section of the cabinet could be maintained at 25°C ±0.2°C. Typical operating conditions are given below;

Room Temperature - 23.8°C
Cooling water flow - 160 cc.per min.
  inlet " - 3.75°C
  outlet " - 22.50°C
Heater operation - 47 sec. in 60 sec.

Heat dissipated - 465 cal. per min. per 1°C Temperature difference between inside and outside.



Fig·VI-B Control System:- Sect B-B

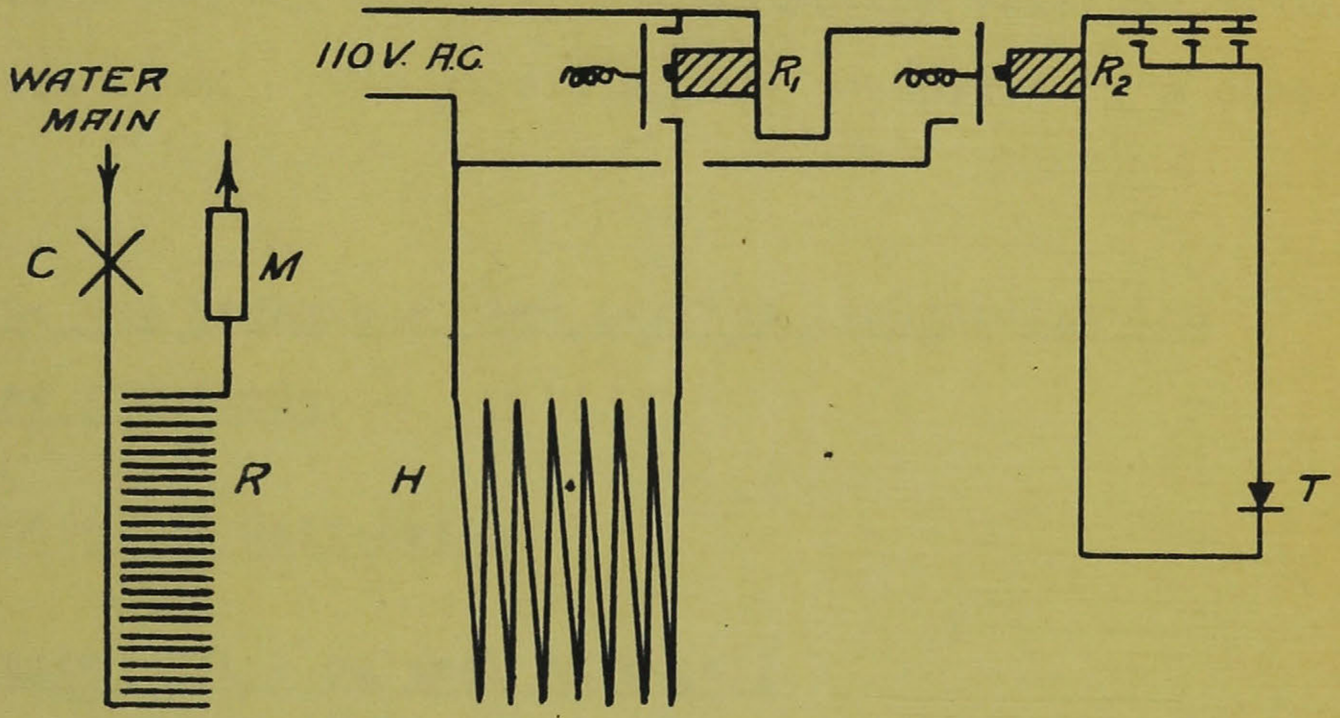


Fig. VI-C Temperature Control System.

Legend:- Fig. VI-B and Fig. VI-C

V, V' - air vent
F - fan
R - cooling coil
H - heater
C' - $CaCl_2$ tray

C - needle valve
M - flowmeter
$R_1$ - power relay
$R_2$ - micro relay
T - regulator

### Shielding

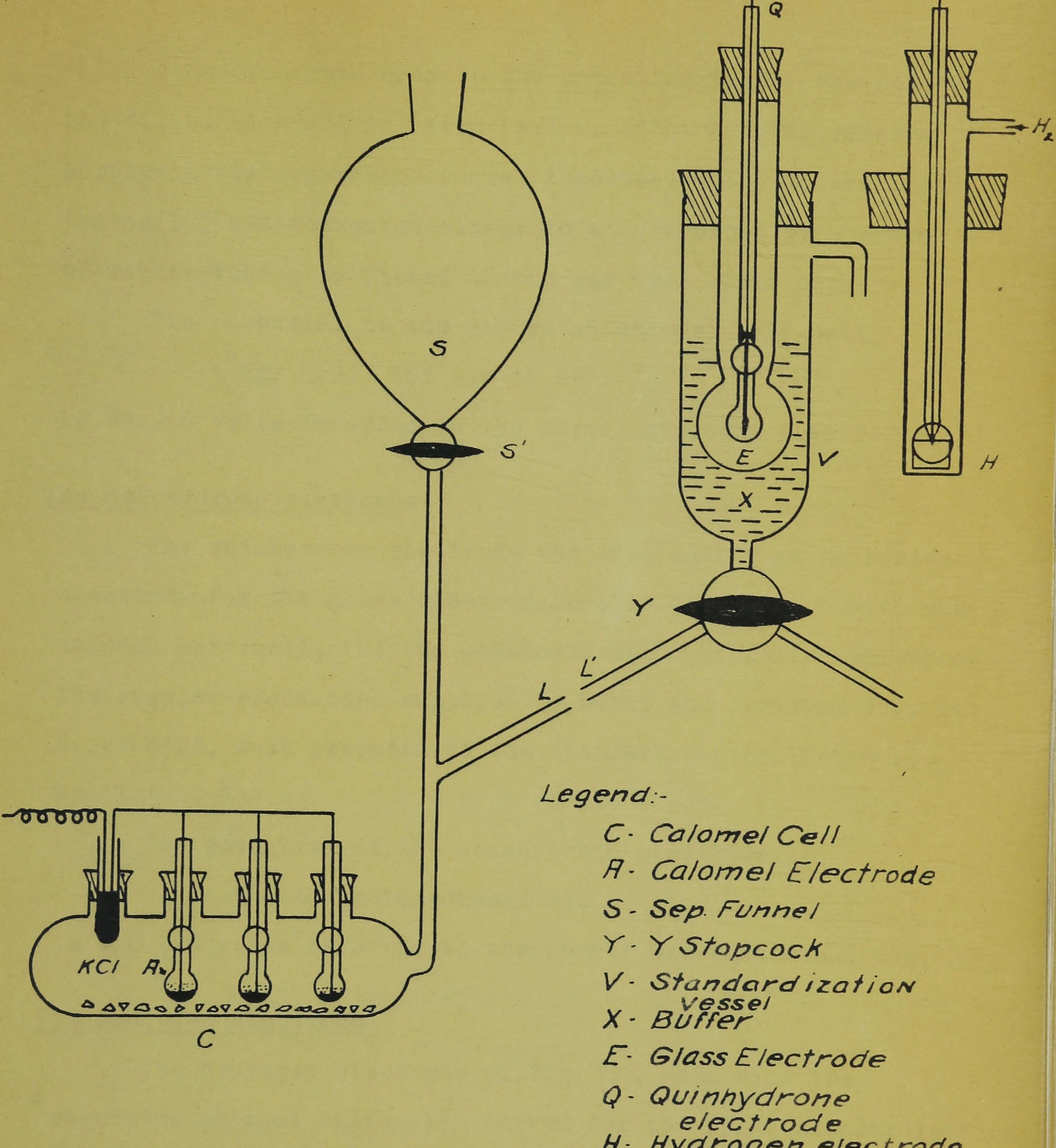
Reproducible measurement of glass electrode potentials requires careful shielding of the apparatus from stray electrical fields. The floor of the lower chamber described above was covered with galvanized iron and soldered to the door frame W. The platform immediately in front of the cabinet and upon which the galvanometer rested was also covered with galvanized iron and soldered to the door frame W. Metal shielded wire was used throughout for electrical connections and all parts of the apparatus shielded with galvanized iron. The shielding was connected to a common ground.

## 2. Apparatus and Technique used for the standardization of the glass electrode.

### a) Description of Half-cells

### The Saturated KCl - calomel half-cell.

The saturated KCl-calomel half-cell, Fig.VII, was used, in conjunction with other half-cells described below, as the working standard throughout the investigation. The regular electrodes, supplied by Leeds and Northrup Co., Cat. No. 7724P1, were prepared in the usual manner, Ref. Bull. 21202-5-435, fitted with rubber stoppers and inserted in the necks of the calomel cell C. The common lead from the three electrodes dipped into a mercury well located in the fourth neck and from



Legend:-

C - Calomel Cell
A - Calomel Electrode
S - Sep. Funnel
Y - Y Stopcock
V - Standardization Vessel
X - Buffer
E - Glass Electrode
Q - Quinhydrone electrode
H - Hydrogen electrode

CELL FOR MEASUREMENT OF HYDROGEN ION CONCENTRATION

Fig. VII

which connection was made to the potentiometer. The cell C was filled with KCl solution (sat. at 25°C) and the reserve supply in the separatory funnel S connected. The arm L of the cell C was connected either to a Y stopcock by a piece of rubber-tubing or closed to the air by a glass plug.

The potential of the saturated calomel half-cell,

Hg/ HgCl/ KCl sat at 25°C /

is +0.246 volts referred to the normal hydrogen electrode.(75)

## The quinhydrone electrode

The quinhydrone electrode was used either as an inside electrode for the glass electrode, or, in conjunction with the calomel half-cell, for the standardization of buffer solutions. The regular electrodes supplied by Leeds and Northrup Co., Cat No. 7685P2, were prepared in the standard manner, Ref.Bull. No 123-10-534.

The potential of the quinhydrone electrode,

$H^+ = 1$ / quinhydrone/ Pt.

is + 0.699 volts referred to the normal hydrogen electrode,(75).

## The hydrogen electrode

The hydrogen electrode, cf. Fig. VII, used with the saturated calomel half-cell, served for the final standardization of buffer solutions. The hydrogen gas was purified by passing over platinized asbestos at 300°C (to remove oxygen), cooled, saturated with water vapour at 25°C and then passed through the gas channel over the electrode. A gold plate ($\frac{1}{2}$ cm$^2$) coated with palladium black and saturated with hydrogen gas served as the hydrogen electrode.

The potential of the hydrogen electrode in a solution normal with respect to hydrogen ions is, by definition, 0 volts.

### The glass electrode

The glass electrode, cf. Fig. VII, was calibrated and used in conjunction with the saturated calomel half-cell to control the hydrogen-ion concentration in the reaction of available chlorine solutions with lignin. The regular electrodes supplied by Leeds and Northrup Co., Cat. No. 7685Pl made of 015 Corning glass, were used with a quinhydrone inside electrode. The latter dipped into a 1 pH HCl solution held in the glass electrode. When not in use the glass electrode was kept in distilled water and the quinhydrone electrode removed.

The potential of the half-cell;

glass// 1 pH HCl/ quinhydrone/ Pt.

is the same as that for the quinhydrone electrode in 1 pH HCl plus the asymmetric potential of the glass electrode.

### b) The Standardization Vessel

The standardization vessel consisted of a short cylinder sealed to a Y stopcock, cf. Fig. VII. The diameter of the cylinder was about twice that of the glass electrode bulb and an overflow tube was provided. The vessel was connected to the calomel cell by the arm L' of the Y stopcock so that saturated KCl could be passed from the separatory funnel S through the stopcock S', to the waste pipe through the Y stopcock.

### c) Buffer solutions and their standardization

A series of buffer solutions, pH 1, 3, 5, 7, and 9, (Clark and Lubs standards (75), were made up from c.p. compounds and $CO_2$-free NaOH. The pH of these buffers was checked with the hydrogen and quinhydrone electrodes as follows:

The standardization vessel was filled with a given buffer and connected to the calomel cell as described above. The hydrogen electrode, previously conditioned by coating with palladium black, saturating with hydrogen gas, and maintained in an atmosphere of hydrogen, was inserted in the vessel and connections made to the potentiometer. (When using the hydrogen electrode a Cambridge potentiometer was used). A liquid junction was made between the saturated KCl and buffer by turning the Y stopcock in a clockwise direction and successively flushing a small quantity of buffer and then KCl to the waste pipe. The separatory funnel stopcock was then closed and the Y stopcock turned to form a new liquid junction between the two solutions.

The following cell was thus connected,

Hg/ HgCl/ sat. KCl at 25°C// Buffer/ $H_2$/ Au

and its e.m.f. balanced potentiometrically.

The balancing potential read in volts on the potentiometer was transformed into pH units by means of the expression,

$$\mathrm{pH} = \frac{+0.246 + (\pm E)}{0.0591}$$

A further check on the pH of the buffer solutions, pH 1 - 7, was obtained by using the quinhydrone electrode in the cell,

Hg/ HgCl/ sat. KCl at 25°C// Buffer/ quinhydrone/ Pt.

The technique used was the same as that described for the hydrogen electrode except that a quinhydrone electrode and a Leeds and Northrup potentiometer were used.

The potential, balancing the e.m.f. of the cell, was read in volts and transformed into pH units by means of the expression;

$$\mathrm{pH} = \frac{0.453 + (\pm E)}{0.0591}$$

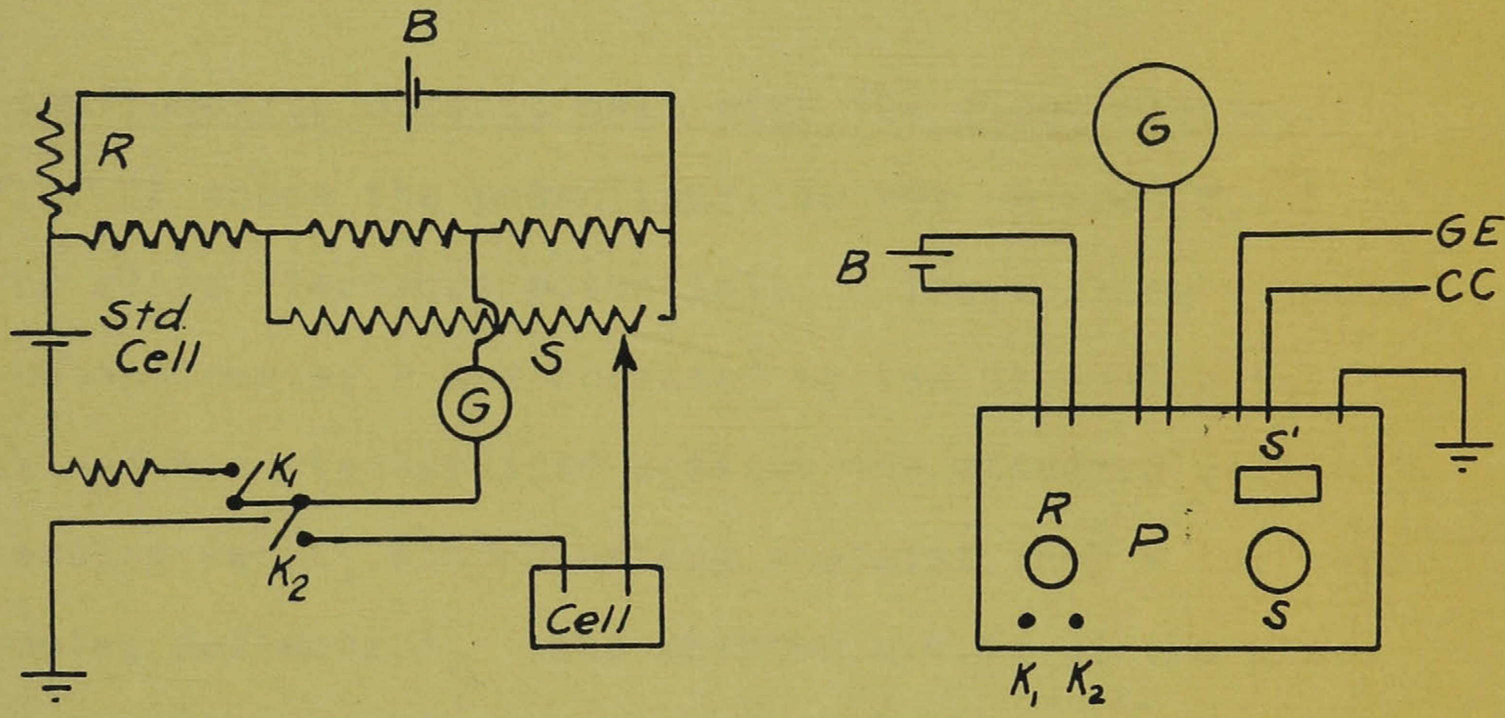
## d.) Standardization of the Glass Electrode

