

REACTIONS OF CELLULOSE IN LIQUID SULFUR DIOXIDE

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A Dissertation

Submitted to The Graduate Committee in partial  
fulfillment of the requirements for the  
Degree of Doctor of Philosophy  
in Chemistry

by

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Virginia Polytechnic Institute  
Blacksburg, Virginia  
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### Acknowledgement

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## TABLE OF CONTENTS

<u>Introduction</u>	page
A. Liquid Sulfur Dioxide as a Solvent and Non-aqueous Reaction Medium .....	1
B. Structure and Properties of Cellulose .....	6
C. Chemical Reactions of Cellulose .....	8
D. Liquid Sulfur Dioxide as a Solvent and Non-aqueous Reaction medium for Cellulose .....	13
 <u>Materials and Laboratory Procedure</u>	
A. Materials used .....	15
B. Laboratory Procedure .....	17
C. Methods of Analysis .....	18
 <u>Experimental</u>	
A. Action of Sulfur Dioxide on Cellulose .....	19
B. Action of Metallic Sodium on Cellulose in Liquid Sulfur Dioxide .....	19
C. Action of Nitrogen Tetroxide on Cellulose in Liquid Sulfur Dioxide. ....	20
D. Action of Nitric Acid on Cellulose in Liquid Sulfur Dioxide .....	23
E. Action of Liquid Sulfur Dioxide on Trisodium Cellulosate .....	28
F. Esterification Reactions in Liquid Sulfur Dioxide .....	37

TABLE OF CONTENTS  
(continued)

	page
G. Hydrolysis of Cellulose .....	41
1. Preliminary Experiments .....	41
2. Degradation of Cellulose with Concentrated Sulfuric Acid Dissolved in Sulfur Dioxide .....	46
3. Degradation of Cellulose with Concentrated Sulfuric Acid Dissolved in Sulfur Dioxide Followed by Hydrolysis of the Product with Dilute Sulfuric Acid ..	48
4. Degradation of Regenerated Cellulose with Concentrated Sulfuric Acid .....	52
5. Degradation of Cellulosic Content of Southern Yellow Pine, and of Wood Pulp with Concentrated Sulfuric Acid .....	55
H. Extraction of Cellulose Dextrins with Liquid Ammonia .....	60
<u>Summary and Conclusions</u> .....	65
<u>Bibliography</u> .....	67

# LIST OF TABLES AND GRAPHS

	page
<u>Table I</u> - Action of Nitric Acid on Cellulose Pulp at $-15^{\circ}\text{C}$ . .....	25
<u>Table II</u> - Action of Nitric Acid on Cellulose Pulp in Liquid Sulfur Dioxide Containing One Gram of $\text{P}_2\text{O}_5$ at $-15^{\circ}\text{C}$ . ..	25
<u>Table III</u> - Action of Nitric Acid on Cellulose Pulp in Liquid Sulfur Dioxide Containing 3 ml. of Concentrated Sulfuric Acid ...	26
<u>Table IV</u> - Action of Nitric Acid on Cellulose Pulp in Liquid Sulfur Dioxide containing one Gram of $\text{P}_2\text{O}_5$ and Saturated with Chlorine Gas .....	26
<u>Table V</u> - Action of Liquid Sulfur Dioxide on Trisodium Cellulosate .....	35
<u>Table VI</u> - Action of Different Organic Acids on Cellulose Acetate Dissolved in Liquid Sulfur Dioxide after 12 Hours at $-15^{\circ}\text{C}$ . ..	38
<u>Table VII</u> - Action of Different Reagents on Cellulose Acetate Dissolved in Sulfur Dioxide after 12 Hours at $-15^{\circ}\text{C}$ . ..	39
<u>Table VIII</u> - Degradation of Regenerated Cellulose in Liquid Sulfur Dioxide with Concentrated Sulfuric Acid ...	50
<u>Table IX</u> - Degradation of Regenerated Cellulose in Liquid Sulfur Dioxide with Concentrated Sulfuric Acid Followed by Hydrolysis with Dilute Sulfuric Acid .	50
<u>Graph I</u> - Degradation of Regenerated Cellulose in Liquid Sulfur Dioxide with Concentrated Sulfuric Acid ....	51
<u>Table X</u> - Degradation of Regenerated Cellulose with Concentrated Sulfuric Acid .....	53
<u>Table XI</u> - Degradation of Regenerated Cellulose with Concentrated Sulfuric Acid Followed by Hydrolysis with Dilute Sulfuric Acid for Five Hours .	53

LIST OF TABLES AND GRAPHS  
(continued)

	page
<u>Graph II</u> - Degradation of Regenerated Cellulose with Concentrated Sulfuric Acid .....	54
<u>Table XII</u> - Degradation of Southern Yellow Pine with Concentrated Sulfuric Acid Followed by Hydrolysis with Dilute Sulfuric Acid for Five Hrs.	57
<u>Graph III</u> - Degradation of Regenerated Cellulose and of Southern Yellow Pine with Concentrated Sulfuric Acid Followed by Hydrolysis with Dilute Sulfuric Acid for Five Hrs. .	58
<u>Table XIII</u> - Degradation of Wood Pulp with Concentrated Sulfuric Acid Followed by Hydrolysis with Dilute Sulfuric Acid for Five Hours ...	60
<u>Table XIV</u> - Extraction of Cellulose Dextrins with Liquid Ammonia .....	62

## INTRODUCTION

### Liquid Sulfur Dioxide as a Solvent and Non-aqueous Reaction Medium.

Sulfur dioxide as a compound has been known since the days of the alchemists. However, its use as a solvent, and non-aqueous reaction medium, is of comparatively recent date.

Pure liquid sulfur dioxide has a boiling point of  $-10.02 \pm 0.01^{\circ}\text{C}$ . as determined by Bergstrom (2), and a density given by the expression,  $D = 2.122 - 0.00232T$ . Where "T" is the temperature in degrees absolute.

The work which has been done on the use of liquid sulfur dioxide as a solvent, and non-aqueous reaction medium, for chemical compounds is not as extensive as that which has been conducted with liquid ammonia. However, sufficient investigations have been carried out to show that liquid sulfur dioxide resembles to a large extent both liquid ammonia and water in its properties as a solvent.

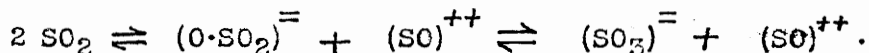
In one of the earliest publications concerning the use of liquid sulfur dioxide as a solvent, Ephraim and Kornblum (10) have shown that some metallic salts, particularly the alkali halides and isocyanates, form addition products with the solvent similarly to the hydrate of copper sulfate which is formed when anhydrous copper sulfate is dissolved in water. Three years later DeForcrand and Toboury (7) showed that the same addition products of sodium,



rubidium, and cesium could be formed by passing dry sulfur dioxide gas over the corresponding iodides.

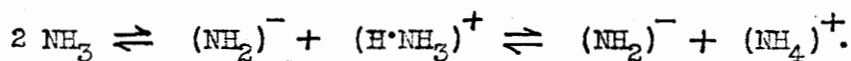
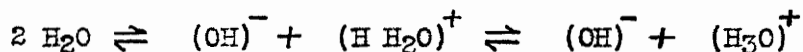
In 1920 Bagster and Cooling (1) carried out experiments on the electrolysis of hydrogen bromide in liquid sulfur dioxide in which they showed that liquid sulfur dioxide is not acidic in nature, but on the contrary is slightly basic. They found that although hydrogen bromide is soluble in liquid sulfur dioxide that it is not appreciably ionized; yet a solution of hydrogen bromide gas in liquid sulfur dioxide dissolves exactly one mole of water for every mole of hydrogen bromide dissolved and the solution is an excellent conductor. When the sulfur dioxide solution of hydrogen bromide and water is electrolyzed, water is set free at the cathode by discharge of the hydronium ion. Furthermore, Bagster and Cooling found that the amount of water set free at the cathode is in excellent agreement with Faraday's laws, i.e. one mole of water is liberated for every faraday of electricity passed through the solution.

More recent experiments on the use of pure liquid sulfur dioxide as a solvent, and a non-aqueous reaction medium, have been conducted by Jander and his coworkers (20) in which they show that liquid sulfur dioxide is a comparatively good solvent for both organic and inorganic compounds, and that pure liquid sulfur dioxide is a poor conductor of electricity whereas its solutions are relatively good conductors just as is the case with pure water and aqueous solutions. However, since the pure liquid does conduct electricity to a small extent Jander and Wickert have proposed the following dissociation scheme:

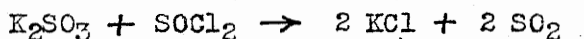


Which is comparable to the dissociation of water and liquid ammonia.

Thus:



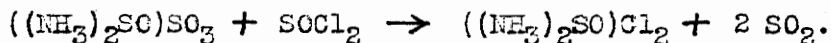
The positive  $(\text{SO})^{++}$  ion corresponds to the hydrogen ion in water, while the negative sulfite ion is the anion corresponding to the hydroxyl ion in water. Using this dissociation scheme as a basis, Jander and Ullmann (21) assumed that thionyl compounds (eg. thionyl chloride) should act as acids in liquid sulfur dioxide, and sulfites as bases. This they found to be the case. The two types of compounds will react in liquid sulfur dioxide forming a salt and sulfur dioxide. The reaction between potassium sulfite and thionyl chloride for example is:



Which is comparable with that between an acid and a base in water, or between an amide and an ammonium salt in liquid ammonia. Furthermore, Jander, Knoll, and Ullmann (24) have set up a system of compounds which is strictly analogous to the ammonia system and the aqua system.