The glass electrode was standardized by measuring the potential of the cell,

$$\mathrm{Hg/\ HgCl/}\ \begin{matrix}\text{sat. KCl}\\ 25^\circ\text{C}\end{matrix}\ //\ \begin{matrix}\text{buffer}\\ \text{std}\end{matrix}\ /\ \text{glass}/\begin{matrix}\text{1 pH}\\ \text{HCl}\end{matrix}/\begin{matrix}\text{quin-}\\ \text{hyd-}\\ \text{rone}\end{matrix}/\ \text{Pt}$$

and comparing the observed e.m.f. with the standard value. The buffer solutions, standardized as previously described, were used so that the standard e.m.f. was known. The deviation of the observed potential from the standard value is due to the asymmetry potential of the glass membrane which

# POTENTIOMETRIC APPARATUS AND ELECTRICAL CIRCUIT.



Legend:-
P - Potentiometer (L.&N. 7652)
G - Galvanometer (L.&N 2500R-b)
B - Battery
GE - Glass Electrode
CC - Calomel "
$K_1K_2$ - Operating keys
R - Rheostat
S - Slide Wire Rheostat
S' - Slide Wire Scale

Fig. VIII

increases very slowly and can be regarded as constant in solutions below pH 10.

The correction factor in volts was added or subtracted, depending upon its polarity, to the e.m.f. observed when the buffer solution in the above cell was replaced by an unknown.

### e.) The potentiometric circuit used with the glass electrode.

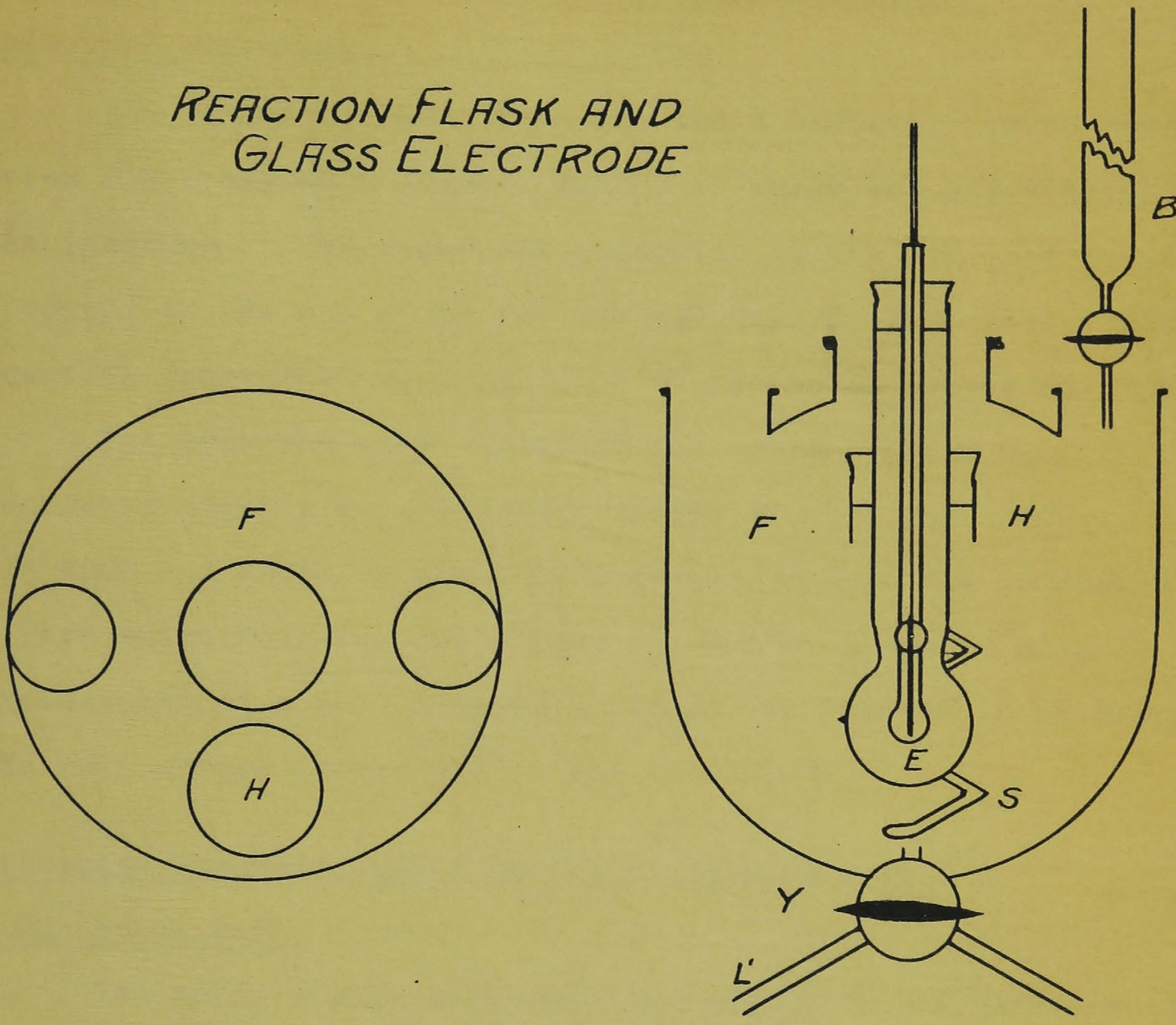
Fig.VIII shows the potentiometric set up used for measuring glass electrode potentials. The working circuit of the potentiometer P was operated by two dry-cells in parallel and was standardized against the standard cell by depressing key $K_1$ and adjusting rheostat knob R for zero galvanometer deflection. The unknown e.m.f. of the glass electrode - calomel cell previously described was then balanced by depressing key $K_2$ and adjusting the slide-wire knob S for zero galvanometer deflection. The balancing potential read in volts on the slide-wire scale S' was converted, after correction for the glass electrode asymmetry potential, to pH units by means of the expression;

$$\mathrm{pH} = \frac{0.453 + (\pm E)}{0.0591}$$

All instruments were shielded with galvanized iron which was brought to a common ground.

The electrical circuit shown in Fig.VIIIis a standard potentiometer circuit which requires no discussion. The keys $K_1$ and $K_2$ were very well made and shielded.

## REACTION FLASK AND GLASS ELECTRODE



Legend:-

| | |
|---|---|
| F | Reaction Flask |
| H | Neck for Glass Electrode |
| E | Glass Electrode |
| S | Stirrer |
| Y | Y Stopcock |
| B | NaOH Burette |

Fig. IX

### 3. Apparatus used for treating Lignin with "available chlorine" solutions.

The reaction flask, Fig. IX, was a one-litre three-necked pyrex flask having a special neck H in which the glass electrode was inserted. The flask was connected by the arm L of the Y stopcock to the arm L' of the calomel cell C, Fig. VII. The reacting components were agitated by the motor driven stirrer S.

The measurement of hydrogen-ion concentration was conducted exactly as previously described, (cf. pg. 123), N/5 NaOH was added to the reaction-mixture from the burette B at a rate which kept the potentiometric bridge balanced at a pre-determined e.m.f. corresponding to the desired pH of reaction. The main change occurs within the first hour.

### 4. Titration apparatus using the glass electrode and a Photronic cell.

The color change accompanying changes in the hydrogen-ion concentration in a solution of alkali lignin, and the pH at which the lignin flocculates was measured in the apparatus sketched in Fig. X.

The apparatus can be regarded as a type of photometer which measures the amount of light transmitted form a standard source through an alkali lignin solution of known concentration and known hydrogen-ion concentration. The glass container, F, was a 400 cc. pyrex beaker with a Y stopcock sealed into the

# TITRATION APPARATUS USING GLASS ELECTRODE AND PHOTRONIC CELL.

Legend:-

| | |
|---|---|
| A | Wooden Container |
| F | Titration Beaker |
| B | HCl Burette |
| G | Galvanometer (L.&N 2500 R-a) |
| C | Photronic Cell |
| D | Iris Diaphragm |
| L, L' | Lenses |
| S | Lamp |
| R | Resistor |
| V | Voltmeter |
| P | Stirrer |
| E | Glass Electrode |
| Y | Y Stopcock |

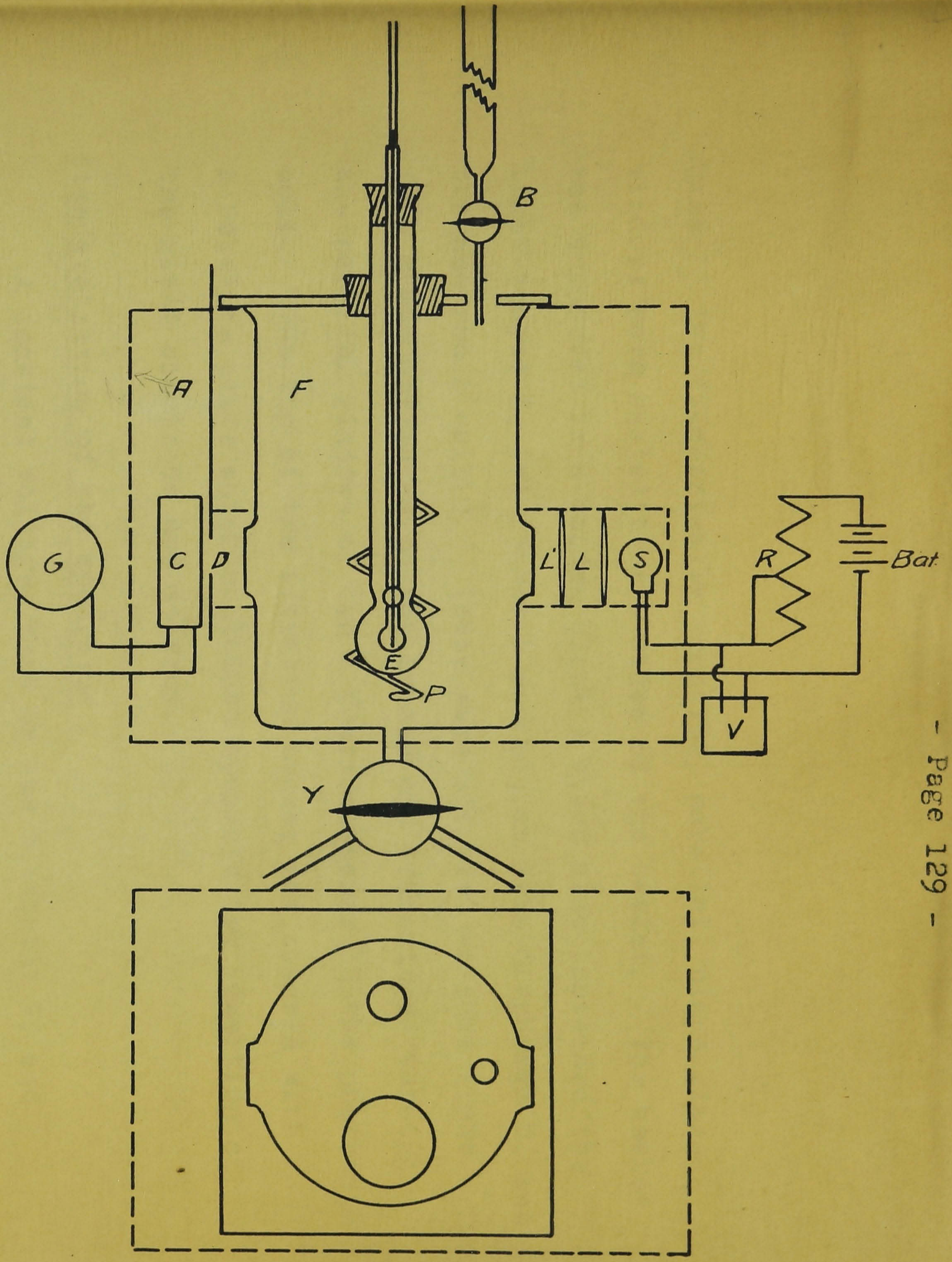


Fig. X

base. Two diametrically opposite, parallel, plane glass windows were sealed to the sides of the beaker. The beaker was supported in a wooden block A which also contained the light source S, two lenses L and L', an iris diaphragm D, and the photronic cell C. These were situated so that light from S was collected by the lenses and transmitted through the parallel windows of the titration beaker to the photronic cell. The top of the titration beaker was covered with a Bakelite plate which contained openings for insertion of the glass electrode and stirrer.

## Standardization of the apparatus

A constant voltage, read on the voltmeter V, and maintained by adjustment of the rheostat R, illuminated the lamp S.

The system was standardized by filling the titration beaker with distilled water and adjusting the area of light falling upon the photronic cell C to give a 20 cm. galvanometer deflection. This operation was carried out by regulating the size of the iris diaphragm D.

The standardized apparatus was checked before and after a titration by again filling the beaker with distilled water and noting the galvanometer deflection. The variation should not be greater than 1 %.

Operation of the apparatus.

A known weight of lignin in approximately N/100 NaOH solution was added to the beaker and the volume adjusted to 300 cc. The stirrer P, and glass electrode E, were placed in position and the Y stopcock connected to the calomel cell C cf. Fig.VII. The glass and calomel electrodes were connected to the potentiometer circuit, cf. Fig.VIII, the light source illuminated, and the stirrer started.

The hydrogen-ion concentration in the titration beaker was measured by forming a liquid junction in the Y stopcock and proceeding with the measurement as previously described cf. pg.123 N/10 HCl was added from the burette B. After each addition of acid the galvanometer deflection was noted and the hydrogen-ion concentration measured.

# PART III. EXPERIMENTAL METHODS

## Description of Experimental and Analytical Methods.

A large number of very similar experiments have been carried out in this investigation so that it has been possible to standardize Experimental and Analytical methods to a large extent. These can be conveniently classified under the following headings;

1. Method of treating alkali lignin with aqueous solutions of chlorine and its derivatives.
2. Process of isolating reaction products; including alkali lignin.
3. Preparation of Hypochlorous acid.
4. Analytical methods.

A complete description of the methods used is given under these headings. Reference thereto is made throughout the dissertation in order to avoid unnecessary repetition and confusion.