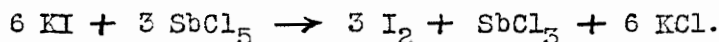
The reaction between ammonia and liquid sulfur dioxide is also analogous to that between ammonia and water, for Jander and Wickert (22) have shown

that it yields a thionyl diammonium sulfite,  $\text{SO}(\text{NH}_3)_2\text{SO}_3$ , which can react with thionyl chloride in liquid sulfur dioxide just as ammonia dissolved in water reacts with an acid. Thus:



Wickert (38) has shown further that liquid sulfur dioxide resembles water as a solvent in that neutralization results in reactions of basic oxides with thionyl chloride in liquid sulfur dioxide.

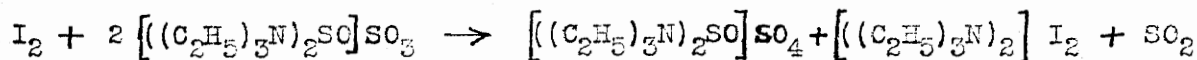
The fact that oxidation-reduction reactions can take place in liquid sulfur dioxide has been established by Jander and Immig (23) in which they show that oxidizing agents will liberate iodine from potassium iodide. Thus antimony pentachloride will liberate iodine according to the following equation:



Similarly iodine will oxidize sulfites to sulfates. For example, the basic compound formed when triethyl amine is added to liquid sulfur dioxide,

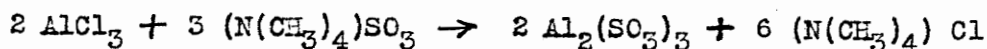
$((\text{C}_2\text{H}_5)_3\text{N})_2\text{SO})\text{SO}_3$ , is readily oxidized by iodine to a sulfate as shown by

the following equation:



As a final example of the analogy between aqueous systems and liquid sulfur dioxide, the amphoteric behavior of aluminum sulfite may be

considered. Jander and Wickert (22) have shown that aluminum sulfite is obtained as a white precipitate on adding tetramethyl ammonium sulfite to a solution of aluminum chloride in liquid sulfur dioxide as shown by the following equation:



On addition of an excess of reagent the precipitate redissolves forming the compound,  $(\text{N}(\text{CH}_3)_4) \text{ Al}_2(\text{SO}_3)_3$ , while reprecipitation of the sulfite can be brought about by adding thionyl chloride. These reactions are very similar to the dissolution of aluminum hydroxide by an excess of sodium hydroxide and its reprecipitation by the addition of an acid.

A large portion of the work described in the preceding pages has been summed up in a review by Emeleus (9) in which he describes the most important reactions which take place in both liquid ammonia and in liquid sulfur dioxide; and in a publication by Jander (25) in which he describes the basis of the chemistry in liquid sulfur dioxide.

In the preceding pages the close analogy of the action of liquid sulfur dioxide to that of water as a solvent and as a non-aqueous reaction medium has been shown. However, in sharp contrast to the action of water as a solvent, liquid sulfur dioxide serves as a good solvent for some of the aromatic and aliphatic hydrocarbons which are completely immiscible with water. In general the investigations (39) which have been conducted

on the use of liquid sulfur dioxide as a solvent for both paraffin and aromatic hydrocarbons show that absolutely water-free liquid sulfur dioxide serves as a good solvent for a large number of these compounds. Also, that fatty oils containing hydroxyl groups have relatively higher solubilities than those which do not contain the hydroxyl group.

### Structure and Properties of Cellulose

Cellulose constitutes the major portion of the plant world. It is a colloidal material which is generally aliphatic in chemical action. Cellulose is not a single chemical compound, but is a class of substances possessing many chemical and physical properties in common. Pure cellulose does not occur as such in nature, but is always found to be in combination with other substances such as lignin, pectin, or other non-cellulosic materials. Whether these non-cellulosic materials are in actual chemical combination with the cellulose, or are held in combination with it by purely physical forces, is a subject which is still under consideration. However, in general, it may be said that three types of compound celluloses exist. They are:

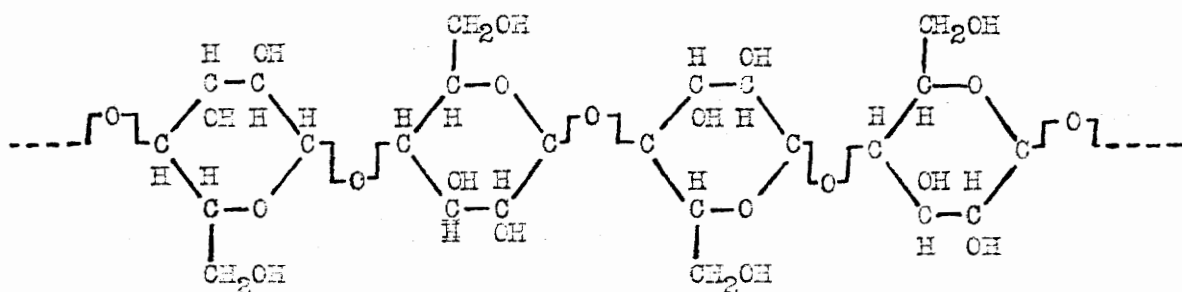
- 1) Lignocellulose. Example - wood.
- 2) Pecto, or muco, cellulose. Example - cotton, flax, rhamie.
- 3) Adipo cellulose. Example - cork.

The purest form of naturally occurring cellulose is found in the cotton plant; which contains over 90% of pure cellulose. The other sources of cellulose (flax, wood, rhamie) all contain less than this. When obtained in the pure state and analyzed, cellulose is found to have the following composition:

Carbon.....	44.4%
Oxygen.....	49.4%
Hydrogen.....	6.2%

which corresponds to an empirical formula of  $(C_6H_{10}O_5)_x$ ; where x varies from fifty to three thousand.

The most widely accepted formula for cellulose is that proposed by Haworth and Machemer (15), who have shown that cellulose is made up entirely of anhydro-beta-glucose units connected together through an oxygen bridge joined to carbon atoms number 1 and 4. Thus:



Further evidence of this structure for the cellulose molecule is shown by the X-ray measurements of Sponsler and Dore (35), who have shown that two anhydro-beta-glucose units will fit along the fiber axis of the cellulose crystal. Also, Monier and Williams (31), and many other investigators too numerous to mention here, have shown that an almost quantitative yield of beta-glucose is obtained on complete hydrolysis of cellulose. Therefore, it is logical to assume from the work which has been done that the cellulose molecule is composed of anhydro-beta-glucose units which are connected

through an oxygen bridge joined to carbon atoms number one and four to give a long chain molecule of colloidal dimensions.

### Chemical Reactions of Cellulose

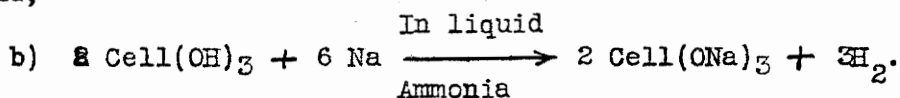
From the above structure of cellulose it can be seen that there are three hydroxyl groups per  $C_6$  unit which contain four hydroxyl groups. Therefore, one would expect the reactions of cellulose to be analogous to those of the polyhydroxy alcohols. This in practice has been found to be true as shown by the following examples:

#### I Action of Alkalies and Alkali Metals

Cellulose forms alcoholates with alkalies, and alkali metals, as shown by the following equations:



and,



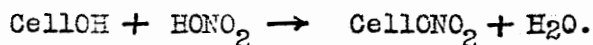
The reaction listed under "a" takes place in a water solution, and it is not definitely known whether two hydrogen atoms are displaced per  $C_6$  unit or whether one hydrogen is displaced in one unit while three hydrogen atoms are displaced in another  $C_6$  unit to correspond to the analysis of the compound formed when an aqueous solution of sodium hydroxide is allowed to act on cellulose. On the other hand, it appears quite certain in the reaction listed under "b" that three hydrogen atoms are displaced per  $C_6$  unit when an alkali

metal is allowed to act on cellulose in a medium of liquid ammonia (32).

## 2) Esterification

Cellulose forms esters with both organic and inorganic acids under the proper conditions. Cellulose nitrate is the oldest and by far the most important ester formed by the action of an inorganic acid on cellulose. Therefore, a discussion of its formation will serve as a representative example for the formation of the cellulose esters of inorganic acids.

The general method for the preparation of cellulose nitrate is essentially the same as that for any other esterification, that is, the elimination of a molecule of water between the alcoholic hydroxyl groups and the reacting acid as shown by the following equation:



Schönbein (33) in 1845, indicated that the most suitable nitrating agent was a mixture of nitric and sulfuric acids. Since this time a very large amount of work has been done on the preparation of cellulose nitrate, but the present day method of preparation remains essentially the same as that proposed by him.

From the above equation, it can be seen that for every nitro group introduced into the cellulose molecule, a molecule of water is formed, and since the extent of nitration, is to a large measure, dependent upon the



amount of water present in the nitrating mixture (23), it is essential that the water be removed as rapidly as it is formed. This is accomplished by the use of some dehydrating agent such as sulfuric acid, phosphorus pentoxide, phosphoric acid, or, in some cases, glacial acetic acid, or acetic anhydride. Lenze and Rubens (27) have shown that a cellulose nitrate containing approximately 14% nitrogen can be prepared when phosphorus pentoxide is used as the dehydrating material. However, experience has shown (17) that one of the best methods for the production of the highest nitrated cellulose, guncotton, is by treating one part of cotton with thirty parts of a bath having the following composition at 15°C:

$\text{H}_2\text{SO}_4$	.....	75.00%
$\text{HNO}_3$	.....	15.75%
$\text{HNO}_2$	.....	1.30%
$\text{H}_2\text{O}$	.....	7.94%

During the process of nitration the temperature is allowed to rise to around 25°C., then toward completion of the reaction it falls to about 20°C..

In the nitration of cellulose, the nitration takes place along the entire length of the chain. As in the case of the action of an alkali on cellulose, there is no indication that the same number of hydroxyl groups on each  $\text{C}_6$  unit is nitrated during the process, and the resultant product is probably a mixture of all stages of esterification. The percentage nitrogen obtained depends upon these mixtures; the pure mono, di, or trinitrate

never being isolated. However, on the basis of a glucose residue, the three nitrates should have the following theoretical nitrogen content:

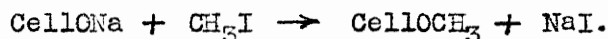
Trinitrate	.....	14.2%
Dinitrate	.....	11.1%
Mononitrate	.....	6.8%

In the case of the esters of organic acids of cellulose, cellulose acetate is by far the most important ester of this group. Therefore, a discussion of its formation will serve as a representative example for the preparation of the cellulose esters of organic acids.

As is the case in the preparation of the nitrate, the formation of cellulose acetate is essentially a reaction in which a molecule of water is eliminated between the alcoholic hydroxyl groups and the reacting acid. However, in sharp contrast to the method of preparation of the nitrate, cellulose acetate can not be prepared efficiently without the use of a suitable catalyst such as zinc chloride, phosphoric acid, sulfuric acid, or chloroacetic acid. The general method of preparation (8) is to treat cellulose of the right moisture content (around 5%) with a mixture of acetic anhydride and glacial acetic acid containing one of the above mentioned catalysts, and allowing the reaction to proceed at a temperature of about five to twenty degrees centigrade until all of the cellulosic material has dissolved. Water is then added to the mixture to promote the hydrolysis of the primary acetate to the secondary acetate.

In passing, it is important to note that the primary acetate; having an acetyl content of 62.5% corresponding to the triacetate, and soluble in such solvents as chloroform, formic acid, acetic acid, and aniline; has very little commercial value due to the fact that threads and films formed from it are weak and brittle. In order to obtain the acetate used in industry today, it is necessary to hydrolyze the triacetate to one soluble in acetone and having an acetyl content of 54.5% corresponding to the diacetate.

3) A final example of reactions typical of polyhydroxy alcohols and exhibited by cellulose is the formation of ethers when an alkyl halide such as methyl iodide is allowed to react with the alcoholate, as shown by the following equation:



Both aliphatic and aromatic, and also mixed ethers of cellulose have been prepared by using the above method of preparation.

#### Hydrolysis of Cellulose

The first recorded attempts to produce sugars and alcohols from vegetable fiber were those of Braconnet (3) in 1819. Since this time an enormous amount of work has been done on this problem, using in general the following means: 1) use of water and pressure alone; 2) use of certain salts, with and without pressure; 3) use of acids, with and without pres-

sure; 4) by regeneration from esters; and 5) use of alkalies. The author will make no attempt to list each investigation separately due to the fact that such a task would be almost unlimited, and, therefore, beyond the scope of this work. Suffice it to say here that most of the references to the earlier work can be found in a book by Schorger (39), and in a publication by The United States Department of Agriculture (26).

The essential chemistry of the hydrolysis of cellulose to glucose involves the degradation of the large cellulose molecule first to hydrocelluloses, then to cellobiose, and finally to glucose by the breaking of the oxygen bonds between the anhydro-glucose units. Theoretically, on the complete hydrolysis of cellulose, 100 grams of cellulose should yield 111.1 grams of glucose. In actual practice, this figure has been approached close enough to show that under the proper conditions a quantitative yield of glucose can be obtained upon the complete hydrolysis of cellulose.

Liquid Sulfur Dioxide as a Solvent and Non-aqueous Reaction Medium for Cellulose and Cellulose Derivatives.

Up to the present time, very little work has been done on the use of liquid sulfur dioxide as a solvent and as a non-aqueous reaction medium for cellulosic materials. The first recorded work is that of Clancy (6) in 1925, who obtained patents on the use of liquid sulfur dioxide as a solvent for both cellulose nitrate and cellulose acetate. Two years later, chemists of The I. G. Farbenind Company (11) succeeded in preparing cellulose acetate

in a medium of liquid sulfur dioxide by the action of acetic anhydride, in the presence of a catalyst such as zinc chloride, on cellulose. The next recorded work is that of Mattox (30) in 1939, whose investigations were primarily of a preliminary nature. Nevertheless, one important fact is contributed by his work; that is, that cellulose is insoluble in, and is unaffected by liquid sulfur dioxide.

#### Object of this Investigation

In view of the fact that a very meager amount of information was available concerning the use of liquid sulfur dioxide as a solvent and as a non-aqueous reaction medium for cellulose and cellulosic materials, it was decided by this laboratory to conduct a thorough investigation on the subject. In carrying out the work, the following typical reactions of cellulose, and cellulose derivatives, were investigated: 1) esterification, 2) etherification, 3) xanthation, and 4) hydrolysis.

Materials and Laboratory Procedure

I. Materials

The sulfur dioxide used during the course of this investigation was, of a necessity, water free and of the purest grade obtainable. The majority of the sulfur dioxide used was obtained from the Virginia Smelting Company of West Norfolk, Virginia, and labeled as extra dry essotoo.

The ammonia used was of the ordinary technical grade of anhydrous ammonia prepared by the E. I. Du Pont National Ammonia Division of Frankford, Philadelphia, Pennsylvania.

The cellulose used during the course of this investigation was of two varieties. 1) Well-fluffed, well-dried, spruce sulfite pulp of a high alpha-cellulose content prepared by The Brown Company of Berlin, New Hampshire, and having the following composition for an air dried sample:

Alpha-cellulose	.....	95.60%
Moisture	.....	3.98%
Lignin	.....	0.50%
Ash	.....	0.14%

and, 2) well-dried regenerated cellulose, rayon, prepared in this laboratory from the sulfite pulp by the well-known viscose process.

The anhydrous soda cellulose used during this investigation was prepared in this laboratory by the action of metallic sodium in liquid ammonia on a sample

of well-dried sulfite pulp. The sodium cellulose prepared by this method had a sodium content of 27.43%; which corresponds fairly closely to that of 30.20% sodium for the trisodium cellulosate.

The cellulose acetate used was obtained from the Hercules Powder Company of Parlin, New Jersey, and had an acetyl content of 54.5%, corresponding to the commercial grade secondary acetate.

The cellulose nitrate used during the course of this investigation was also obtained from the Hercules Powder Company, and had a nitrogen content of 13.44%; corresponding very closely to the trinitrate.

The wood used in the hydrolysis experiments was well-dried, seasoned, second-growth Southern Yellow Pine sawdust; having the following composition on an air dried sample:

Total cellulose	.....	53.0%
CCl <sub>4</sub> extract	.....	4.0%
Lignin	.....	34.2%
Moisture	.....	5.1%
Ash	.....	0.43%

The cellulose was determined by Brownley (5) according to the method of Cross and Bevan (18), and the lignin was determined by the procedure devised by Becker (19).

The nitrogen tetroxide used in the nitration experiments was pre-

pared in this laboratory by heating lead nitrate. The gas was dried by passing it over calcium chloride, and then over phosphorous pentoxide, then condensed by means of a salt-ice bath to a reddish-brown liquid and reserved for use.

The nitric acid used in the nitrating experiments was prepared in this laboratory by the distillation of the nitric acid from a mixture of sodium nitrate and concentrated sulfuric acid.

The sulfuric acid used for the hydrolysis experiments was of two varieties: 1) Twenty per cent fuming, chemically pure grade sulfuric acid, and 2) the ordinary chemically pure concentrated sulfuric acid.

The other chemicals used during the course of this investigation were, unless otherwise specified, of the highest chemically pure grade obtainable.

## II. Laboratory Procedure

The laboratory procedure, unless otherwise specified, was as follows: A large test tube, 30 by 300 mm., was immersed in a salt-ice bath and sulfur dioxide condensed in the tube. The material or materials to be investigated were then added to the liquid sulfur dioxide and allowed to remain in contact with it for a specified time with agitation, either with the tube still immersed in the salt-ice bath, or while subjecting the reaction mixture to room temperature by closing the end of the reaction



tube with an appropriate device. At the end of a specified time the reaction mixture was analyzed to determine what reaction, if any, had taken place.

### III. Methods of Analysis

The methods of analysis will be discussed under each separate investigation.

## Experimental

### A). Preliminary Experiments

#### 1) Action of Sulfur Dioxide on Cellulose

A one gram sample of cellulose was introduced into the reaction tube, and 50 ml. of sulfur dioxide condensed upon it. The reaction tube was closed and allowed to stand at room temperature for 48 hours. At the end of this time the sulfur dioxide was distilled off, and the last traces removed by means of a vacuum. A sodium fusion test on the cellulose was negative, showing that no sulfur had been introduced into the cellulose molecule.

#### 2) Action of Metallic Sodium on Cellulose in Sulfur Dioxide

The procedure was the same as that for experiment one, except that about one-half a gram of finely-divided metallic sodium was added to the sulfur dioxide-cellulose mixture. The sodium did not dissolve in the sulfur dioxide, but remained as a suspension. At the end of 48 hours, the sulfur dioxide was allowed to evaporate, and the residue of cellulose and sodium was washed thoroughly with ethyl alcohol to remove all traces of metallic sodium. The cellulose was dried in an oven at 100°C. for two hours, and the following test made on it:

a) Flame test for sodium, and (b) sodium fusion test for sulfur. Both of the above tests were negative, and since the cellulose in all appearances

was unchanged, it can be said that metallic sodium has no effect on cellulose dispersed in a medium of liquid sulfur dioxide.