### 1. Method of treating alkali lignin with "available chlorine" solutions.

The action of chlorine and hypochlorous acid upon alkali lignin was studied under conditions of controlled hydrogen-ion concentration. The significance of the hydrolysis constant for chlorine and the dissociation constant for hypochlorous acid has been discussed previously and the following equations shown to apply;

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HClO \qquad (1)$$

$$HClO + NaOH \rightleftharpoons NaClO + H_2O \qquad (2)$$

The dissociation constant for hypochlorous acid ($3.7 \times 10^{-8}$ at 25°C) shows that this acid, formed by the hydrolysis of chlorine, exists in the undissociated state at about pH = 4.75 (conc. = N/10) together with only minute quantities of molecular chlorine and hypochlorite ion. At higher pH values, brought about by the addition of NaOH, hypochlorite ion appears, the ratio of hypochlorous acid to hypochlorite ion being defined by the Oeman equation,

$$\log \frac{\text{salt}}{\text{acid}} = pKa + pH$$

$$\text{where } pH = \frac{1}{\log H^+}$$

$$pKa = \frac{1}{\log Ka}$$

Ka = dissociation constant.

In more acidic media, less than pH 4.75, equation (1) is reversed. Hypochlorous acid, combining with the hydrochloric acid reacts to form molecular chlorine and water. The position of the equilibrium in this case is defined both by the hydrogen-ion concentration and that of the chloride ion;-- the slight dissociation of the weak acid, HClO, and of water being negligible in comparison with that of HCl.

The conditions of reaction for solutions of "available chlorine" after addition to solutions of alkali lignin are therefore well defined provided the pH of the medium is maintained constant and the chloride ion concentration in solutions more acid than pH 4.75 is known.

The experimental methods used to maintain these conditions can be divided into two classes;

1. Those in which the pH was directly controlled with the glass electrode without the addition of buffer salts. (In this method the only buffering action was due to the concentration of acid (pH 2) or alkali (pH 10) added to the solution to maintain constant pH.)
2. Those in which the pH of the solution was directly controlled with the glass electrode and to which buffer salts had been previously added to facilitate this control.

The technique employed in either case was very similar. The "available chlorine" present in the chlorine or hypochlorous acid solution was first determined by titration and the number of cc. required to give a pre-determined number of milli-equivalents of "available chlorine" per gm. of lignin calculated. A volume of standard solution, containing a known amount of alkali lignin was then placed in the reaction flask (F•). In the first method above, an amount of $CO_2$-free water was added to the flask such that the final volume after the addition of the "available chlorine" solution was 750 cc. The flask stirrer (S)* was started, the electrode (E)* inserted in the neck (H)* of the flask and the electrical connections made to the potentiometer (P)**. The potentiometer slide-wire was set to an e.m.f. value corresponding to the desired reaction pH and the calomel half-cell connected to the arm L of the Y stopcock of the flask (F)* . A solution of $H_2SO_4$ (10%) was then added dropwise to the reaction flask until the galvanometer gave no deflection upon completing the electrical circuit. The latter was effected by forming a new liguid junction in the Y stopcock and then depressing key $K_2$.

Having thus adjusted the pH of the alkali lignin solution to the desired value, the standard solution of "available chlorine" was slowly added (within a period of five minutes) to the flask from a pipette. The pH of the mixture was kept constant during, and after the addition by adding N/5 NaOH from the burette (B)*. The quantity of alkali necessary to neutralize the HCl fromed in the reaction was

---

* Fig. IX.

**Fig. VIII.

gauged by repeatedly forming a liquid junction in the Y stopcock, depressing $K_2$ and noting the direction and extent of the galvanometer deflection.

In those cases where the alkali lignin solution was artifically buffered to facilitate hydrogen-ion control a standard buffer solution was added simultaneously with the $CO_2$ free water to the lignin solution. The standard "available chlorine" solution was also mixed in a separatory funnel with a quantity of the buffer prior to addition to the reaction flask. The total amount of buffer used was such that the reacting mixture was M/40 in buffer salt.

The "available chlorine" solution was allowed to react to completion with the lignin. A separate series of experiments showed that the rate of reaction was extremely rapid to eighty percent completion (within 30 minutes) after which it decreased slowly to zero. Depending upon the amount of reagent added, 2 to 5 days was found to be ample for complete reaction. The solution was then removed from the flask, acidified with HCl and the flocculent precipitated lignin isolated in the usual manner.

## 2. Method of isolating reaction products. (including alkali lignin)

A fundamental property of alkali lignin and of its reaction products with "available chlorine" solutions is their complete solubility in alkalies and their insolubility in acid solution. Their isolation can thus be readily effected. The reaction products when isolated directly from aqueous solutions become horny, insoluble substances on drying so that anhydrous media have to be used for their isolation. The use of dioxan as a lignin solvent, and of ether as precipitant has been attended with a great deal of success in these laboratories. A description of this technique as applied to alkali lignin and the above mentioned reaction products follows:

The sodium lignate, in alkaline solution, on the addition of acid yields the free lignin acid as a light buff- to brown-colored flocculent precipitate. This is freed from $Na^+$ ion etc. by alternately centrifuging and washing the precipitate with dilute acid (0.01N) and is finally reduced to a thick paste on a Büchner funnel. Washing this paste with distilled water removes excess chloride ion.

The precipitate is then dissolved in absolute dioxan and the residual moisture, together with any $Cl^-$ ion, present as HCl, removed by 3 to 5 repeated distillations with fresh solvent The resulting solution, adjusted to contain approximately ten percent of alkali lignin, is then slowly dropped into about 10 times its volume of vigorously-stirred anhydrous ether.

The alkali lignin settles out from the ethereal solution as a light, buff-colored product and the mother-liquor is removed by decantation and filtration on a cone funnel. The precipitate is washed with- 1)fresh ether to remove dioxan; 2) ligroin (80-90°C) to remove ether; 3)ligroin (30-50°C). The product is dried in a vacuum desiccator and samples for analysis are finally dried at 80-100°C over $P_2O_5$ in an Abderhalden drier.

N.B. Large quantities of product are difficult to handle by filtration so that a variation is necessary in the above procedure. In these cases the precipitates are alternately centrifuged and washed with the above mentioned solvents and then dried. The dried product however, possesses a strong electrostatic charge, is very lumpy and generally difficult to work with.

## 3. Preparation and Standardization of Hypochlorous acid solutions.

Hypochlorous acid, freshly distilled, was used throughout the investigation as the standard source of "available chlorine" solutions. Its preparation from bleaching powder has been thoroughly investigated by Taylor and Bostock (73) whose method was used.

50 gms. of "bleaching powder" was rolled to a fine powder between two sheets of paper and mixed with 500 cc. of distilled water in the two litre flask of an all-glass distillation apparatus. 1000 cc. of hot water, containing 100 gm. boric acid, was then added to the flask and the liberated hypochlorous acid distilled. 1000 cc. distillate was collected into two 500cc. brown, glass-stoppered bottles and placed in the constant temperature cabinet. Solutions approximately 0.1 N in $HClO$ were obtained in this way.

The strength of "available chlorine" solutions was determined by adding a volumetric sample to an acidified solution of KI and titrating the liberated iodine with N/20 thiosulphate using starch as indicator (69).

The equations represent the reactions taking place;

$$HClO + H_2SO_4 + 2\ KI \longrightarrow K_2SO_4 + H_2O + HCl + I_2 \quad (1)$$

$$Cl_2 + H_2SO_4 + 2\ KI \longrightarrow H_2SO_4 + 2\ HCl + I_2 \quad (2)$$

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\ NaI \quad (3)$$

The potentiometric titration curve for hypochlorous acid, Fig. II, explains clearly equation (1) in that the addition of HClO to an acid solution results in the reversal of the chlorine hydrolysis equation,

$$Cl_2 + H_2O \rightleftharpoons HClO + HCl$$

The iodine liberated by the action of chlorine upon KI is titrated with thiosulphate, equation (3).

The potentiometric titration curve also indicates that the relative composition of the hypochlorous acid solution is dependent upon its hydrogen-ion concentration. The "available chlorine" solutions, prepared and standardized in the above manner, were allowed to react with alkali lignin under conditions of controlled pH so that their composition was at all times completely defined.

## 4. Analytical Methods.

Standard analytical methods were used throughout the investigation.

a) Measurement of hydrogen-ion concentration.

Hydrogen-ion concentrations were measured using the cell,

Hg/ HgCl/ sat. KCl 25°C/ unknown solution//1 pH HCl/ Quin./ Pt.

as previously described, (Experimental Part 2). The glass electrode was calibrated frequently in buffer standards. The overall accuracy of the determination was 3 millivolts corresponding to 0.05 pH unit.

b) Determination of Lignin.

Lignin was determined according to the method proposed by Mehta (12). The lignin, precipitated in acid solution, was centrifuged free from sodium ion etc. by washing with dilute acid. The moist centrifuged paste was washed finally on to a tared asbestos Gooch crucible with dilute HCl, dried at 100°C and weighed to constant weight. The accuracy of the determination was about 2%.

c) Determination of Methoxyl.

Samples for analysis were dried at 100°C in an Abderhalden drier, accurately weighed out, (± 0.01 mgm.), and analysed using the semi-micro Zeisel apparatus (76) with the Vieböch-Schwappach modification (77). The accuracy of the determination was ± 0.1%.

d) Determination of Halogen.

Samples for analysis were dried at 100°C in an Abderhalden drier, accurately weighed out, (± 0.01 mgm.) and analysed for chlorine using the Willard-Thompson semi-micro method. (78). The accuracy of the determination was 0.2%.

### e) Determination of "available chlorine"

"Available chlorine" was determined by adding a volumetric sample of the hypochlorous acid solution to an acidified KI solution and titrating the liberated iodine with thiosulphate (69). The overall accuracy covering the titration and addition of the reagent to the alkali lignin solution was 0.1 milliequivalent of "available chlorine".

### f) Determination of Carbon and Hydrogen.

The carbon and hydrogen analysis of alkali lignin was carried out by the Liebig macro method (80). The accuracy of the determination was one-tenth of one percent for both carbon and hydrogen.

# PART IV EXPERIMENTAL RESULTS

## Action of Available Chlorine Solutions upon Alkali Lignin at Constant Hydrogen-Ion Concentration

The experimental results of the investigation dealing with the action of chlorine and its derivatives upon lignin are recorded in Tables XVII to XXIV.

The results obtained from each series of experiments, conducted at constant **pH** are arranged in separate tables and each table is divided into two sections, A and B. Section A of any table gives the analytical results of the individual experiments, namely; the quantity of reactant used, and the methoxyl and halogen analysis of the product isolated. Section B contains the data, calculated from the analytical results, by means of which the individual experiments can be compared with each other and with those appearing in other (B) sections. Section B therefore shows;

(a) the milliequivalents of available chlorine solution used per gm. of lignin. (Calculated from the amount of reactant added and the weight of lignin used).

(b) the percentage of chlorine found in the product expressed as milliequivalents.

(c) the percentage and milliequivalents of methoxyl lost in the reaction. (Obtained by calculating the percent methoxyl of the product on a chlorine free basis and subtracting the result from the methoxyl content of alkali lignin). (see also pg. 147 A)

(d) the equivalent ratio of methoxyl lost to chlorine introduced.

(e) the equivalents of available chlorine per gm. of lignin required to remove one equivalent of methoxyl from the lignin.

(f) the equivalents of available chlorine required to introduce one atom of chlorine into the lignin.

The number of any given experiment appears in both A and B sections and shows,

(a) the order of the experiment, and

(b) the pH of the reaction medium.

The experimental methods, both for treating alkali lignin with available chlorine and for isolation of the reaction products, has been previously described, Experimental Part III.

## 1. Reaction of Available Chlorine Solutions with Alkali Lignin at pH 2

The results of the experiments carried out at pH 2 are given in Table XVII and are represented graphically in Fig. XI.

The reaction medium was strongly buffered by the acid present ($H_2SO_4$) and the HCl formed, so that the reaction could be readily controlled without the use of buffering salts. According to Bergqvist (68) the ratio of $Cl_2$:HClO:ClO' is 1:1:4.3 x $10^{-6}$ at pH 2.

## 2. Reaction of Available Chlorine Solutions with Alkali Lignin at pH 3.5

The reaction of "available chlorine" with alkali lignin is attended with the formation of HCl. Neutralization of the latter with NaOH maintains a constant hydrogen ion-concentration but the consequent formation of the highly dissociated sodium salt tends to reverse the chlorine hydrolysis and results in an increase in the concentration of molecular chlorine,

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl$$

Two experiments were conducted at pH 3.5 to determine the effect of chloride ion upon the reaction of "available chlorine" solutions with lignin. The first experiment was carried out in the usual manner, chloride ion arising solely from the HCl formed in the reaction, while the second was conducted in a medium made initially 0.015 M in chloride ion. The results are given in Table XVIII.

## 3. Reaction of Available Chlorine Solutions with Alkali Lignin at pH 4

The results of the experiments carried out at pH 4 are given in Table XIX and are represented graphically in Fig. XII.

The reaction medium was not buffered by the addition of buffering salts but the hydrogen ion concentration was directly controlled, potentiometrically, by the addition of N/5 NaOH solution. According to Bergqvist (68) the ratio of $Cl_2$:HClO:ClO' is 1:130:5.6 x 10 $^{-2}$ at pH 4.

## 4. Reaction of Available Chlorine Solutions with Alkali Lignin at pH 5

The experiments conducted at pH 5 were performed in a medium made intially M/20 in a buffer salt. Constant hydrogen ion concentration was maintained potentiometrically, by the addition of N/5 NaOH. The results of the experiments are given in Table **XX**. The ratio of $Cl_2$:HClO:ClO' is 1:1300:5.6 at pH 5 (68).

## 5. Reaction of Available Chlorine Solutions with Alkali Lignin at pH 6

The results of the experiments carried out at pH 6 are given in Table XXI and are represented graphically in Fig. XIII. Experiments 6 - 5, 6 - 7, and 6 - 9 were performed in a medium initially made M/20 in a buffer salt. All experiments were maintained at constant pH, potentiometrically, by the addition of N/5 NaOH. According to Bergqvist (68) the ratio of Cl:HClO:ClO' is 1:13000:560 at pH 6.

### 6. Reaction of Available Chlorine Solutions with Alkali Lignin at pH 7

The results of the experiments performed at pH 7 are given in Table XXII. Experiment 7 - 4 was conducted in a buffered medium. The concentration of molecular chlorine at pH 7 may be neglected, the ratio of HClO:Cl being 2.3:1 according to Bergqvist (68)

### 7. Reaction of Available Chlorine Solutions at Alkali Lignin at pH 8

The results of experiments conducted in pH 8 media are given in Table XXIII and are represented graphically in Fig. XIV. The ratio of HClO:ClO' is 1:4 according to Bergqvist (68). The hydrogen-ion concentration was controlled, potentiometrically, by the addition of N/5 NaOH and without the use of buffers.

### 8. Reaction of Available Chlorine Solutions with Alkali Lignin at pH 10

The results of the experiments conducted at pH 10 are given in Table XXIV and are represented in Fig. XV. The reaction was sufficiently well buffered in the alkaline medium to permit direct control of the hydrogen-ion concentration, potentiometrically, by the addition of N/5 NaOH. According to Bergqvist (68) the ratio of $HClO:ClO^-$ is 1:440 at pH 10.

<u>Sample calculation:</u> Tables XVII to XXIV.