## B). Nitration

### 1) Action of Nitrogen Tetroxide on Cellulose

#### Experiment I

Nitrogen tetroxide, prepared as described on page 16 and 17 was passed through a drying tube containing phosphorous pentoxide then bubbled into 50 ml. of sulfur dioxide contained in the reaction tube, which was immersed in a salt-ice bath at  $-15^{\circ}\text{C}$ . The gas appeared to be completely soluble in the sulfur dioxide, A deep red to brown solution was formed. The end of the reaction tube was closed and the solution of nitrogen tetroxide in sulfur dioxide allowed to stand at room temperature for two hours. No sign of a reaction was evident at the end of this time; the homogeneous, brown solution remaining as such in the reaction tube. The reaction tube was transferred to a salt-ice bath at  $-15^{\circ}\text{C}$ ., and the pressure released by opening the end of the reaction tube to the atmosphere. Two grams of cellulose were then added, in small quantities with stirring, to this brown, homogeneous solution. At first no reaction was evident, the cellulose appeared to be unaffected. At the end of ten minutes a vigorous reaction took place. The reaction, which lasted about five minutes, left a white solid in the reaction tube. All except traces of the sulfur dioxide and the nitrogen tetroxide were driven off due to the heat of reaction.

The white solid obtained above was washed with 50 ml. portions of sulfur dioxide until the nitrogen tetroxide was completely removed, as shown by the lack of coloration in the sulfur dioxide wash. The last traces of sulfur dioxide were removed by means of a vacuum. The white solid obtained in this way was tested as follows:

- 1) A small portion of the solid was exposed to the atmosphere. A viscous solution formed after an hours standing. On allowing the solution to stand for an additional two hours charring was observed.
- 2) The rest of the solid left from "1" was added, in small quantities, with stirring, to 200 ml. of water. Upon contact with water a vigorous reaction resulted with the evolution of brown fumes of nitrogen dioxide. A small amount of solid material, having all appearances of highly degraded cellulose, was left undissolved, this was filtered off and washed free of acid as shown by a litmus paper test on the wash water, dried in an oven at 100°C. for two hours, and a sodium fusion test made for nitrogen. Results showed that no nitrogen was in the final product.

The filtrate obtained from dissolving the original solid in water was evaporated to about one half its volume, and a test made for the sulfate ion with barium chloride solution, a heavy white precipitate, insoluble in hydrochloric acid, was formed, showing the presence of the sulfate ion.

The sulfur dioxide wash solution containing the nitrogen tetroxide was evaporated to dryness. No residue was left in the beaker.

#### Experiment II

The procedure for this experiment was the same as that for Experiment I with the exception that the cellulose was added to the sulfur dioxide before the nitrogen tetroxide. The results were identical with those of Experiment I except that the reaction took place while the reaction tube was still immersed in the salt-ice bath after a period of fifteen minutes.

#### Experiment III

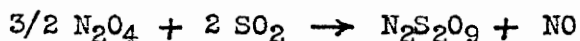
The procedure for this experiment was identical with that of Experiment I with the exception that instead of passing the nitrogen tetroxide into the sulfur dioxide as a gas, 5 ml. of the liquid nitrogen tetroxide were added to the sulfur dioxide. The results were identical with those of Experiment I.

#### Experiment IV

The procedure for this experiment was identical with that of Experiment III with the exception that the cellulose was added to the sulfur dioxide before the nitrogen tetroxide. The results were the same as those of Experiment I except that the reaction took place while the reaction tube was still immersed in the salt-ice bath after a period of fifteen minutes.

The results of the foregoing experiments indicate that it is probably impossible to nitrate cellulose in a medium of sulfur dioxide with nitrogen tetroxide due to the fact that the primary reaction is

that of the formation of the compound,  $\text{N}_2\text{S}_2\text{O}_9$ , as shown by the following equation: (29)



Briner and coworkers (4) have shown that the above reaction is exothermic, and that the product reacts with water with an evolution of nitrogen dioxide and the formation of sulfuric acid. These results agree with those obtained during this investigation.

## 2) Action of Nitric Acid on Cellulose

The experimental work on the action of nitric acid on cellulose was divided into four separate series of investigations in which varying amounts of nitric acid were used. 1) The action of nitric acid alone, 2) the action of nitric acid in the presence of phosphorus pentoxide, 3) the action of nitric acid in the presence of concentrated sulfuric acid, and 4) the action of nitric acid in the presence of phosphorus pentoxide, and chlorine gas.

The experimental procedure for each of the above investigations was essentially the same.

- 1) The required amount of sulfur dioxide was introduced into the reaction tube, which was immersed in a salt-ice bath at  $-15^{\circ}\text{C}$ .
- 2) The dehydrating agent used, was added to and mixed well with the sulfur dioxide.

- 3) The required amount of nitric acid was added to and mixed well with the mixture of sulfur dioxide and dehydrating agent.
- 4) One gram of cellulose was added to and mixed well with the contents of the reaction tube.
- 5) The reaction mixture was allowed to remain for two hours, with intermittent stirring, in a salt-ice bath at  $-15^{\circ}\text{C}$ .
- 6) The liquid portion of the reaction mixture was decanted, evaporated, and tested for solid matter. The solid material left in the reaction tube was added cautiously, with stirring, to 500 ml. of water.
- 7) Solid material filtered off.
- 8) Solid portion, if any, washed free of acid to litmus, and dried at  $100^{\circ}\text{C}$ . for two hours.
- 9) Qualitative test for nitrogen made on the cellulosic residue by means of the sodium fusion method.
- 10) A qualitative test for the sulfate ion was made on the filtrate with 10% barium chloride solution.

The results of each of the four investigations are listed separately in TABLES I, II, III, and IV.

TABLE I

The Action of Nitric Acid on Cellulose Pulp  
in Liquid Sulfur Dioxide at - 15°C.

<u>Number of Experiment</u>	<u>Vol. of HNO<sub>3</sub> in ml./gram of Cellulose</u>	<u>Volume of SO<sub>2</sub> in ml.</u>	<u>Time of Reaction In Hours</u>	<u>Qualitative test for Nitrogen</u>
1	1	29	2	Negative
2	2	28	2	"
3	3	27	2	"
4	4	26	$\frac{1}{2}$	"
5	5	25	*	"

TABLE II

Action of Nitric Acid on Cellulose Pulp in Liquid Sulfur Dioxide  
containing one Gram of Phosphorus Pentoxide at - 15°C.

<u>Number of Experiment</u>	<u>Vol. of HNO<sub>3</sub> in ml. /gram of Cellulose</u>	<u>Volume of SO<sub>2</sub> in ml.</u>	<u>Time of Reaction in Hours</u>	<u>Qualitative test for Nitrogen</u>
1	1	50	2	Negative
2	2	50	2	"
3	3	50	2	"
4	5	50	2	"
5	10	50	*	"

\*A very vigorous reaction took place on the addition of the  
Cellulose to the reaction mixture.



TABLE III

Action of Nitric Acid on Cellulose Pulp in Liquid Sulfur Dioxide containing 3 ml. of Concentrated Sulfuric Acid at  $-15^{\circ}\text{C}$ .

<u>Number of Experiment</u>	<u>Vol. of <math>\text{HNO}_3</math> in ml./gram of Cellulose</u>	<u>Volume of <math>\text{SO}_2</math> in ml.</u>	<u>Time of Reaction In Hours</u>	<u>Qualitative test for Nitrogen</u>
1	1	50	2	Negative
2	3	50	2	"
3	5	50	2	"
4	7	50	$\frac{1}{2}$	"*

TABLE IV

Action of Nitric Acid on Cellulose Pulp in Liquid Sulfur Dioxide containing One Gram of Phosphorus Pentoxide, and saturated with Chlorine Gas.

<u>Number of Experiment</u>	<u>Vol. of <math>\text{HNO}_3</math> in ml./gram of Cellulose</u>	<u>Volume of <math>\text{SO}_2</math> in ml.</u>	<u>Time of Reaction in Hours</u>	<u>Qualitative test for Nitrogen</u>
1	1	40	2	Negative
2	2	40	2	"
3	3	40	2	"
4	4	40	2	"
5	5	40	2	"
6	6	40	$\frac{1}{2}$	"*
7	7	40	**	"*

\*Product completely water soluble.

\*\*A very vigorous reaction took place on the addition of the cellulose to the reaction mixture.

From an inspection of TABLES I to IV inclusive, it can be seen that it was found to be impossible to nitrate cellulose in a medium of liquid sulfur dioxide either with fuming nitric acid alone, a mixture of fuming nitric acid and phosphorus pentoxide, a mixture of fuming nitric acid and concentrated sulfuric acid, or with a mixture of fuming nitric acid, phosphorus pentoxide, and chlorine. This is attributed to the fact that in each case the primary reaction is that of the formation of the compound,  $N_2S_2O_9$ , as shown on page 23.

In each of the four series of experiments on the use of fuming nitric acid as a nitrating agent for cellulose in a medium of sulfur dioxide, the important facts observed were as follows:

- 1) Fuming nitric acid is soluble in sulfur dioxide, and reacts with it to form the compound,  $N_2S_2O_9$ .
- 2) The higher the concentration of nitric acid, the greater the degradation of the cellulose, and the shorter the time of formation of the compound,  $N_2S_2O_9$ .
- 3) Concentrated sulfuric acid is soluble in sulfur dioxide.
- 4) Phosphorus pentoxide is insoluble in sulfur dioxide.
- 5) Chlorine gas is soluble in sulfur dioxide, and gives a homogeneous, yellow solution similar to that of chlorine in water.

### III Action of Liquid Sulfur Dioxide on Trisodium Cellulosate

#### a) Preliminary Experiments

1) One gram of soda cellulose was added to liquid sulfur dioxide. The soda cellulose was charred immediately upon contact with the sulfur dioxide fumes, and to a greater extent when it came in contact with the liquid.

2) One gram of phosphorus pentoxide was added to, and mixed well, with 30 ml. of sulfur dioxide, and one gram of soda cellulose was added to this mixture. The charring of the soda cellulose was greater than when only sulfur dioxide was used.

3) About 5 ml. of methyl iodide was dissolved in 30 ml. of sulfur dioxide, and one gram of soda cellulose was added to this solution. The soda cellulose was charred immediately upon contact with the sulfur dioxide fumes.

4) One gram samples of soda cellulose were moistened with the following reagents: 1) benzene, 2) carbon disulfide, 3) methyl alcohol, 4) ethyl alcohol, 5) chloroform, 6) carbon tetrachloride, and 7) methyl iodide. On adding to liquid sulfur dioxide results showed that no charring occurred in any of these samples even after standing an hour.

5) Two grams of soda cellulose were moistened with benzene, and added to 50 ml. of sulfur dioxide with stirring, and allowed to remain in the sul-

fur dioxide, with intermittent stirring, for two hours. At the end of this time, the solid material was separated from the sulfur dioxide by filtration with a fritted-glass, pressure filter. The last traces of sulfur dioxide were removed from the residue by means of a vacuum, and the following tests made on the product.

- 1) A qualitative test for sulfur by the sodium fusion method was positive.
- 2) About  $\frac{1}{2}$  gram of the residue was boiled with methyl alcohol for one hour. The insoluble material, separated by filtration, was washed several times with boiling methyl alcohol, dried at 100°C. for two hours, and a qualitative test for sulfur made on it. Results showed that sulfur was still in the residue.

The filtrate from the boiling methyl alcohol extraction of the solid was evaporated to dryness. A small amount of a yellow residue remained in the evaporating dish.

From the results of the four preliminary experiments on the action of sulfur dioxide on trisodium cellulosate, the following facts are evident:

- 1) Trisodium cellulosate is charred upon contact with sulfur dioxide fumes.
- 2) When trisodium cellulosate is moistened with either benzene, carbon disulfide, methyl alcohol, ethyl alcohol, chloroform, carbon tetrachloride, or with methyl iodide, and then added to liquid sulfur dioxide, no charring

results.

3) When trisodium cellulosate is moistened with benzene, and subjected to the action of liquid sulfur dioxide for two hours, a substance containing sulfur is obtained.

4) Boiling methyl alcohol extracts part of the sulfur content from the substance obtained by the action of liquid sulfur dioxide on trisodium cellulosate.

In order to determine what compound, if any, was formed by the action of sulfur dioxide on trisodium cellulosate, an investigation was carried out in which the following procedure was used.

1) Five grams of trisodium cellulosate were moistened with benzene and added to the reaction tube (immersed in a salt-ice bath at  $-15^{\circ}\text{C}.$ ) containing 200 ml. of sulfur dioxide.

2) The reaction was allowed to proceed for two hours with intermittent stirring at  $-15^{\circ}\text{C}.$

3) The end of the reaction tube was closed, and the reaction allowed to proceed at room temperature for 10 hours.

4) The reaction tube was immersed in a salt-ice bath at  $-15^{\circ}\text{C}.$ , and the pressure released by opening the end of the tube to the atmosphere. The reaction was allowed to proceed, with intermittent stirring for six hours.

- 5) The end of the reaction tube was closed, and the reaction allowed to proceed at room temperature for five hours.
- 6) The reaction tube was immersed in a salt-ice bath at  $-15^{\circ}\text{C}.$ , and the pressure released by opening the end of the reaction tube to the atmosphere. The reaction was allowed to proceed for one hour.
- 7) The now powdery substance, was separated from the sulfur dioxide-benzene solution by filtration with a fritted-glass, pressure filter, and washed with several portions of sulfur dioxide.
- 8) The filtrate was tested for any solid material after the sulfur dioxide was evaporated. Results showed that only benzene, which burned with a sooty flame, remained from the evaporation.
- 9) The residue obtained in step seven was freed of the last traces of sulfur dioxide by means of a vacuum.
- 10) The sulfur dioxide-free sample was passed through a 60 mesh screen, dried at  $100^{\circ}\text{C}.$  for two hours, and four separate samples subjected to the following quantitative analyses.

Sample #1

A weighed portion of the product was refluxed for one hour with 100 ml. of methyl alcohol. At the end of this time, the cellulosic material was filtered off by means of a fritted-glass filter, washed with six sep-

arate 10 ml. portions of boiling methyl alcohol, dried<sup>at</sup> 100°C. for two hours, and reserved for analysis. The filtrate, including the wash portions, was diluted with water to exactly 250 ml., and reserved for analysis.

Sample #2

The same procedure as that for sample #1 was followed with the exception that the extraction was carried out at room temperature.

Sample #3

The same procedure as that for sample #1 was followed with the exception that water was used as the extracting agent instead of methyl alcohol.

Sample #4

The same procedure as that for sample #1 was followed with the exception that extraction was carried out at room temperature with water as the extracting agent.

Analysis of Filtrates

a) Volumetric Determination of Sulfur

A measured amount of approximately 0.1 N standard iodine solution was made acid with sulfuric acid, and a sufficient amount of each of the filtrates was added to titrate the iodine.

From the volume of the filtrates required to use up a known volume of the standard iodine solution, the amount of sulfur present in each of the filtrates was calculated as per cent sulfur.

b) Gravimetric Determination of Sulfur

The procedure for the gravimetric determination of sulfur was the same as that used by Gotsch (14). A measured volume of each of the filtrates was added to 100 ml. of 6% sodium hydroxide contained in a 400 ml. beaker. Approximately 2 ml. of bromine were added to the alkaline solutions, and the contents kept just below the boiling point for one hour. At the end of this time, the solutions were made acid with hydrochloric acid, and the excess bromine expelled by boiling. The slightly acid solutions were filtered, if necessary, and diluted to exactly 200 ml. Aliquot portions of 50 ml. of each of the filtrates were then heated to boiling, and an excess of barium chloride solution added to precipitate the sulfur as barium sulfate. The solutions were kept hot for at least ten hours, then filtered while hot. The precipitate was washed free of chlorides with boiling water, transferred to a weighed crucible and ignited at 900°C. for two hours. The per cent sulfur was calculated from the weight of barium sulfate.

c) Gravimetric Determination of Sulfur in the Original Product and in each of the Extracted Residues

The same procedure as that for the gravimetric determination of sulfur in the filtrates was used with the exception that a weighed sample of the solids were used.



The results of the investigation of the action of liquid sulfur dioxide on trisodium cellulosate are given in TABLE V on page 35.

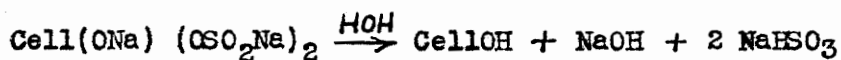
TABLE V

Action of Liquid Sulfur Dioxide on Trisodium Cellulosate

	<u>Total S</u> <u>in Product</u> <u>in Per Cent</u>	<u>Total S</u> <u>in Product</u> <u>in Per Cent</u>	<u>Total S in</u> <u>Filtrates</u> <u>In Per Cent</u>	<u>Total S</u> <u>Accounted</u> <u>for in %</u>
	17.91	....	....	17.91
1) From Boiling CH <sub>3</sub> OH	....	9.13	6.92	17.05
2) From R.T. CH <sub>3</sub> OH	....	10.43	6.60	17.03
3) From Boiling H <sub>2</sub> O	....	17.03	0.00	17.03
4) From R.T. H <sub>2</sub> O	....	17.51	0.00	17.51

From an inspection of TABLE V, it can be seen that a substance containing 17.91% sulfur was obtained from the action of liquid sulfur dioxide on trisodium cellulosate for 24 hours. The experimental value for the amount of sulfur obtained agrees remarkably well with the value, 17.97% sulfur, calculated for the compound, trisodium, disulfite cellulosate, having the formula  $\text{Cell}(\text{ONa})(\text{OSO}_2\text{Na})_2$ .

Also, from TABLE V, it can be seen that the filtrate from the extraction of the sample with water at room temperature contains all of the sulfur. Therefore, it can be said that the compound, which is formed by the action of liquid sulfur dioxide on trisodium cellulosate is completely hydrolyzed by the action of water with the regeneration of cellulose, and the formation of one mole of sodium sulfite and one mole of sodium acid sulfite, or two moles of sulfur, per mole of trisodium, disulfite cellulosate, as shown by the following equations:



A simple calculation shows that 1.93 moles of sulfur per mole of trisodium disulfite cellulosate were obtained by experiment. Therefore it appears quite probable that a compound containing at least 17% sulfur is formed by the action of liquid sulfur dioxide on trisodium cellulosate.

#### IV Esterification Reactions in Liquid Sulfur Dioxide

Due to the fact that trisodium cellulosate reacts with liquid sulfur dioxide, the ordinary type etherification reactions with dimethyl sulfate, methyl iodide, etc., and the xanthation reaction carbon disulfide were not attempted. However, an attempt was made to prepare mixed esters of cellulose. According to F.P. 702,116 (13), and U.S.P. 1,785,466 (37), both aliphatic and aromatic mixed esters of cellulose have been prepared by reacting cellulose acetate, or some other organic ester of cellulose, with an organic acid of higher ionization constant. Preferably, the acid used should be one in which the initial ester is soluble. Now, since cellulose acetate is soluble in liquid sulfur dioxide, it appeared possible that the sulfur dioxide might be used instead of the acid as a dispersing medium, and that solid organic acids with higher ionization constants could be reacted with cellulose acetate. With this idea in mind, several experiments were carried out with the use of organic acids, some with higher and some with lower ionization constants than acetic acid.

The procedure for each of the experiments was essentially the same. Three grams of cellulose acetate were dissolved in 25 ml. of sulfur dioxide, and a definite amount of the acid to be investigated was added to this solution, and the contents allowed to remain at  $-15^{\circ}\text{C}.$ , with intermittent stirring, for a specified time. At the end of the reaction time, the

entire contents of the reaction tube were added to approximately 600 ml. of water, the solid material filtered off, and washed free of the acid used either with water, or some solvent, in which the particular acid was soluble. The solid material was dried, and a sodium fusion test made for the identifying element.

The results of the above group of experiments are given in  
TABLE VI.

TABLE VI

Action of Different Organic Acids on Cellulose Acetate Dissolved in Liquid Sulfur Dioxide after 15 Hours at  $-15^{\circ}\text{C}$ .