<u>Data;</u>

<u>Experiment 2 - 1</u>

Lignin used - 0.627 gm.
Reagent added - 1.89 milliequivalents.
$OCH_3$ of reaction product - 13.75 %
Cl of reaction product - 1.59 %
$OCH_3$ of alkali lignin - 15.20 %

Calculation;

% $OCH_3$ on Cl free basis - $13.75 \times \frac{100}{100 - 1.59}$

% $OCH_3$ lost in reaction - $15.20 - 13.98$

Milliequivalents $OCH_3$ lost per gm. lignin - $\frac{1.22}{31.0} \times \frac{1000}{100}$

Milliequivalents Cl introduced in lignin - $\frac{1.59}{35.5} \times \frac{1000}{100}$

Equivalents "available chlorine" required to

a) introduce one equiv. Cl per gm. lignin - $\frac{3.02}{0.33}$

b) remove one equiv $OCH_3$ per gm. lignin- $\frac{3.02}{0.39}$

## Table XVII (Section A)

### Action of "available chlorine" solutions upon alkali lignin at pH 2.

| Exp. | Lignin used gm | "available chlorine" solution |  |  | Methoxyl analysis |  |  | Halogen analysis |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  | cc. N/20 thio.req. by 10 cc. sample. | cc. reagent added | Milli-equiv. reagent added | Mgm. subs. | cc. N/20 thio. req. | %OCH$_3$ | Mgm. subs. | Mgm. AgCl | %Cl |
| 2- 1 | 0.627 | 18.90 | 20 | 1.89 | 54.63 | 29.03 | 13.75 | 21.24 | 1.37 | 1.59 |
| 2- 2 | 0.627 | 37.15 | 10 | 1.81 | 16.53 | 8.76 | 13.70 | 27.69 | 2.22 | 1.98 |
| 2- 3 | 0.627 | 18.87 | 40 | 3.77 | 40.29 | 19.11 | 12.25 | 20.75 | 2.69 | 3.18 |
| 2- 4 | 0.627 | 25.75 | 30 | 3.86 | 16.82 | 7.83 | 12.00 | 42.61 | 5.87 | 3.41 |
| 2- 5 | 0.627 | 18.74 | 60 | 5.63 | 25.16 | 10.41 | 10.70 | 68.14 | 15.47 | 5.60 |
| 2- 6 | 0.627 | 17.45 | 80 | 6.98 | 18.90 | 7.04 | 9.61 | 43.09 | 12.34 | 7.09 |
| 2- 7 | 0.627 | 19.20 | 80 | 7.66 | 25.92 | 9.12 | 9.08 | 35.49 | 11.89 | 8.18 |
| 2- 8 | 0.650 | 19.83 | 80 | 7.93 | 21.05 | 7.13 | 8.77 | 30.66 | 10.41 | 8.41 |
| 2- 9 | 0.650 | 21.32 | 100 | 10.20 | 29.64 | 8.12 | 7.09 | 25.82 | 14.34 | 9.92 |
| 2-10 | 0.650 | 20.10 | 110 | 11.00 | 35.92 | 8.90 | 6.41 | 31.46 | 13.68 | 10.76 |
| 2-11 | 0.650 | 17.38 | 150 | 13.00 | 24.32 | 4.98 | 5.30 | 21.53 | 11.28 | 12.97 |
| 2-12 | 0.650 | 19.69 | 150 | 14.80 | 43.89 | 7.57 | 4.46 | 23.84 | 13.85 | 14.37 |

## Table XVII (Section B)

## Action of "available chlorine" solutions upon alkali lignin at pH 2

| Experimental Data | | | | | | Calculations | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exp. | Lignin used gm | Chlorinated product | | | Reagent added Milli-equiv. per gm lignin | % $OCH_3$ on Cl free basis | % $OCH_3$ lost | Milliequivalents of $OCH_3$ lost per gm. lignin | Milliequivalents of Cl introduced per gm. lignin | equiv. ratio $OCH_3$ / Cl | "available chlorine" equivs. reagent req. per equiv. $OCH_3$ lost | "available chlorine" equivs. reagent req. per equiv. Cl introduced |
| | | Yield gm. | % $OCH_3$ | % Cl | | | | | | | | |
| | | | | | | alkali lignin - 15.20% methoxyl. | | | | | | |
| 2- 1 | 0.627 | 0.61 | 13.75 | 1.59 | 3.02 | 13.98 | 1.22 | 0.39 | 0.33 | 1.21 | 7.76 | 9.15 |
| 2- 2 | 0.627 | 0.68 | 13.70 | 1.98 | 2.88 | 13.98 | 1.22 | 0.39 | 0.56 | 0.71 | 7.39 | 5.16 |
| 2- 3 | 0.627 | 0.68 | 12.25 | 3.18 | 6.01 | 12.66 | 2.54 | 0.83 | 0.90 | 0.92 | 7.32 | 6.67 |
| 2- 4 | 0.627 | 0.61 | 12.00 | 3.41 | 6.15 | 12.41 | 2.79 | 0.90 | 0.96 | 0.94 | 6.84 | 6.40 |
| 2- 5 | 0.627 | 0.62 | 10.70 | 5.60 | 8.97 | 11.36 | 3.84 | 1.24 | 1.58 | 0.78 | 7.23 | 5.67 |
| 2- 6 | 0.627 | 0.62 | 9.61 | 7.09 | 11.1 | 10.34 | 4.86 | 1.57 | 1.99 | 0.79 | 7.06 | 5.58 |
| 2- 7 | 0.627 | 0.65 | 9.08 | 8.18 | 12.2 | 9.89 | 5.31 | 1.71 | 2.30 | 0.74 | 7.14 | 5.30 |
| 2- 8 | 0.650 | 0.60 | 8.77 | 8.41 | 12.2 | 9.52 | 5.68 | 1.83 | 2.37 | 0.77 | 6.66 | 5.14 |
| 2- 9 | 0.650 | 0.62 | 7.09 | 9.92 | 15.7 | 7.88 | 7.32 | 2.36 | 2.79 | 0.85 | 6.65 | 5.64 |
| 2-10 | 0.650 | 0,60 | 6.41 | 10.76 | 17.0 | 7.18 | 8.02 | 2.59 | 3.04 | 0.85 | 6.56 | 5.60 |
| 2-11 | 0.650 | 0.63 | 5.30 | 12.97 | 20.0 | 6.07 | 9.13 | 2.94 | 3.56 | 0.83 | 6.80 | 5.62 |
| 2-12 | 00650 | 0.50 | 4.46 | 14.37 | 22.8 | 5.22 | 9.98 | 3.22 | 4.05 | 0.80 | 7.10 | 5.64 |

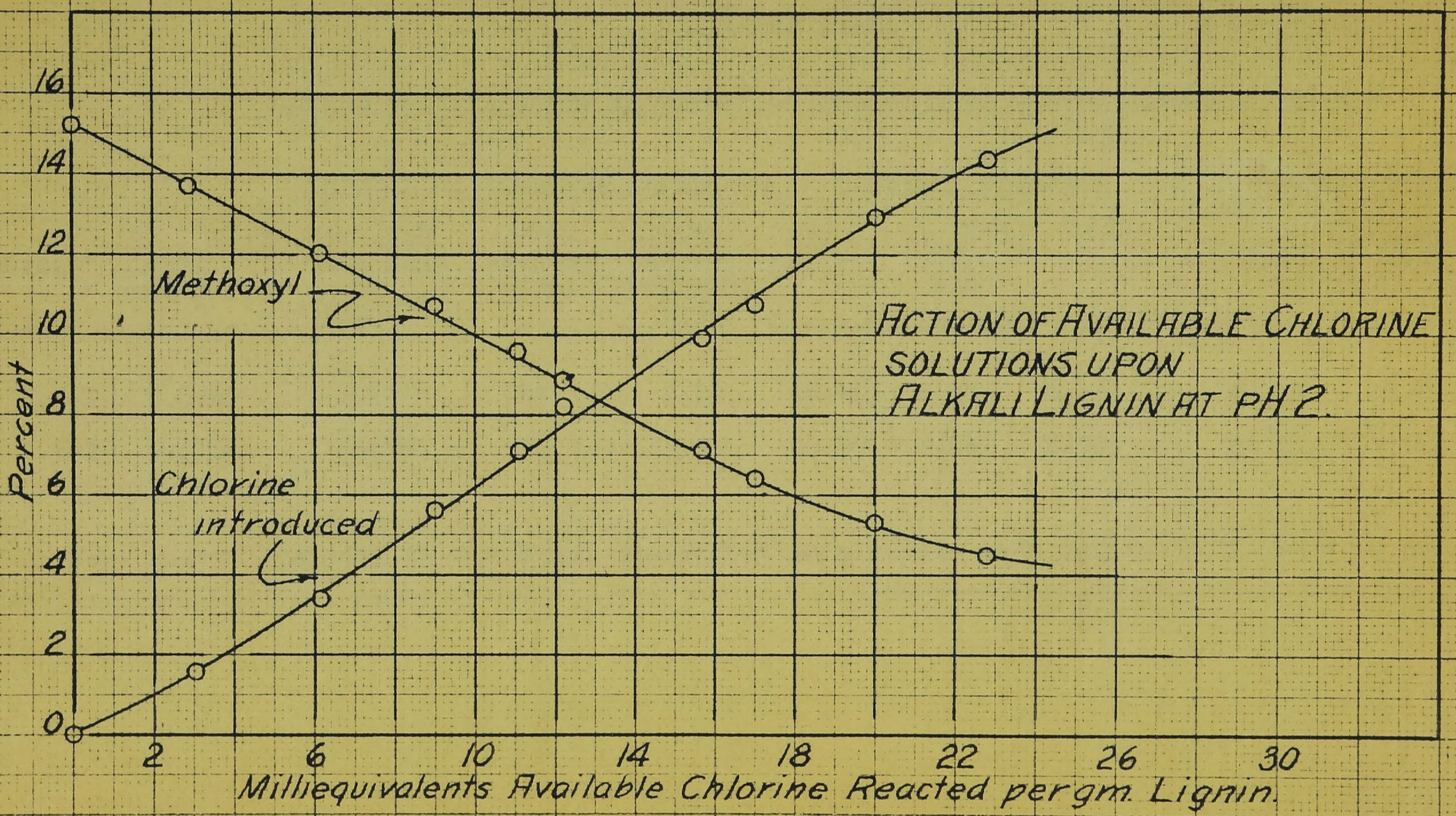

ACTION OF AVAILABLE CHLORINE
SOLUTIONS UPON
ALKALI LIGNIN AT PH 2.

FIG. XI

## Table XVIII

### Action of "available chlorine" solutions upon alkali lignin at pH 3.5

| | | "available chlorine" solution | | | Methoxyl analysis | | | Halogen analysis | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Exp. | Lignin used gm | cc. N/20 thio.req. by 10 cc. sample | cc. reagent added | Milli-equiv. reagent added | Mgm. subs. | cc. N/20 thio. req. | %$OCH_3$ | Mgm. subs. | Mgm. AgCl | %Cl |
| 3.5-1 | 0.626 | 22.78 | 80 | 9.11 | 26.47 | 8.83 | 8.62 | 36.80 | 11.01 | 7.40 |
| 3.5-2 | 0.626 | 22.78 | 80 | 9.11 | 25.98 | 8.44 | 8.40 | 28.71 | 8.61 | 7.47 |

Exp. 3.5-2 conducted in the usual manner but in a medium made initially 0.015 M in Cl' ion.

## Table XIX (Section A)

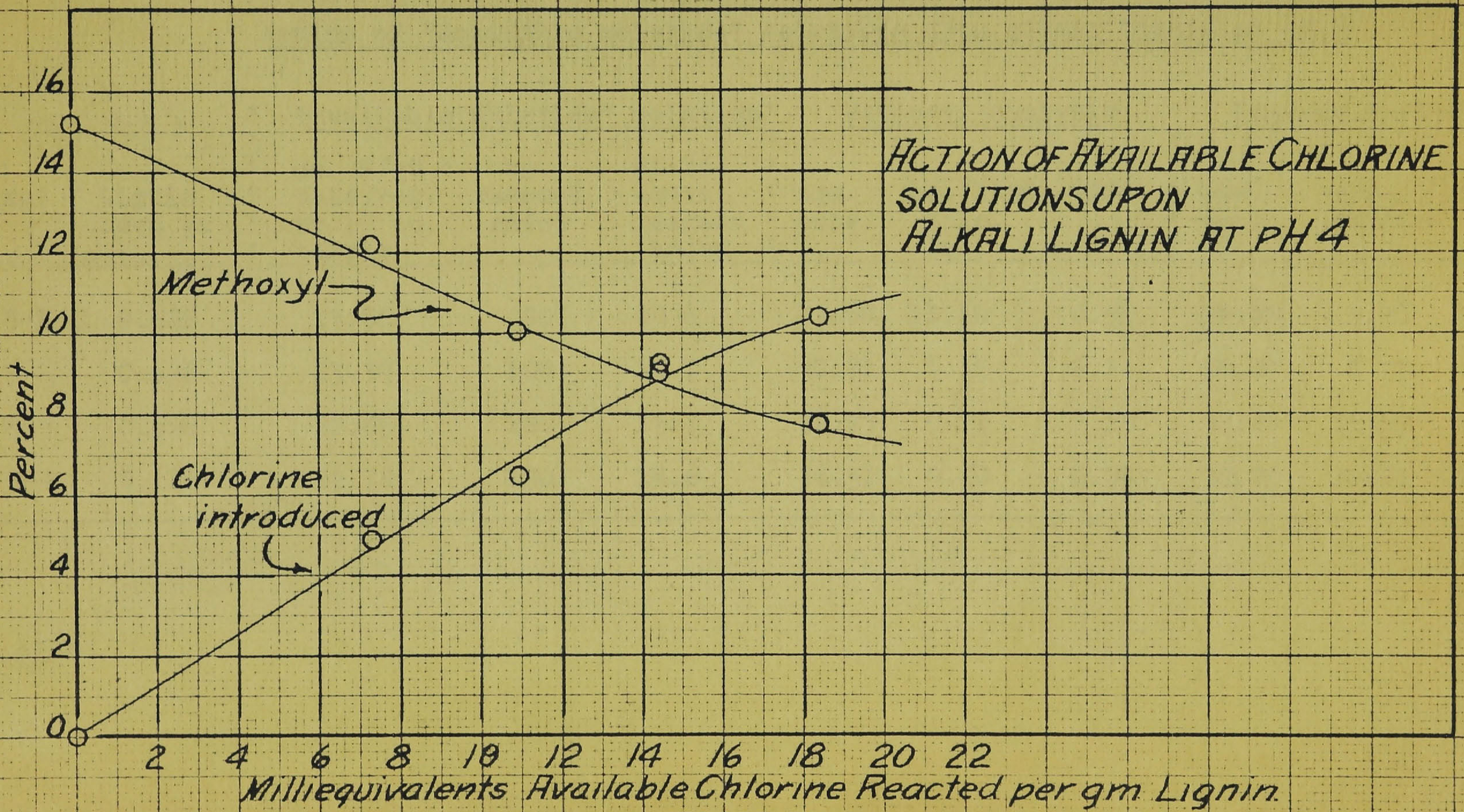
### Action of "available chlorine" solutions upon alkali lignin at pH 4

|  |  | "available chlorine" solution N |  |  | Methoxyl analysis |  |  | Halogen analysis |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| Exp. | Lignin used gm. | cc. N/20 thio.req. by 10 cc. sample | cc. reagent added | Milli-equiv. reagent added | Mgm. subs. | cc. N/20 thio. req. | %$OCH_3$ | Mgm. subs. | Mgm. AgCl | %Cl |
| 4-1 | 0.659 | 24.23 | 40 | 4.85 | 34.60 | 16.32 | 12.20 | 34.11 | 6.71 | 4.86 |
| 4-2 | 0.659 | 24.12 | 60 | 7.23 | 30.83 | 12.52 | 10.05 | 37.15 | 9.64 | 6.43 |
| 4-3 | 0.659 | 23.87 | 80 | 9.55 | 30.70 | 10.98 | 9.25 | 29.49 | 10.72 | 9.00 |
| 4-4 | 0.659 | 16.12 | 150 | 12.1 | 26.82 | 8.03 | 7.74 | 24.61 | 10.04 | 10.40 |