<u>Number of Experiment</u>	<u>Acid Used</u>	<u>Solubility of Acid in <math>\text{SO}_2</math></u>	<u>Grams of Acid/gram of Acetate</u>	<u>Qualitative Test for Identifying Element</u>
1	Chloroacetic	s.s*	2/3	Negative
2	Trichloroacetic	c.s **	"	"
3	Picric	c.s.	"	"
4	Uric	s.s.	"	"
5	Nitrobenzoic	s.s.	"	"
6	Sulfanilic	s.s.	"	"
7	3, Nitro- phthalic	s.s.	"	"
8	1 Amino, 2 Napthalic, 4 Sulfonic	s.s.	"	"

\* Slightly soluble

\*\*Completely soluble

Experiments were carried out to investigate the action of thionyl chloride, phosphoric acid, perchloric acid, chloral hydrate, and phosphorus oxychloride on cellulose acetate dissolved in liquid sulfur dioxide.

The procedure was identical with that for the investigation of the action of the different organic acids on cellulose acetate dissolved in sulfur dioxide.

The results of the above group of experiments are listed in TABLE VII.

TABLE VII

Action of Different Reagents on Cellulose acetate Dissolved in Liquid Sulfur Dioxide after 12 Hours at  $-15^{\circ}\text{C}$ .

<u>Number of Experiment</u>	<u>Reagent Used</u>	<u>Solubility of Reagent in <math>\text{SO}_2</math></u>	<u>Grams of Reagent/gr. of Acetate</u>	<u>Qualitative Test for Identifying Element</u>
1	Thionyl chloride	c.s.	1	Positive for S
2	Phosphoric acid	c.s.	"	Negative
3	Chloral hydrate	c.s.	"	"
4	Phosphorus Oxy-chloride	s.s.	"	"
5	Perchloric Acid	c.s.	"	"
5	Urea 2 m. of sulfuric acid	s.s.	"	"

From an inspection of TABLES VI and VII, it can be seen that only the product from the action of thionyl chloride on cellulose acetate dissolved in sulfur dioxide gave a test for an identifying element. A sulfur analysis on the product obtained from this reaction showed that the product contained only 0.65% sulfur. Therefore, since the product was acetone soluble, and burned as does cellulose acetate, it was concluded that the thionyl chloride was not in actual chemical combination with the cellulose acetate molecule; but was merely adsorbed by it.

## V. Hydrolysis of Cellulose

During the course of this investigation it was found that concentrated sulfuric acid is miscible with sulfur dioxide in all proportions, and that glucose is insoluble in, and apparently unaffected by sulfur dioxide. It appeared, therefore, that it might be possible to first degrade cellulose in liquid sulfur dioxide with concentrated sulfuric acid, then remove the sulfuric acid by washing with sulfur dioxide. Thus, it should be possible to obtain the glucose in a pure form by using a simple extraction method. With this thought in mind, a thorough investigation of the problem was carried out.

### A) Preliminary Experiments

#### Experiment I

Ten ml. of concentrated sulfuric acid were added to the reaction tube, immersed in a salt-ice bath at  $-15^{\circ}\text{C}$ , and 40 ml. of sulfur dioxide condensed on it. The sulfuric acid and the sulfur dioxide formed a water-clear, homogeneous solution. One gram of cellulose was added slowly, with stirring, to the sulfuric acid-sulfur dioxide solution. The cellulose was not charred. The reaction was allowed to proceed for two hours, with intermittent stirring, and at the end of this time, the cellulose material had a light brown color. The sulfur dioxide-sulfuric acid solution was decanted, and the residue washed with six 25 ml. portions of sulfur dioxide. The final sulfur dioxide wash did not give a precipitate insoluble in hydrochloric



acid when the sulfur dioxide was evaporated and the residue dissolved in water and tested with 10% barium chloride solution.

The residue from the sulfur dioxide wash, which was a brown semi-solid, was transferred to a vacuum desiccator, and allowed to remain under vacuum over night. Examination of the product showed that it had charred to a black mass. A sulfate test with 10% barium chloride solution on the product dissolved in water gave a heavy white precipitate insoluble in hydrochloric acid, which showed that the product still contained sulfuric acid.

#### Experiment II

Exactly the same procedure as that for Experiment I was followed with the exception that the cellulose was allowed to remain in contact with the sulfur dioxide-sulfuric acid solution for six hours. The results were identical with those of Experiment I with the exception that the cellulose had lost all of its fiber form, and instead of obtaining a semisolid as in Experiment I, a brown, viscous syrup, insoluble in sulfur dioxide, was obtained.

#### Experiment III

Three grams of cellulose were dissolved in 10 ml. of concentrated sulfuric acid at  $-15^{\circ}\text{C}$ . As soon as all of the cellulose had dissolved, the reaction tube was transferred to an ice bath at  $0^{\circ}\text{C}$ ., and the reaction allowed to proceed for ten hours at this temperature. At the end of this time,

the brown, viscous syrup was washed with six separate 25 ml. portions of sulfur dioxide. The brown, viscous syrup formed a froth with the sulfur dioxide when agitated by means of a mechanical stirrer, but, on standing, the syrup again settled to the bottom of the reaction tube. A barium chloride test on both the sulfur dioxide wash, and the brown, viscous syrup gave a heavy white precipitate insoluble in hydrochloric acid.

### Experiment III

Approximately five grams of cellulose was moistened with sulfur dioxide then added, with stirring, to a large test tube containing 40 ml. of concentrated sulfuric acid. The reaction tube was immersed in an ice bath and the sulfur dioxide allowed to evaporate. The reaction mixture was kept at 0°C. for twenty hours. At the end of this time, the following series of experiments were carried out on the brown, viscous solution.

1) About 5 ml. of the syrup were added drop by drop, with stirring, to 400 ml. of sulfur dioxide. The syrup appeared to form a homogeneous solution with the sulfur dioxide. However, on standing the brown, viscous syrup settled to the bottom of the reaction tube. The upper layer of clear solution was decanted, and the syrup treated with three additional 200 ml. portions of sulfur dioxide. Each time, the viscous, brown syrup settled to the bottom of the reaction tube on allowing it to stand several minutes. A sulfate test on both the sulfur dioxide wash, and on the brown, viscous syrup was positive.

2) About 5 ml. of the brown, viscous syrup were added to 100 ml. of sulfur

dioxide, and approximately 5 ml. of ether added to this mixture. A brown, homogeneous solution formed. On the addition of more ether, a brown precipitate formed. This precipitate was dissolved by the addition of more sulfur dioxide with the formation of the brown, viscous syrup. More ether was added, and again the brown precipitate formed. This precipitate was filtered off, and washed several times with ether. A brown gum, which charred when left exposed to room temperature, was formed. This indicated that all of the sulfuric acid had not been removed. A sulfate test on the ether-sulfur dioxide wash, and on a water solution of the residue was positive, showing that one part of the sulfuric acid had been removed from the product.

3) About 5 ml of the brown, viscous syrup were added to 100 ml. of sulfur dioxide, and enough ether was added to form a homogeneous solution. The solution was agitated by means of a mechanical stirrer for five minutes, then sufficient ether to form a precipitate was added. The liquid portion in the reaction tube was decanted, and 100 ml. of sulfur dioxide added to the precipitate. The gummy precipitate formed a brown, viscous syrup which settled to the bottom to the reaction tube when allowed to stand several minutes. The foregoing process of first forming a homogeneous solution by the addition of ether, then the formation of a precipitate by the addition of an excess of ether, followed by decanting the liquid, and redissolving the precipitate with sulfur dioxide was repeated four times. The final precipitate was transferred to a vacuum desiccator and allowed to remain under vacuum over night in order to remove the last traces of sulfur dioxide.

Examination of the product showed that it had charred to a black mass, indicating the presence of sulfuric acid.

4) About 5 ml. of the brown, viscous syrup were added to 100 ml. of sulfur dioxide, and 25 ml. of benzene added to the mixture a little at a time. The benzene formed a clear, homogeneous solution with the sulfur dioxide, but did not seem to affect the brown, viscous syrup in any way. More benzene was added slowly with stirring until about 200 ml. had been added. The brown, viscous syrup remained as such at the bottom of the reaction tube. The sulfur dioxide-benzene solution was decanted, and the syrup exposed to room temperature. Examination of the product after two hours showed that it had charred to a black mass, showing that sulfuric acid was still present.

A series of experiments, identical with the above preliminary experiments with the exception that fuming sulfuric acid was used instead of concentrated sulfuric acid, were carried out. The results were identical with those of the four preliminary experiments just described.

From the foregoing preliminary experiments, it can be seen, that although some of the sulfuric acid is removed from the degradation product by washing with sulfur dioxide, it appears impossible to remove all of the sulfuric acid either with sulfur dioxide alone, a mixture of sulfur dioxide and ether, or with a mixture of benzene and sulfur dioxide.

Degradation of Cellulose with Concentrated Sulfuric Acid Dissolved in Sulfur Dioxide.

In order to determine the amount of glucose formed by the action of concentrated sulfuric acid dissolved in sulfur dioxide on cellulose a series of experiments were carried out in which a known volume of sulfuric acid dissolved in a known volume of sulfur dioxide was allowed to act on cellulose for various periods of time.

The procedure for each of the experiments was as follows:

- 1) Exactly three grams of regenerated cellulose (rayon) were added to a solution of 10 ml. of concentrated sulfuric acid and 50 ml. of sulfur dioxide, and allowed to remain in contact with it at  $-15^{\circ}\text{C}$ . for a specified time, with intermittent stirring.
- 2) At the end of the reaction time, the sulfur dioxide-sulfuric acid solution was decanted, and the product washed with sulfur dioxide until the wash sulfur dioxide gave no test for the sulfate ion.
- 3) The sulfuric acid remaining in the product was neutralized by the careful addition of a suspension of 20 grams of calcium carbonate in 100 ml. of water. The contents of the reaction tube were kept at  $-15^{\circ}\text{C}$ ., by means of a salt-ice bath throughout the neutralization of the sulfuric acid.
- 4) The excess calcium carbonate and calcium sulfate was removed by filtering under suction. The precipitate was washed with five separate 10 ml. portions of cold distilled water.

- 5) The filtrate was transferred to 250 ml. volumetric flask and diluted to the mark with distilled water.
- 6) The amount of glucose in the sample was determined by means of a polariscope which had been calibrated with a standard glucose solution.

The results of the investigation of the action of concentrated sulfuric acid on cellulose in a medium of sulfur dioxide are given in TABLE VIII, and represented graphically on page 51.

From an examination of TABLE VIII, it can be seen that the optical activity of the product is at first negative, then passes through zero and becomes positive, and increases rapidly up to a degradation time of 25 hours. After which time, only a small increase in the optical activity of the product is shown with an increased time of degradation. These results seem to be contradictory to the fact that cellulose is made up of beta-glucose units. However, Honig and Schubert (16) have shown that on the hydrolysis of cellulose with concentrated sulfuric acid at low temperatures, sulfuric acid esters of cellulose, which have a negative optical activity, are first formed. Honig and Schubert have shown further that on prolonged hydrolysis, these sulfuric acid esters of cellulose are broken down with the formation of glucose. Therefore, in view of the fact that the investigation was carried out at  $-15^{\circ}\text{C.}$ , it is not surprising that the product has a negative optical activity for the first few hours of degradation.

Degradation of Cellulose with Concentrated Sulfuric Acid Dissolved in Sulfur Dioxide followed by Hydrolysis of the Product with Dilute Sulfuric Acid

Stern (35) has shown that the sulfuric acid esters of cellulose, which are formed at low temperatures by the action of concentrated sulfuric acid on cellulose, can be hydrolyzed to glucose by boiling with dilute sulfuric acid.

In order to see if the water soluble product obtained from the action of concentrated sulfuric acid dissolved in sulfur dioxide on regenerated cellulose could be hydrolyzed to glucose by boiling with dilute sulfuric acid, a series of experiments were carried out in which the procedure was identical with that for the degradation of cellulose with a solution of sulfuric acid in sulfur dioxide with the exception that the filtrate from step 4 on page 46 was diluted to approximately 200 ml., and refluxed for five hours with 2 ml. of concentrated sulfuric acid. At the end of this time, the solution was neutralized by the careful addition of four grams of calcium carbonate, clarified by the addition of one gram of activated charcoal, filtered, transferred to a 250 ml. volumetric flask, and diluted to the mark with distilled water. The amount of glucose obtained was determined by means of a polariscope.

The results of the degradation of cellulose with concentrated sulfuric acid dissolved in sulfur dioxide followed by the hydrolysis of the water-soluble product with dilute sulfuric acid are given in TABLE IX, and

represented graphically on pages 51 and 58.



TABLE VIII

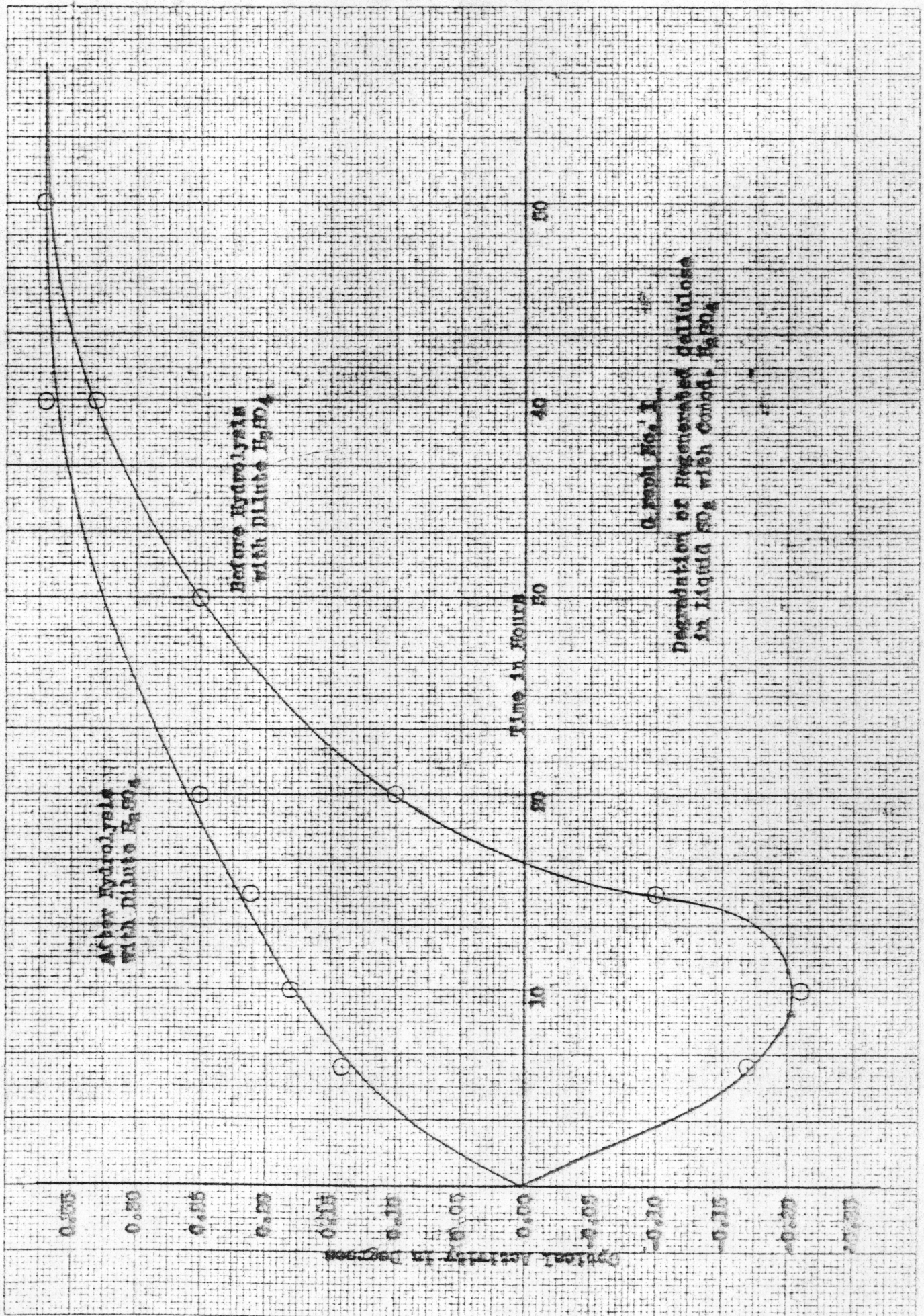
Data for Degradation of Regenerated Cellulose in Liquid Sulfur Dioxide with Concentrated Sulfuric Acid.

<u>Number of Experiment</u>	<u>Time of Degradation in Hours</u>	<u>Optical Activity in Degrees</u>	<u>Grams of Glucose Obtained</u>	<u>Per Cent Yield (Actual)</u>	<u>Per Cent Yield (Theory)</u>
1	6	-0.17	...	...	...
2	10	-0.21	...	...	...
3	15	-0.10	...	...	...
4	20	0.10	0.40	13.33	12.01
5	30	0.25	1.00	33.33	30.03
6	40	0.28	1.12	37.33	33.63
7	50	0.32	1.28	42.66	38.43

TABLE IX

Data for Degradation of Regenerated Cellulose in Liquid Sulfur Dioxide with Concentrated Sulfuric Acid Followed by Hydrolysis with Dilute Sulfuric Acid for Five Hours.

<u>Number of Experiment</u>	<u>Time of Degradation in Hours</u>	<u>Optical Activity in Degrees</u>	<u>Grams of Glucose Obtained</u>	<u>Per Cent Yield (Actual)</u>	<u>Per Cent Yield (Theory)</u>
1	6	0.14	0.56	18.66	16.81
2	10	0.18	0.72	24.00	21.62
3	15	0.21	0.84	28.00	25.22
4	20	0.25	1.00	33.33	30.03
5	30	0.25	1.00	33.33	30.03
6	40	0.32	1.28	42.66	38.43
7	50	0.32	1.28	42.66	38.43



From an examination of TABLE IX, it can be seen that although all of the water-soluble product, obtained by the action of concentrated sulfuric acid dissolved in sulfur dioxide on cellulose, appears to be hydrolyzed to glucose, the yield obtained was not sufficient to warrant further study of the problem. Therefore, the use of sulfur dioxide as a solvent for the concentrated sulfuric acid during the actual degradation of cellulose was discontinued.

#### Degradation of Regenerated Cellulose with Concentrated Sulfuric Acid

A series of experiments, identical with those of the degradation of cellulose by the use of concentrated sulfuric acid dissolved in sulfur dioxide, were conducted in which only concentrated sulfuric acid was used.

The procedure for each of the experiments, both before and after hydrolysis, was the same as that for the degradation of cellulose in the previous series with the exception that the actual degradation was carried out at 0°C. instead of at -15°C.

The results of the degradation of the regenerated cellulose with concentrated sulfuric acid are given in TABLES X and XI, and represented graphically on page 54 in Graph No. II.