## Table XIX (Section B)

## Action of "available chlorine" solutions upon alkali lignin at pH 4

| Experimental Data | | | | | | Calculations | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exp. | Lignin used gm | Chlorinated product | | | Reagent added Milli-equiv. per gm lignin | % $OCH_3$ on Cl free basis | % $OCH_3$ lost | Milliequivalents of $OCH_3$ lost per gm. lignin | Milliequivalents of Cl introduced per gm. lignin | equiv. ratio $\frac{OCH_3}{Cl}$ | "available chlorine" equivs. reagent req. per equiv. $OCH_3$ lost | "available chlorine" equivs. reagent req. per equiv Cl introduced |
| | | Yield gm. | % $OCH_3$ | % Cl | | | | | | | | |
| | | | | | | | | alkali lignin = 15.20% methoxyl | | | | |
| 4-1 | 0.659 | 0,58 | 12.20 | 4.86 | 7.38 | 12.83 | 2.37 | 0.76 | 1.37 | 0.56 | 9.7 | 5.4 |
| 4-2 | 0.659 | 0.55 | 10.05 | 6.43 | 10.97 | 10.72 | 4.48 | 1.51 | 1.81 | 0.87 | 7.0 | 6.1 |
| 4-3 | 0.659 | 0.50 | 9.25 | 9.00 | 14.50 | 10.15 | 5.05 | 1.63 | 2.53 | 0.65 | 8.9 | 5.7 |
| 4-4 | 0.659 | 0.50 | 7.74 | 10.40 | 18.4 | 8.63 | 6.57 | 2.12 | 2.93 | 0.72 | 9.1 | 6.3 |



ACTION OF AVAILABLE CHLORINE SOLUTIONS UPON ALKALI LIGNIN AT PH 4

FIG. XII

# Table XX (Section A)

## Action of "available chlorine" solutions upon alkali lignin at pH 5

| Exp. | Lignin used gm. | "available chlorine" solution | | | Methoxyl analysis | | | Halogen analysis | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | cc. N/20 thio.req. by 10 cc. sample | cc. reagent added | Milli-equiv. reagent added | Mgm. subs. | cc. N/20 thio. req. | $\%OCH_3$ | Mgm. subs. | Mgm. AgCl | %Cl |
| 5-1 | 0.626 | 23.58 | 90 | 10.6 | 33.68 | 11.10 | 8.51 | 39.21 | 9.31 | 5.88 |
| 5-2 | 0.626 | 23.39 | 100 | 11.7 | 30.71 | 9.65 | 8.14 | 30.07 | 8.23 | 6.75 |
| 5-3 | 0.626 | 22.85 | 120 | 13.7 | 32.83 | 9.21 | 7.25 | 33.24 | 11.07 | 8.25 |
| 5-4 | 0.626 | 22.78 | 130 | 14.8 | 36.51 | 9.80 | 6.94 | 32.99 | 10.91 | 8.25 |

# Table XX (Section B)

## Action of "available chlorine" solutions upon alkali lignin at pH 5

| Experimental Data | | | | | | Calculations | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exp. | Lignin used gm | Chlorinated product | | | Reagent added Milli-equiv. per gm lignin | % $OCH_3$ on Cl free basis | % $OCH_3$ lost | Milliequivalents of $OCH_3$ lost per gm lignin | Milliequivalents of Cl introduced per gm. lignin | equiv. ratio $\frac{OCH_3}{Cl}$ | "available chlorine" equivs. reagent req. per equiv. $OCH_3$ lost | "available chlorine" equivs. reagent req. per equiv Cl introduced |
| | | Yield | % $OCH_3$ | % Cl | | | | | | | | |
| | | | | | | | | alkali lignin - 15.20% methoxyl | | | | |
| 5-1 | 0.626 | 0.55 | 8.51 | 5.88 | 16.9 | 9.05 | 6.15 | 1.98 | 1.65 | 1.20 | 8.4 | 10.2 |
| 5-2 | 0.626 | 0.52 | 8.14 | 6.75 | 18.7 | 8.73 | 6.47 | 2.08 | 1.93 | 1.08 | 9.0 | 9.7 |
| 5-3 | 0.626 | 0.48 | 7.25 | 8.25 | 21.9 | 7.90 | 7.30 | 2.35 | 2.32 | 1.01 | 8.9 | 9.0 |
| 5-4 | 0.626 | 0.45 | 6.94 | 8.25 | 23.6 | 7.46 | 7.74 | 2.50 | 2.32 | 1.08 | 9.4 | 10.2 |

## Table XXI (Section A)

## Action of "available chlorine" solutions upon alkali lignin at pH 6

| Exp. | Lignin used gm. | "available chlorine" solution |  |  | Methoxyl analysis |  |  | Halogen analysis |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  | cc. N/20 thio. req. by 10 cc. sample | cc. reagent added | Milli-equiv. reagent added | Mgm. subs. | cc. N/20 thio. req. | %$OCH_3$ | Mgm. subs. | Mgm. AgCl | %Cl |
| 6- 1 | 0.627 | 20.05 | 10 | 1.0 | 51.21 | 29.39 | 14.82 | 29.50 | 0.45 | 0.38 |
| 6- 2 | 0.627 | 19.98 | 30 | 3.0 | 62.49 | 33.78 | 13.85 | 39.64 | 2.97 | 1.85 |
| 6- 3 | 0.627 | 19.68 | 60 | 5.9 | 31.43 | 14.96 | 12.70 | 35.61 | 4.23 | 2.94 |
| 6- 4 | 0.627 | 13.48 | 120 | 8.1 | 36.72 | 16.71 | 11.60 | 36.79 | 5.35 | 3.58 |
| 6- 5 | 0.650 | 20.45 | 110 | 11.3 | 22.37 | 8.37 | 9.70 | 32.50 | 7.29 | 5.55 |
| 6- 6 | 0.650 | 19.49 | 120 | 11.7 | 26.67 | 9.65 | 9.36 | 39.98 | 9.16 | 5.65 |
| 6- 7 | 0.650 | 26.23 | 90 | 11.8 | 23.49 | 8.47 | 9.35 | 41.80 | 9.57 | 5.65 |
| 6- 8 | 0.650 | 18.70 | 130 | 12.1 | 25.56 | 8.67 | 8.78 | 45.06 | 11.40 | 6.26 |
| 6- 9 | 0.627 | 20.40 | 140 | 14.3 | 32.32 | 10.55 | 8.32 | 38.34 | 10.83 | 7.01 |
| 6-10 | 0.650 | 18.55 | 180 | 16.7 | 26.85 | 6.46 | 6.23 | 36.74 | 13.20 | 8.90 |
| 6-11 | 0.650 | 21.35 | 200 | 21.4 | 23.74 | 5.76 | 6.28 | 40.97 | 15.09 | 9.11 |

# Table XXI (Section B)

## Action of "available chlorine" solutions upon alkali lignin at pH 6

| Experimental Data | | | | | | Calculations | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exp. | Lignin used gm | Chlorinated product | | | Reagent added Milli-equiv. per gm lignin | % $OCH_3$ on Cl free basis | % $OCH_3$ lost | Milliequivalents of $OCH_3$ lost per gm. lignin | Milliequivalents of Cl introduced per gm. lignin | equiv. ratio $\frac{OCH_3}{Cl}$ | "available chlorine" equivs. reactant req. per equiv. $OCH_3$ lost | "available chlorine" equivs. reactant req. per equiv. Cl introduced |
| | | Yield gm. | % $OCH_3$ | % Cl | | | | | | | | |
| | | | | | | | | alkali lignin - 15.20% methoxyl | | | | |
| 6- 1 | 0.627 | 0.68 | 14.82 | 0.38 | 1.6 | 14.88 | 0.32 | 0.10 | 0.11 | 0.96 | 15.7 | 15.0 |
| 6- 2 | 0.627 | 0.64 | 13.85 | 1.85 | 4.8 | 14.12 | 1.08 | 0.35 | 0.52 | 0.68 | 13.7 | 9.21 |
| 6- 3 | 0.627 | 0.65 | 12.70 | 2.94 | 9.4 | 13.08 | 2.12 | 0.68 | 0.83 | 0.82 | 13.8 | 11.3 |
| 6- 4 | 0.627 | 0.65 | 11.60 | 3.58 | 12.9 | 12.00 | 3.20 | 1.03 3 | 1.01 | 1.02 | 12.5 | 12.8 |
| 6- 5 | 0.650 | 0.53 | 9.70 | 5.55 | 17.4 | 10.28 | 4.92 | 1.58 | 1.56 | 1.02 | 11.0 | 11.2 |
| 6- 6 | 0.650 | 0.50 | 9.36 | 5.65 | 18.0 | 9.93 | 5.27 | 1.70 | 1.59 | 1.07 | 10.6 | 11.3 |
| 6- 7 | 0.650 | 0.45 | 9.35 | 5.65 | 18.2 | 9.91 | 5.29 | 1.70 | 1.59 | 1.07 | 10.7 | 11.4 |
| 6- 8 | 0.650 | 0.42 | 8.78 | 6.26 | 18.7 | 9.36 | 5.84 | 1.88 | 1.76 | 1.07 | 10.0 | 10.6 |
| 6- 9 | 0.627 | 0.40 | 8.32 | 7.01 | 22.4 | 8.95 | 6.25 | 2.02 | 1.78 | 1.13 | 11.1 | 12.6 |
| 6-10 | 0.650 | 0.38 | 6.23 | 8.90 | 25.8 | 6.84 | 8.36 | 2.69 | 2.51 | 1.07 | 9.6 | 10.3 |
| 6-11 | 0.650 | 0.35 | 6.28 | 9.11 | 31.0 | 6.91 | 8.27 | 2.67 | 2.56 | 1.04 | 11.6 | 12.1 |

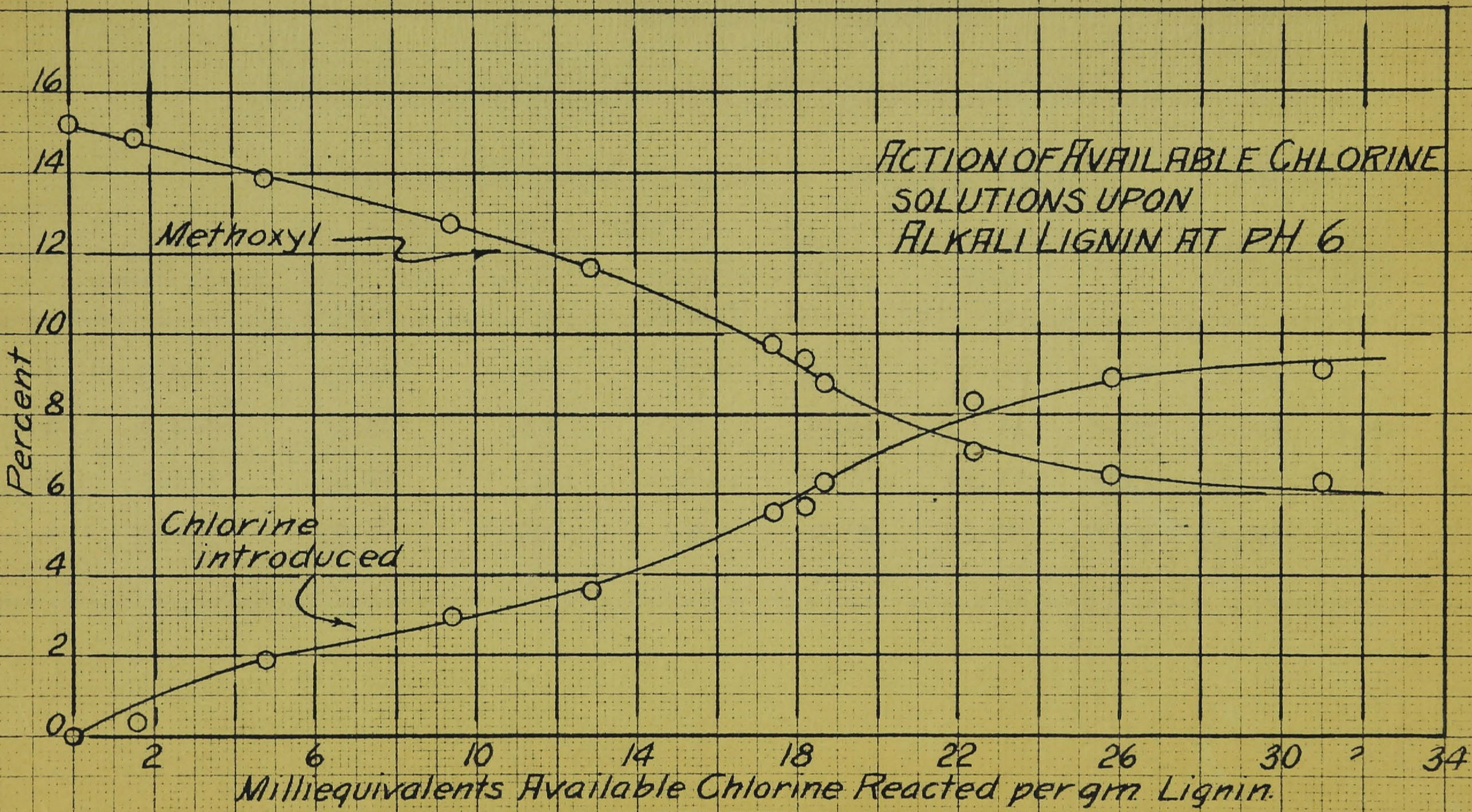

ACTION OF AVAILABLE CHLORINE
SOLUTIONS UPON
ALKALI LIGNIN AT PH 6
Methoxyl
Chlorine introduced
Percent
0
2
4
6
8
10
12
14
16
2
6
10
14
18
22
26
30
?
34
Milliequivalents Available Chlorine Reacted per gm Lignin.

FIG. XIII

## Table XXII (Section A)

### Action of "available chlorine" solutions upon alkali lignin at pH 7

| Exp. | Lignin used gm. | "available chlorine" solution | | | Methoxyl analysis | | | Halogen analysis | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | cc. N/20 thio.req. by 10 cc. sample | cc. reagent added | Milli-equiv. reagent added | Mgm. subs. | cc. N/20 thio. req. | $\%OCH_3$ | Mgm. subs. | Mgm. AgCl | %Cl |
| 7-1 | 0.659 | 15.98 | 150 | 12.0 | 25.42 | 10.68 | 10.84 | 32.92 | 7.76 | 3.56 |
| 7-2 | 0.659 | 26.87 | 110 | 14.7 | 33.18 | 12.78 | 9.95 | 27.25 | 3.86 | 4.40 |
| 7-3 | 0.659 | 26.57 | 130 | 17.3 | 41.73 | 13.97 | 8.65 | 35.10 | 8.15 | 5.75 |
| 7-4 | 0.659 | 23.80 | 160 | 19.1 | 31.98 | 10.08 | 8.15 | 25.49 | 5.78 | 5.61 |

## Table XXII (Section B)

## Action of "available chlorine" solutions upon alkali lignin at pH 7

| Experimental Data | | | | | | Calculations | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exp. | Lignin used gm | Chlorinated product | | | Reagent added Milli-equiv. per gm lignin | % $OCH_3$ On Cl free basis | % $OCH_3$ lost | Milliequivalents | | equiv. ratio $\frac{OCH_3}{Cl}$ | "available chlorine" equivs. reagent req. | |
| | | Yield gm. | % $OCH_3$ | % Cl | | | | of $OCH_3$ lost per gm. lignin | of Cl introduced per gm lignin | | per equiv. $OCH_3$ lost | per equiv Cl introduced |
| | | | | | | | | alkali lignin - 15.20 % methoxyl. | | | | |
| 7-1 | 0.659 | 0.42 | 10.84 | 3.56 | 18.2 | 11.53 | 3.67 | 1.18 | 1.00 | 1.18 | 15.4 | 18.2 |
| 7-2 | 0.659 | 0.35 | 9.95 | 4.40 | 22.4 | 10.20 | 5.00 | 1.61 | 1.24 | 1.30 | 13.9 | 18.0 |
| 7-3 | 0.659 | 0.25 | 8.65 | 5.75 | 26.2 | 9.18 | 6.02 | 1.94 | 1.62 | 1.20 | 13.5 | 16.2 |
| 7-4 | 0.659 | 0.35 | 8.15 | 5.61 | 30.5 | 8.64 | 6.56 | 2.12 | 1.58 | 1.34 | 14.4 | 19.3 |

## Table XXIII (Section A)

### Action of "available chlorine" solutions upon alkali lignin at pH 8

| | | "available chlorine" solution | | | Methoxyl analysis | | | Halogen analysis | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Exp. | Lignin used gm. | cc. N/20 thio.req. by 10 cc. sample | cc. reagent added | Milli-equiv. reagent added | Mgm. subs. | cc. N/20 thio. req. | $\%OCH_3$ | Mgm. subs. | Mgm. AgCl | %Cl |
| 8-1 | 0.659 | 20.23 | 100 | 10.1 | 29.28 | 12.88 | 11.38 | 37.22 | 4.42 | 2.94 |
| 8-2 | 0.659 | 20.23 | 130 | 13.2 | 26.67 | 10.71 | 10.40 | 36.64 | 5.80 | 3.72 |
| 8-3 | 0.659 | 19.93 | 160 | 15.9 | 23.41 | 8.70 | 9.60 | 33.16 | 4.84 | 3.62 |
| 8-4 | 0.659 | 24.77 | 160 | 19.8 | 38.44 | 13.22 | 8.88 | 34.81 | 6.53 | 4.64 |

## Table XXIII (Section B)

## Action of "available chlorine" solutions upon alkali lignin at pH 8

| Experimental Data | | | | | | Calculations | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exp. | Lignin used gm | Chlorinated product | | | Reagent added Milli-equiv. per gm lignin | % $OCH_3$ on Cl free basis | % $OCH_3$ lost | Milliequivalents of $OCH_3$ lost per gm lignin. | Milliequivalents of Cl introduced per gm. lignin. | equiv. ratio $\frac{OCH_3}{Cl}$ | "available chlorine" equivs reagent req. per equiv. $OCH_3$ lost | "available chlorine" equivs reagent req. per equiv Cl introduced |
| | | Yield gm. | % $OCH_3$ | % Cl | | | | | | | | |
| | | | | | | | alkali lignin - 15.20% methoxyl | | | | | |
| 8-1 | 0.659 | 0.63 | 11.38 | 2.94 | 15.4 | 11.72 | 3.48 | 1.12 | 0.83 | 1.35 | 13.7 | 18.6 |
| 8-2 | 0.659 | 0.45 | 10.40 | 3.72 | 20.0 | 10.82 | 4.38 | 1.41 | 1.05 | 1.34 | 14.2 | 19.1 |
| 8-3 | 0.659 | 0.35 | 9.60 | 3.62 | 24.2 | 9.97 | 5.23 | 1.69 | 1.02 | 1.65 | 14.3 | 23.7 |
| 8-4 | 0.659 | 0.25 | 8.88 | 4.64 | 30.0 | 9.34 | 55.86 | 1.89 | 1.30 | 1.45 | 15.9 | 20.7 |

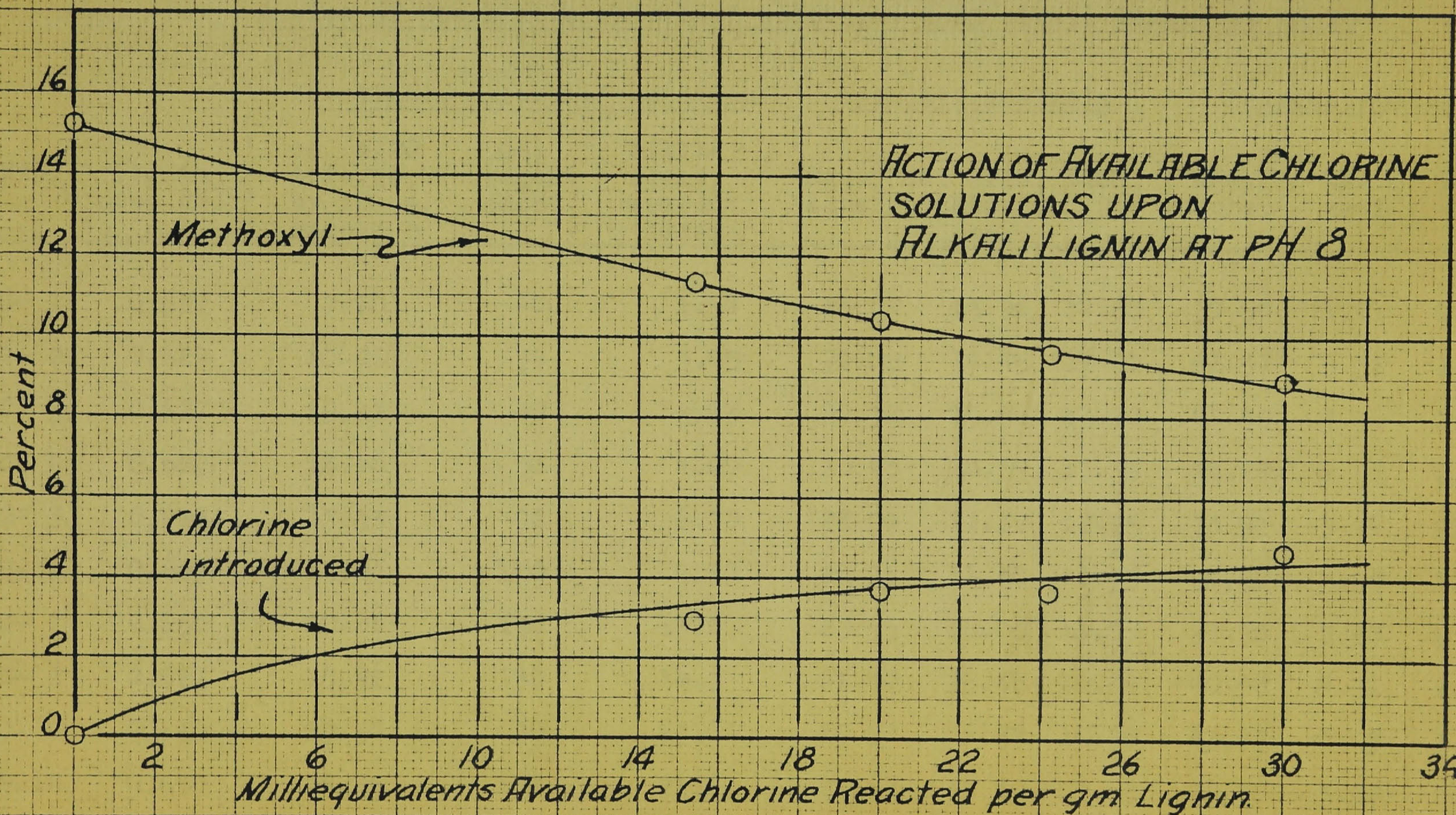

ACTION OF AVAILABLE CHLORINE
SOLUTIONS UPON
ALKALI LIGNIN AT PH 8
Methoxyl
Chlorine
introduced
Percent
16
14
12
10
8
6
4
2
0
2
6
10
14
18
22
26
30
34
Milliequivalents Available Chlorine Reacted per gm Lignin

FIG. XIV

## Table XXIV (Section A)

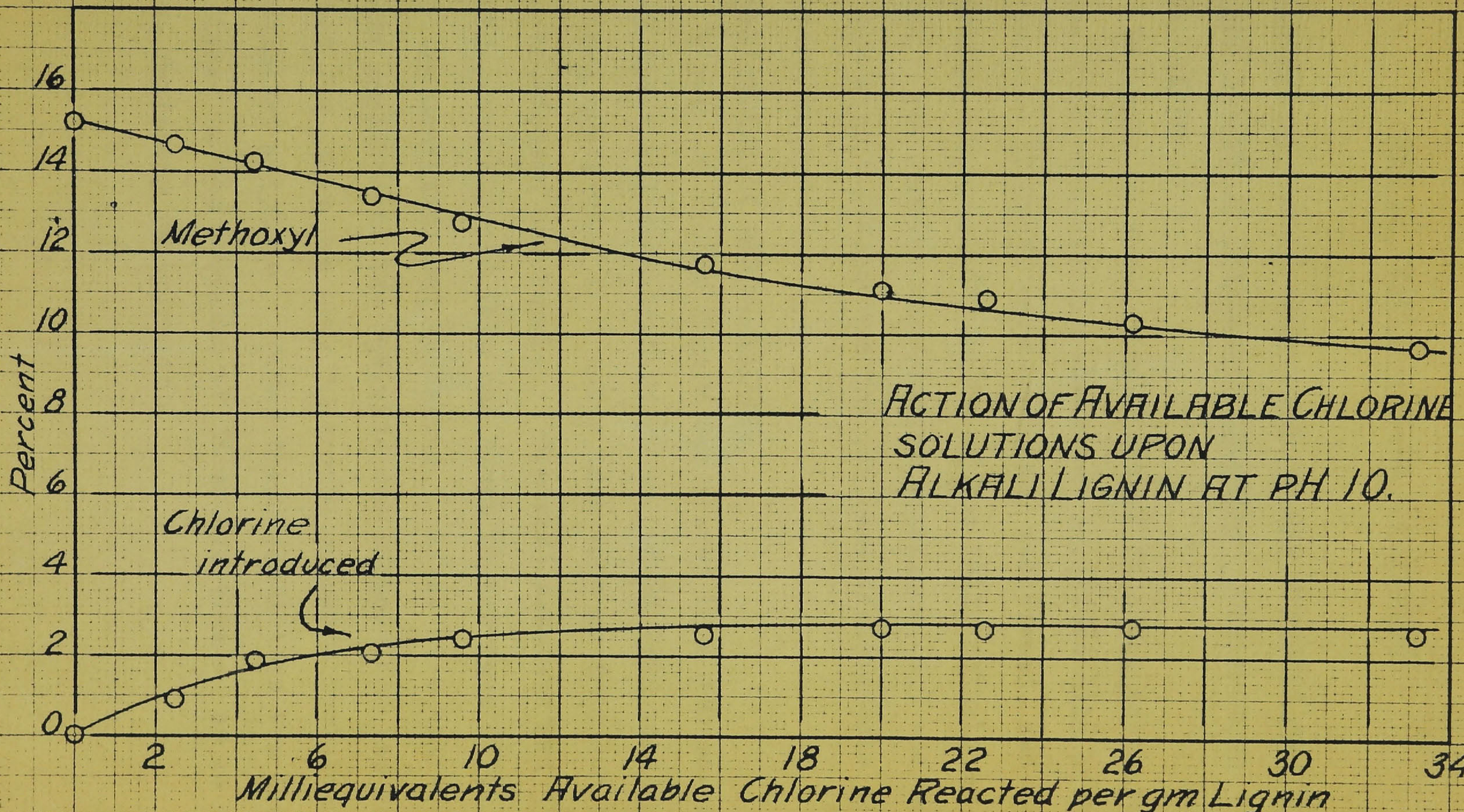
### Action of "available chlorine" solutions upon alkali lignin at pH 10

| | | "available chlorine" solution | | | Methoxyl analysis | | | Halogen analysis | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Exp. | Lignin used gm. | cc. N/20 thio. req. by 10 cc. sample | cc. reagent added | Milli-equiv. reagent added | Mgm. subs. | cc. N/20 thio. req. | %$OCH_3$ | Mgm. subs. | Mgm. AgCl | %Cl |
| 10- 1 | 0.627 | 7.70 | 40 | 1.54 | 24.64 | 13.96 | 14.62 | 30.90 | 1.11 | 0.88 |
| 10- 2 | 0.627 | 20.29 | 30 | 3.05 | 70.09 | 38.45 | 14.21 | 81.57 | 5.32 | 1.88 |
| 10- 3 | 0.627 | 19.13 | 40 | 3.83 | 29.37 | 15.56 | 13.70 | 41.59 | 3.36 | 2.00 |
| 10- 4 | 0.627 | 18.40 | 50 | 4.60 | 20.48 | 10.59 | 13.38 | 30.28 | 2.47 | 2.02 |
| 10- 5 | 0,627 | 13.33 | 90 | 6.00 | 24.00 | 11.82 | 12.75 | 38.92 | 3.74 | 2.40 |
| 10- 6 | 0.627 | 19.00 | 100 | 9.50 | 25.71 | 11.80 | 11.75 | 30.50 | 3.08 | 2.50 |
| 10- 7 | 0.650 | 20.00 | 130 | 13.0 | 23.55 | 10.08 | 11.09 | 27.58 | 2.97 | 2.67 |
| 10- 8 | 0.627 | 18.92 | 150 | 14.2 | 61.40 | 25.85 | 10.84 | 40.58 | 4.31 | 2.63 |
| 10- 9 | 0.650 | 19.95 | 170 | 17.0 | 15.90 | 6.33 | 10.30 | 43.77 | 4.99 | 2.76 |
| 10-10 | 0.650 | 24.05 | 180 | 21.6 | 31.67 | 11.80 | 9.65 | 34.16 | 3.07 | 2.59 |

## Table XXIV (Section B)

### Action of "available chlorine" solutions upon alkali lignin at pH 10

| Experimental Data | | | | | | Calculations | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exp. | Lignin used gm | Chlorinated product | | | Reagent added Milli-equiv. per gm lignin | % $OCH_3$ on Cl free basis | % $OCH_3$ lost | Milliequivalents of $OCH_3$ lost per gm lignin | Milliequivalents of Cl introduced per gm lignin | equiv. ratio $\frac{OCH_3}{Cl}$ | "available chlorine" equivs reagent req. per equiv. $OCH_3$ lost | per equiv Cl introduced |
| | | Yield gm. | % $OCH_3$ | % Cl | | | | | | | | |
| | | | | | | | | alkali lignin - 15.20% methoxyl | | | | |
| 10- 1 | 0.627 | 0.70 | 14.62 | 0.88 | 2.46 | 14.75 | 0.45 | 0.14 | 0.25 | 0.59 | 17.0 | 4.16 |
| 10- 2 | 0.627 | 0.66 | 14.21 | 1.88 | 4.86 | 14.50 | 0.70 | 0.22 | 0.53 | 0.42 | 21.8 | 9.15 |
| 10- 3 | 0.627 | 0.61 | 13.70 | 2.00 | 7.12 | 13.98 | 1.22 | 0.39 | 0.56 | 0.71 | 18.1 | 12.6 |
| 10- 4 | 0.627 | 0.61 | 13.38 | 2.02 | 7.34 | 13.67 | 1.53 | 0.49 | 0.57 | 0.87 | 14.8 | 12.9 |
| 10- 5 | 0.627 | 0.68 | 12.75 | 2.40 | 9.58 | 13.07 | 2.13 | 0.69 | 0.68 | 1.01 | 13.9 | 14.4 |
| 10- 6 | 0.627 | 0.60 | 11.75 | 2.50 | 15.16 | 12.05 | 3.15 | 1.02 | 0.70 | 1.44 | 14.8 | 21.5 |
| 10- 7 | 0.650 | 0.50 | 11.09 | 2.67 | 20.0 | 11.40 | 3.80 | 1.22 | 0.75 | 1.63 | 16.4 | 26.7 |
| 10- 8 | 0.627 | 0.60 | 10.84 | 2.63 | 22.6 | 11.26 | 3.96 | 1.28 | 0.74 | 1.73 | 17.6 | 30.6 |
| 10- 9 | 0.650 | 0.45 | 10.30 | 2.76 | 26.2 | 10.60 | 4.60 | 1.48 | 0.78 | 1.90 | 17.7 | 33.6 |
| 10-10 | 0.650 | 0.35 | 9.65 | 2.59 | 33.2 | 9.91 | 5.29 | 1.70 | 0.73 | 2.33 | 19.5 | 45.5 |



ACTION OF AVAILABLE CHLORINE SOLUTIONS UPON ALKALI LIGNIN AT PH 10.

FIG. XV

# PART V. MISCELLANEOUS EXPERIMENTS

## 1. Methylation of alkali lignin and of the products resulting from the action of "available chlorine" solutions on alkali lignin.

In order to obtain some insight into the mechanism of the reaction of "available chlorine" solutions with alkali lignin, some of the reaction products were isolated, methylated, and their properties compared with those of the fully methylated alkali lignin. The Haworth methylation technique (81) was used both for alkali lignin and for its reaction products as indicated below:

### a) Methylation of alkali lignin.

2 gms. of alkali lignin was placed in a 250 cc. three-necked flask and dissolved in 25 cc. of 4% NaOH solution. The flask was placed in a water bath kept at 25°C and its contents stirred vigorously. Dimethyl sulphate and 35% NaOH solution were dropped into the flask at the rate of 10 cc. and 25 cc. respectively per half-hour. After five half-hour periods addition of the reagents was stopped and the flask stirred for about one hour to ensure complete hydrolysis of the dimethyl sulphate. Under these conditions the lignin was methylated in the presence of 5% excess alkali as is shown in the following calculation;

$Me_2SO_4 \quad + \quad 2\ NaOH \quad = \quad Na_2SO_4 \quad +$

126 gms. $\longleftrightarrow$ 80 gms.

126 gms. $\longleftrightarrow$ 84 gms.using 5% excess alkali.

(1.33 sp.gr.)

96 cc. $\longleftrightarrow$ 240 cc. of 35% NaOH.

10 cc. $\longleftrightarrow$ 25 cc.

The partially methylated alkali lignin was insoluble in the mixture after the first methylation indicating the methylation of phenolic/or enolic hydroxyl groups. The product was separated by pouring the methylation mixture into a large volume of water and and centrifuging off the precipitate. This was dissolved in acetone and re-methylated under the same conditions.

The product from the second methylation was removed in the acetone layer which separated from the alkaline solution. The acetone-lignin solution was poured into a large volume of water and the flocculent precipitate isolated in the usual manner, (Experimental Part 3). The partially methylated lignin was analysed and then dissolved in acetone for re-methylation; in the case of alkali lignin five methylations were necessary to prepare the fully methylated derivative.

Yield - 0.7 gms.

Analysis- 34.76 mgm. req. 41.00 cc. N/20 thio.

= 30.40 % $OCH_3$

## b) Methylation of the products resulting from the action of "available chlorine" solutions on alkali lignin.

The methylation of these products was conducted under the same conditions as in (a) above for alkali lignin.

Exp. 22 In this case the fully methylated derivative could not be prepared due to lack of material. The lignin,here again, became insoluble upon methylation and in the final three methylations acetone was employed as solvent. The methylated product was isolated by the same method as used for alkali lignin.

Starting material - product from Exp. 22, namely, 0.3 gms. of alkali lignin which been partially de-methylated and chlorinated with 14.2 milliequivalents of "available chlorine" solution per gm. lignin at pH 10.

Analysis - 28.34 mgm. subs. req. 13.50 cc. N/20 thio.
= 12.30 % $OCH_3$
- 35.30 mgm. subs. gave 4.75 mgm. AgCl
= 3.33 % Cl.

Methylated product- Yield 0.07 gms.

Analysis - 18.21 mgm. subs. req. 17.98 cc. N/20 thio.
= 25.45 % $OCH_3$
- 33.47 mgm. subs. gave 3.95 mgm. AgCl.
= 2.92 % Cl.

Exp. 26 In this case the de-methylated lignin product did not become alkali insoluble upon methylation. This would seem to indicate that a sufficient number of carboxyl groups had been formed in the reaction with "available chlorine" to maintain alkali solubility of the methylated product. The methylated product was separated by acidification of the methylation mixture and centrifuging off the precipitate. This was then isolated for analysis in the usual manner; nine methylations were necessary to prepare the fully methylated derivative.

Starting material - product from Exp. 26, namely, 0.5 gms. of alkali lignin which had been partially de-methylated and chlorinated with 29.8 mil-equivalents of "available chlorine" solution per gm. of lignin at pH 10.

Analysis - In order to obtain sufficient material for methylation the reaction product was not isolated. The methoxyl and chlorine content, taken from Fig. XV. were,

10.00 % $OCH_3$

2.70 % Cl.

Methylated product- Yield 0.15 gms.

Analysis - 16.30 mgm. subs. req. 14.66 cc. N/20 thio.

= 23.20 % $OCH_3$

44.86 mgm. subs. gave 2.00 mgm., AgCl

= 1.10 % Cl

Table XXV gives the results of the methylation experiments and a comparison of the increase in methoxyl content obtained by methylation of the reaction products with that obtained by methylation of alkali lignin.

## Table XXV

### Summary of Methylation Experiments

| Product | %$OCH_3$ of original lignin | fully methylated deriv. | Increase in %$OCH_3$ |
|---|---|---|---|
| alkali lignin | 15.20 | 30.40 | 15.20 |
| Exp. No. 22 | 12.72 | 26.25 | 13.53 |
| Exp. No. 26 | 10.14 | 23.48 | 13.34 |

(% $OCH_3$ calculated on chlorine free basis)

2. Dehalogenation of the products resulting from the action of "available chlorine" solutions upon alkali lignin.

The action of "available chlorine" solutions upon lignin results in a de-methylation and chlorination of the compound, the ratio of the two effects being a function of the pH of the reaction medium. The halogen atoms introduced in the lignin are firmly bound and require more severe treatment for their removal than the action of 35% NaOH solution at room temperature but can be removed as indicated below:

0.4 gm. of alkali lignin which had been partially de-methylated and chlorinated at pH 2 was placed in a 100 cc. r.b. flask and dissolved in 50 cc. N/2 NaOH solution. Zinc dust was added ($\frac{1}{2}$ gm.) to the solution and the contents of the flask refluxed on a water bath at 100°C for 12 hrs. The flask was then cooled and the zinc removed by centrifuging, precipitating with $H_2S$ gas and filtering off the ZnS. The lignin was separated by the addition of HCl, centrifuged, thoroughly washed with dilute HCl, and filtered to a moist paste on a Büchner funnel. The precipitate was then separated into two fractions with dioxan; a) a fraction soluble in dioxan and isolated in the usual manner,(Experimental Part III), and, b) a fraction insoluble in dioxan. The latter was extracted with absolute dioxan, absolute ether, petroleum ether and finally dried in an Abderhalden drier for analysis.

The analysis of the starting material and of the two products is given in Table XXVI, together with a calculation of the methoxyl content on a chlorine free basis.

Table XXVI

Dehalogenation Experiment

| Product | % CL. | % $OCH_3$ | % $OCH_3$ on Cl free basis | Yield |
|---|---|---|---|---|
| Starting material | 10.76 | 6.41 | 7.18 | |
| Dioxan-sol. fraction | 6.89 | 6.95 | 7.38 | 0.15 gm. |
| Dioxan-insol. fraction | 1.61 | - | - | 0.07 gm. |

## 3. Rate of Reaction of "available chlorine" solutions with alkali lignin.

A series of experiments was conducted in order to determine the rate of reaction of "available chlorine" solutions with alkali lignin. No attempt was made to define the "order of reaction", the object being to find the time necessary for complete reaction of the "available chlorine" solution.

The experiments were carried out in the usual manner (Experimental Part 3), a known quantity of hypochlorous acid solution being added to the alkali lignin solution at pH 6 and the hydrogen-ion concentration maintained constant by the addition of N/5 NaOH. The quantity of alkali necessary was determined by measurement of the hydrogen-ion concentration using the glass electrode. The reaction was interrupted in the three separate experiments after 10, 30 and 180 min. respectively by addition of excess sodium sulphite solution.

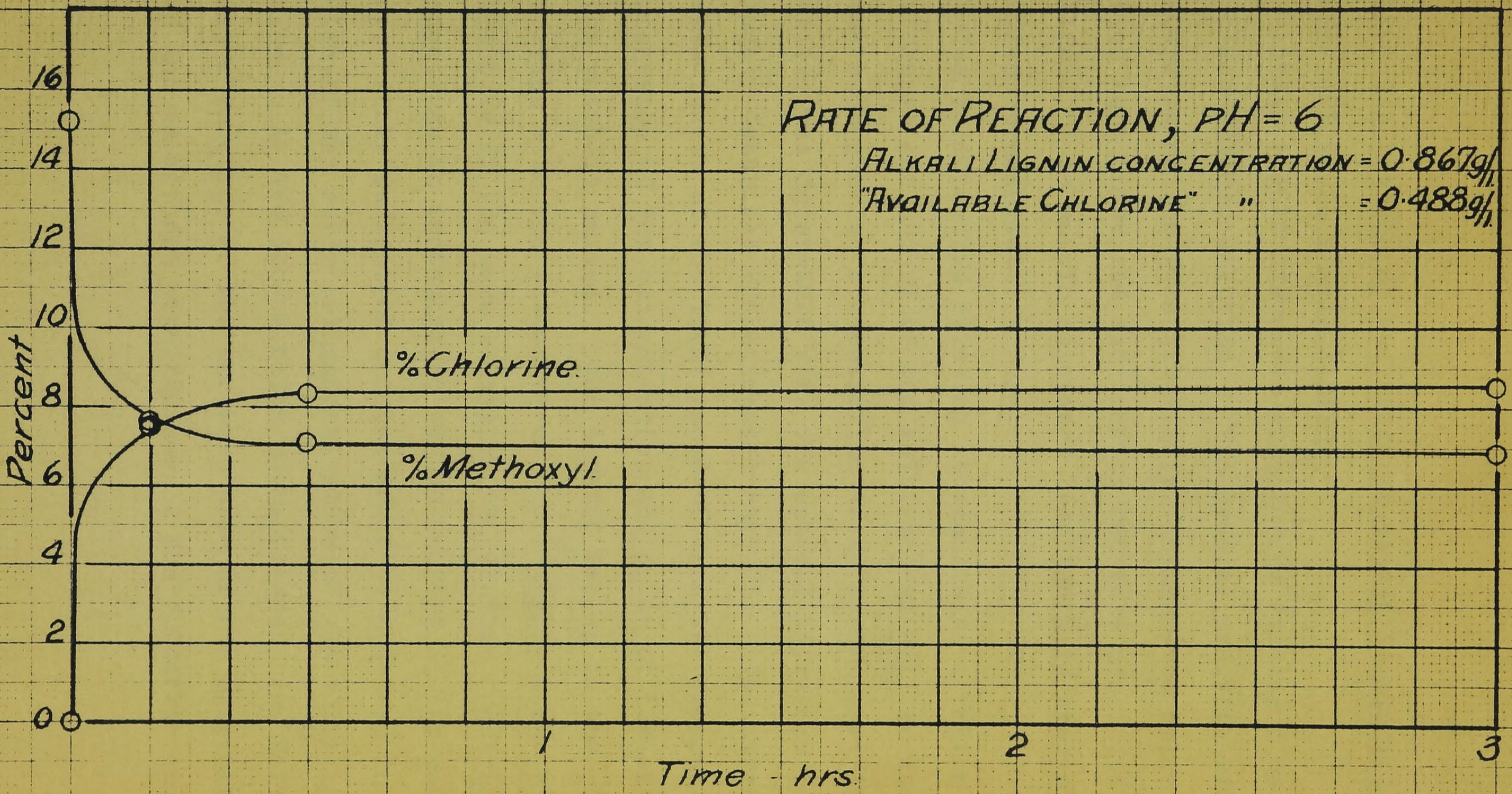
The reaction product was separated by addition of HCl, isolated in the usual manner and analysed. The experimental results are given in Table XXVII, the rate of reaction being represented graphically in Fig. XVI.

## Table XXVII

### Reaction of "available chlorine" solutions with alkali lignin at pH 6

### T. = 25°C

| | | | "available chlorine" solution | | | Methoxyl analysis | | | Halogen analysis | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | Vol. cc. | Alkali lignin used gm. | cc. N/20 thio.req. by 10 cc. sample | cc. reagent added | Milli-equiv. reagent added | Mgm. subs. | cc. N/20 thio. req. | %$OCH_3$ | Mgm. subs. | Mgm. subs. | % Cl |
| 0 | - | - | - | - | - | 19.28 | 11.33 | 15.20 | - | - | - |
| 10 | 750 | 0.65 | 20.45 | 200 | 20.4 | 17.97 | 5.23 | 7.54 | 43.55 | 13.46 | 7.65 |
| 30 | 750 | 0.65 | 17.90 | 230 | 20.6 | 17.91 | 4.82 | 7.10 | 23.88 | 8.05 | 8.34 |
| 180 | 750 | 0.65 | 20.62 | 200 | 20.6 | 28.93 | 7.72 | 6.90 | 41.90 | 14.54 | 8.58 |



RATE OF REACTION, PH = 6
ALKALI LIGNIN CONCENTRATION = 0·867 g/l
"AVAILABLE CHLORINE" " = 0·488 g/l

FIG XVI.

## 4. Relationship between pH and Color of alkali lignin solutions: Flocculation pH of alkali lignin.

Alkali lignin dissolves in alkalies forming a dark-brown to black-colored solution. The gradual addition of acid, by neutralizing the free alkalinity, changes the color of the solution to a light red and finally causes a precipitation of the lignin. In acidic solutions the lignin is present as a flocculent precipitate.

The relationship existing between this variation in color change and the pH of the solution, as well as the maximum hydrogen-ion concentration associated/with alkali lignin solubility was determined with the optical titration apparatus previously described (Experimental Part 2). The intensity and wave-length of the light incident upon the photronic cell is a function of the concentration and color of the solution through which it passes. The current set up in the photronic cell varies with the intensity of the incident light, almost irrespective of its wave-length in the visible spectrum, and its magnitude is indicated by the deflection of the galvanometer mirror. This deflection can therefore be regarded as a function of the color and concentration of the solution in question. At the flocculation point, however, the deflection becomes a function of the particle size of the precipitate formed and is without significance. The titration curve is thus composed of two sections, the latter portion of which is irreversible.

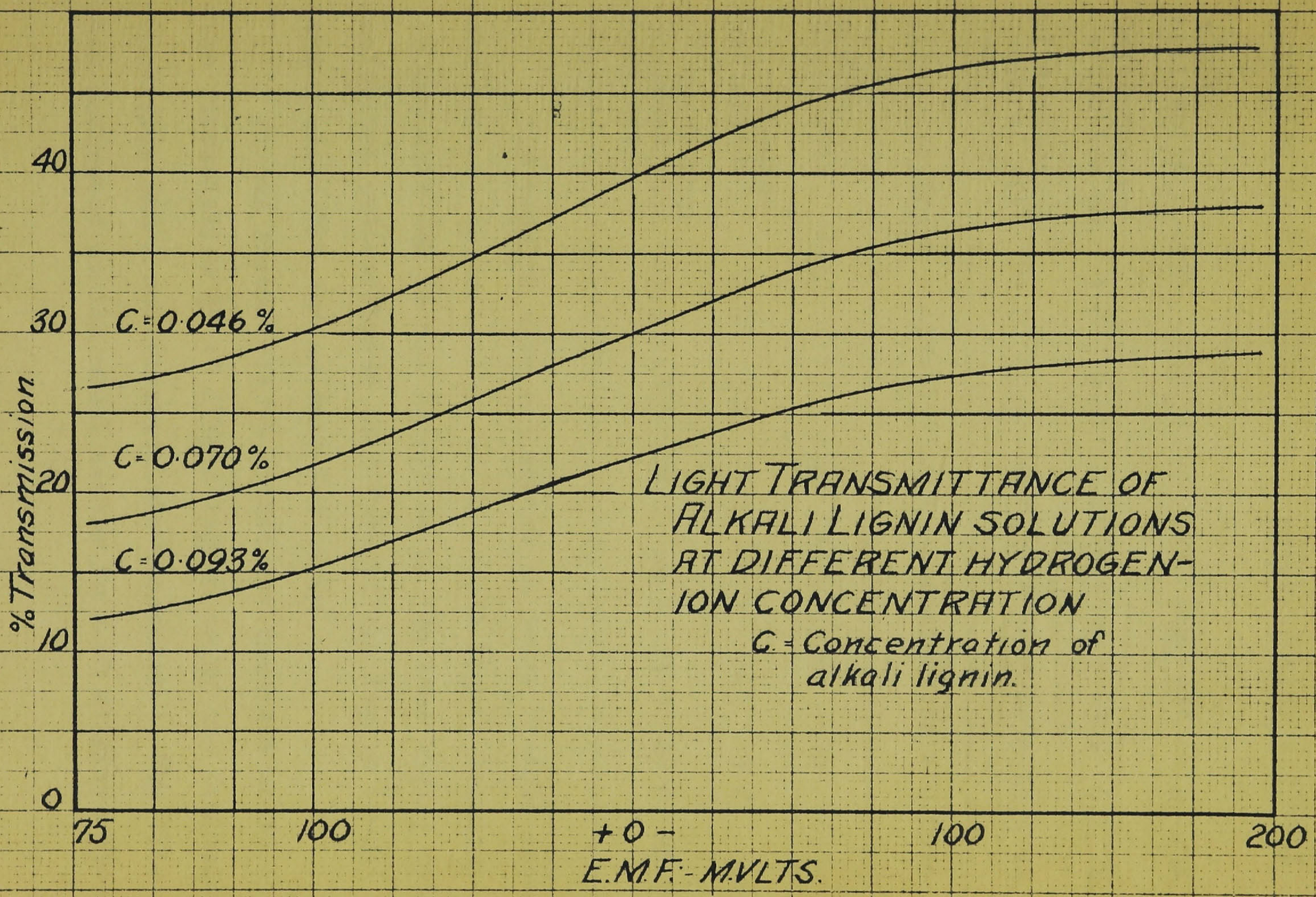
The apparatus was connected up as for hydrogen-ion concentration measurement and standardized to give a 20 cm. galvanometer deflection using distilled water in the titration beaker. The beaker was then emptied, a known weight of alkali lignin, in dilute alkali solution, introduced and the volume brought to 300 cc. The titration was performed by adding N/10 HCl dropwise from a burette and measuring, at intervals, the galvanometer deflection and hydrogen-ion concentration. The results of three titrations using different concentrations of alkali lignin are given in Table XXVIII.

## Table XXVIII

Potentiometric and photometric titration of alkali lignin

Titration No. 1 - alkali lignin concentration = 0.046%

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| e.m.f. millivolts | +147 | +137 | +117 | +90 | +62 | +25 | -24 | -70 | -119 |
| Galvanometer Deflection cm. | 5.4 | 5.6 | 5.8 | 6.3 | 6.7 | 7.5 | 8.4 | 9.1 | 9.4 |
| %Transmission compared with pure water | 27.0 | 28.0 | 29.0 | 31.5 | 33.5 | 37.5 | 42.0 | 45.5 | 47.0 |



LIGHT TRANSMITTANCE OF ALKALI LIGNIN SOLUTIONS AT DIFFERENT HYDROGEN-ION CONCENTRATION

C = Concentration of alkali lignin.

FIG XVII

Table XXVIII (continued)

Titration No.2 - alkali lignin concentration = 0.070%

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| e.m.f. millivolts | +170 | +135 | +125 | +82 | +48 | +25 | - 2 | -34 | -89 | -163 |
| Galvanometer Deflection cm. | 3.6 | 3.9 | 4.1 | 4.8 | 5.2 | 5.6 | 6.1 | 6.6 | 7.1 | 7.6 |
| %Transmission compared with pure water | 18.0 | 19.5 | 20.5 | 24.0 | 26.0 | 28.0 | 30.5 | 33.0 | 35.5 | 38.0 |

Titration No. 3 - alkali lignin concentration = 0.093%

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| e.m.f. millivolts | +170 | +117 | +32 | -33 | -58 | -96 | -153 | -177 |
| Galvanometer Deflection | 2.4 | 3.9 | 4.1 | 4.9 | 5.1 | 5.2 | 5.6 | 5.7 |
| %Transmission compared with pure water | 12.0 | 19.5 | 20.5 | 24.5 | 25.5 | 26.0 | 28.0 | 28.5 |

The results show the change in color brought about by the gradual acidification of an alkali lignin solution. This is probably due to the formation of the less highly colored, or colorless, undissociated acid form of the lignin (R-OH) from its dissociated sodium salt $R\text{-}O^- + Na^+$.

It was impossible to obtain any accurate measurement of the flocculation pH of alkali lignin using the standardized apparatus and a modification was necessary. The titration was conducted in the usual manner to a pH slightly above that in which flocculation had been found to occur. The galvanometer deflection was then increased to about 10 cms. by enlarging the iris diaphragm opening D (Fig.X), and the titration continued. The apparatus was thus made more sensitive to changes in the intensity of transmitted light and the following results were obtained, Table XXIX.

### Table XXIX

### Flocculation of alkali lignin

Titration No.1 - alkali lignin concentration = 0.0625%

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| e.m.f. millivolts | - 135 | -162 | -192 | -203 | -209 | -223 | -232 | -243 |
| Galvanometer Deflection cm. | 12.40 | 12.95 | 13.30 | 13.35 | 13.35 | 13.20 | 13.05 | 12.80 |

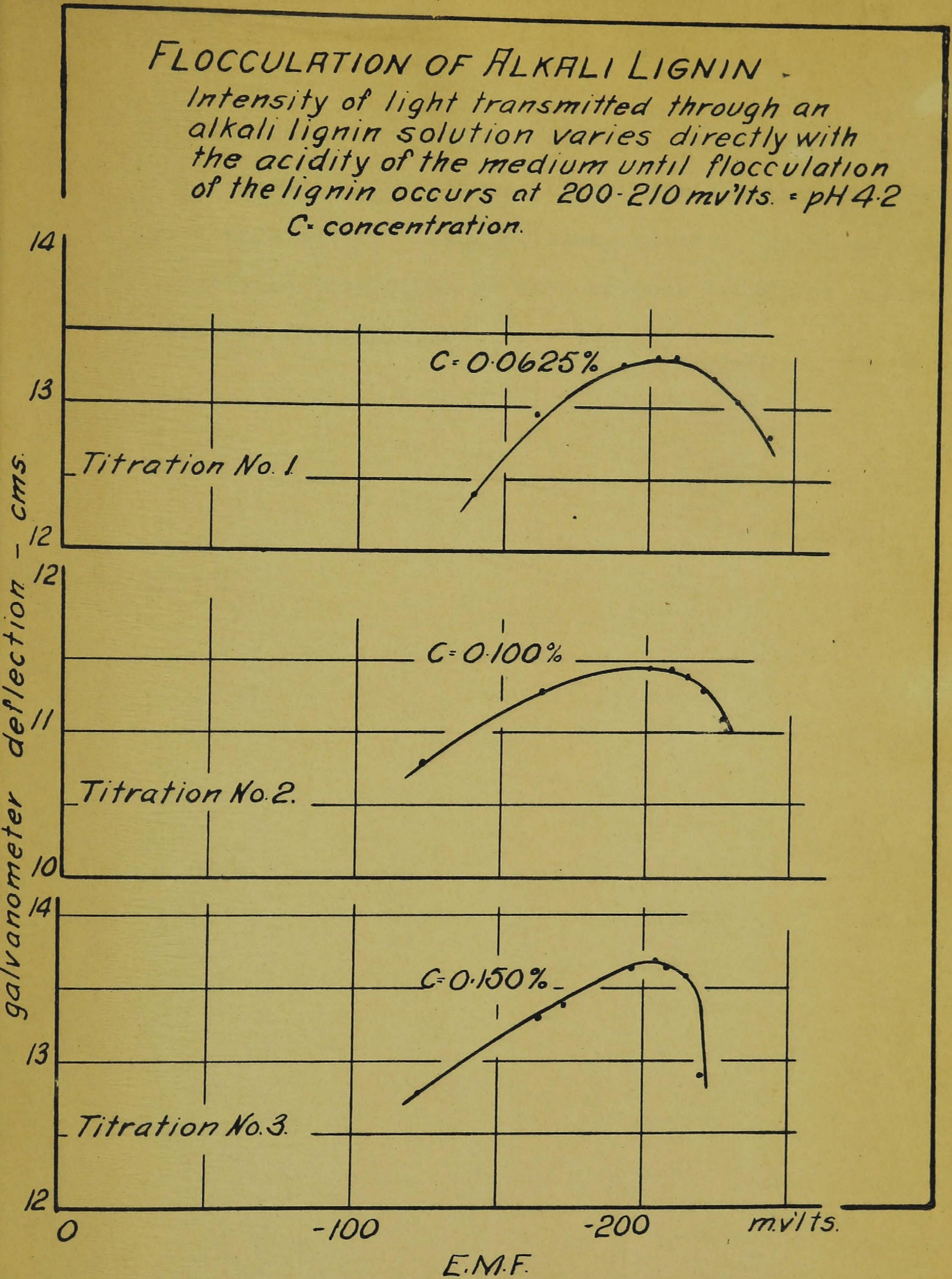
Titration No. 2 - alkali lignin concentration = 0.100%

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| e.m.f. millivolts | -123 | -164 | -202 | -209 | -214 | -219 | -226 |
| Galvanometer Deflection cm. | 10.80 | 11.30 | 11.45 | 11.45 | 11.40 | 11.30 | 11.10 |

Titration No. 3 - alkali lignin concentration = 0.150%

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| e.m.f. millivolts | -123 | -164 | -173 | -196 | -205 | -208 | -217 | -220 |
| Galvanometer deflection cm. | 12.80 | 13.30 | 13.40 | 13.65 | 13.70 | 13.65 | 13.60 | 12.90 |

A series of curves, representing the change in intensity of transmitted light is given in Fig. XVIII. Since a standardized apparatus could not be used the ordinates represent



FLOCCULATION OF ALKALI LIGNIN -
Intensity of light transmitted through an alkali lignin solution varies directly with the acidity of the medium until flocculation of the lignin occurs at 200-210 mv'lts. = pH 4.2
C = concentration.

FIG. XVIII.

merely change in centimeters of the galvanometer deflection for the individual titrations and these cannot be co-ordinated with each other. The abcissae, however, represent definite, comparable relationships with respect to pH and corresponding point of flocculation.

## SUMMARY

This investigation was undertaken in order to obtain fundamental data relating to the bleaching of wood cellulose pulps by the use of chlorine and its oxygenated derivatives. The action of these agents upon the main substance being removed in the process, namely, the lignin, was studied under conditions of controlled hydrogen-ion concentration.

Alkali lignin, since it most closely resembles the residual lignin in alkaline pulps, was used as starting material. This substance was isolated from spruce wood according to the procedure proposed by Mehta and was purified by a new method, based upon fundamental fractionation principles, yielding a uniform, reproducible compound.

The action of aqueous solutions of chlorine and its oxygenated derivatives upon alkali lignin results in,

a) chlorination of the lignin,

b) simultaneous de-methylation of the lignin.

The two reactions a) and b) are intimately related, the extent to which each proceeds being a function of the hydrogen-ion concentration of the medium in which the reactions occur. Both tend toward final constant values in solutions of pH 6 and greater while in more acidic media, although the methoxyl content tends to become constant, the chlorine content of the lignin continues to increase with increasing quantities of

reagent added to the reaction mixture. In acid solutions the equivalent ratio of "methoxyl lost" to "chlorine introduced" is less than unity, namely, 0.75 - 0.85, while in less acidic media the same ratio, after the early stages of the reaction, becomes sensibly constant at a value slightly above unity. In alkaline solutions the equivalent ratio (less than unity when only small quantities of reagent are used) proceeds through unity to a considerably higher value. In all reaction media, pH 2 - 10, the loss of methoxyl is preceeded by the introduction of chlorine in the lignin molecule.

The quantity of reagent required to bring about, a) equivalent de-methylation of the lignin, b) equivalent chlorination of the lignin, was also found to be a function of the hydrogen-ion concentration of the medium and is different for a) as compared with b).

The reaction product obtained at pH 10 (having colloidal properties similar to those of alkali lignin) can be methylated with dimethyl sulphate and alkali, and the <u>increase</u> in methoxyl content amounts to about ninety percent of that obtained when alkali lignin is fully methylated under the same conditions. In other words, the chemical changes involved in the removal of methoxyl groups by the action of "available chlorine" solutions upon alkali lignin does not result in the formation of potential or active hydroxyl groups capable of methylation under these conditions; at the same time the hydroxyl groups of the latter type pre-existing in the lignin and capable of methylation, are not affected by the "available chlorine" solution.

The solubility relationships of alkali lignin in solutions of different hydrogen-ion concentration was investigated and it was found that alkali lignin is flocculated in solutions of greater acidity than represented by pH 4.2.

The results of the investigation show that optimum conditions as regards removal of lignin from wood cellulose involving minimum consumption of chlorine, can best be obtained by conducting bleaching operations in media of controlled hydrogen-ion concentration, pH 5 - 6.

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