TABLE X

Data for Degradation of Regenerated Cellulose with Concentrated Sulfuric Acid

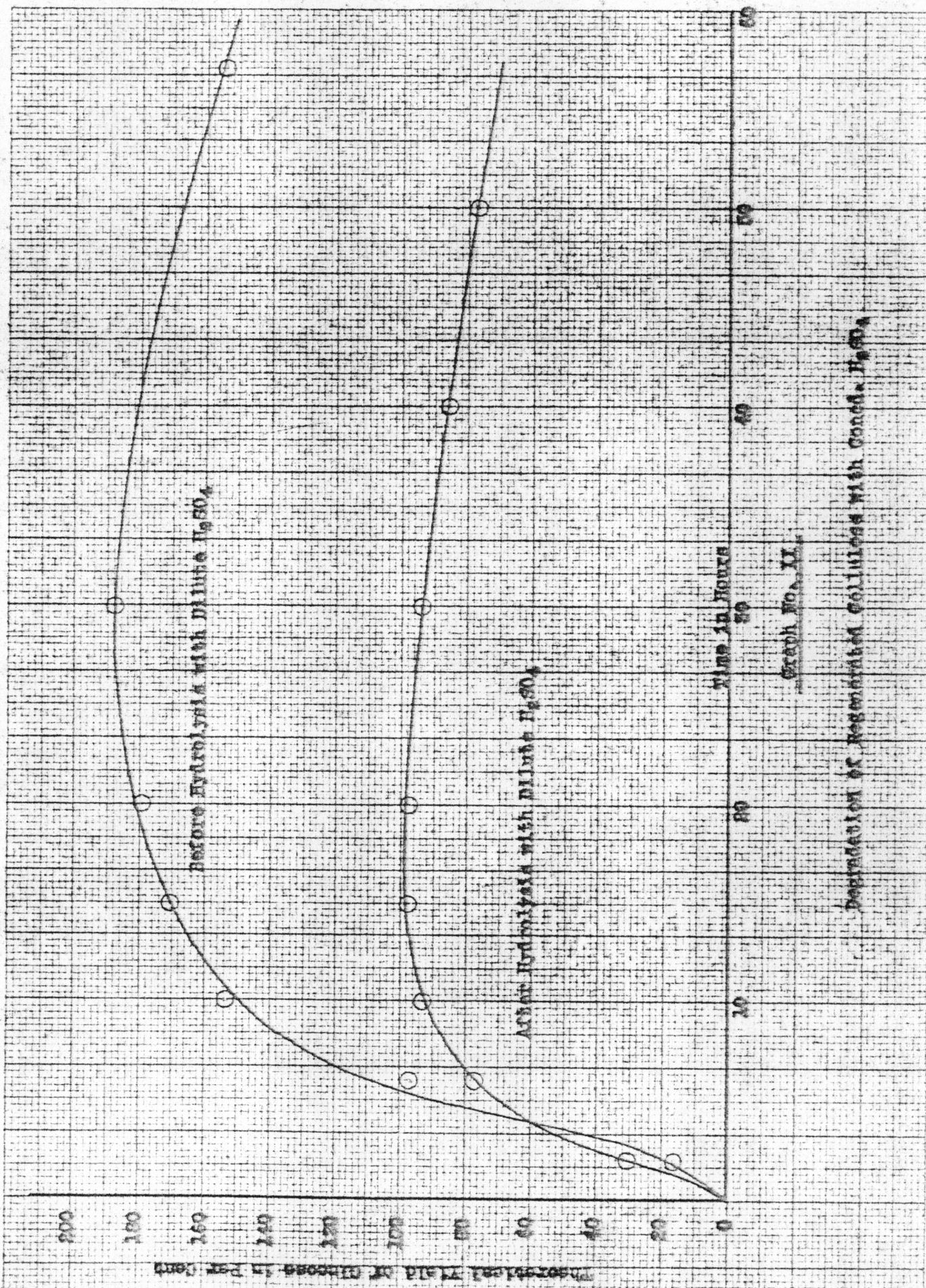
<u>Number of Experiment</u>	<u>Time of Degradation in Hours</u>	<u>Optical Activity in Degrees</u>	<u>Grams of Glucose Obtained</u>	<u>Per Cent Yield (Actual)</u>	<u>Per Cent Yield (Theory)</u>
1	2	0.14	0.56	18.66	16.81
2	6	0.81	3.24	108.00	97.26
3	10	1.28	5.12	170.06	153.75
4	15	1.42	5.68	189.33	170.57
5	20	1.49	5.96	198.66	178.98
6	30	1.56	6.24	208.00	187.38
7	40	0.68	2.72	90.66	81.63
8	57	1.28	5.12	170.06	153.75

TABLE XI

Data for Degradation of Regenerated Cellulose with Concentrated Sulfuric Acid Followed by Hydrolysis with Dilute Sulfuric Acid for Five Hours

<u>Number of Experiment</u>	<u>Time of Degradation in Hours</u>	<u>Optical Activity in Degrees</u>	<u>Grams of Glucose Obtained</u>	<u>Per Cent Yield (Actual)</u>	<u>Per Cent Yield (Theory)</u>
1	2	0.25	1.00	33.33	30.03
2	6	0.64	2.56	85.33	76.87
3	10	0.78	3.12	104.00	93.69
4	15	0.81	3.24	108.00	97.26
5	20	0.81	3.24	108.00	97.26
6	30	0.78	3.12	104.00	93.69
7	40	0.71	2.84	94.66	85.28
8	50	0.64	2.56	85.33	76.87





Graph No. XI.

Percentage of Regenerated Cellulose with Cond. H<sub>2</sub>SO<sub>4</sub>

From an examination of TABLE X, it can be seen that the optical activity of the product, before hydrolysis, is greater by far, than that of pure glucose. This phenomenon, as explained by Stern (36), is attributed to the formation of cellulose esters of sulfuric acid, which have a much greater optical activity than that of glucose. Stern points out further, that on prolonged hydrolysis with concentrated sulfuric acid, or on hydrolysis with dilute sulfuric acid at a high temperature, the cellulose esters of sulfuric acid are broken down with the formation of glucose.

From an inspection of TABLE XI, it can be seen that on hydrolysis of the water-soluble product obtained by the action of concentrated sulfuric acid on regenerated cellulose with dilute sulfuric acid an almost quantitative yield of glucose is obtained after a degradation time of 15 hours. After this time, the amount of glucose obtained is seen to decrease gradually with an increased time of degradation. This is attributed to the fact that the glucose formed is broken down into further degradation products by the prolonged action of concentrated sulfuric acid.

Degradation of Cellulosic content of Southern Yellow Pine, and of Wood Pulp with Concentrated Sulfuric Acid.

A series of experiments, identical with those of the previous investigation with the exception that Southern Yellow Pine sawdust was

used instead of regenerated cellulose, were carried out.

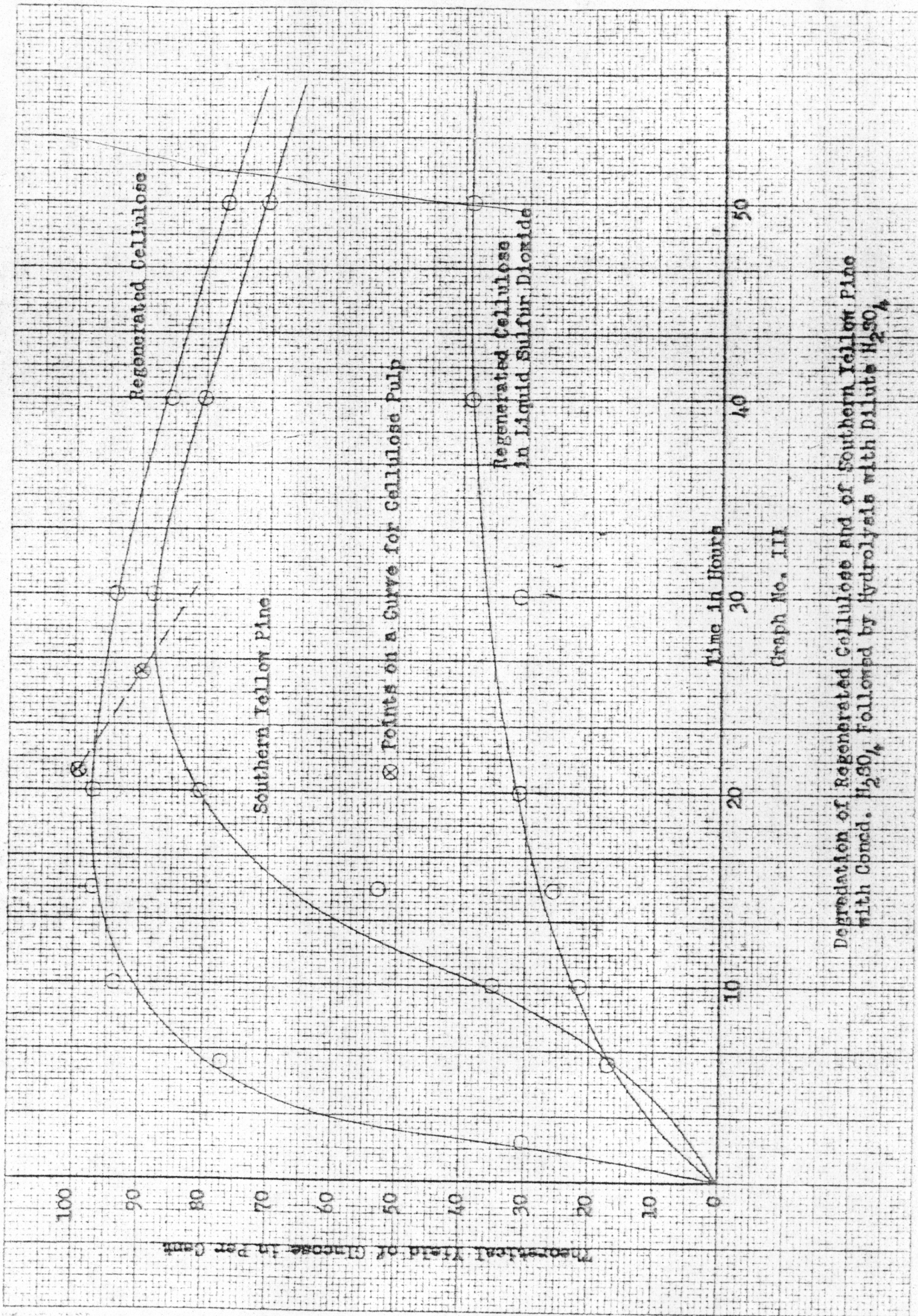
The results of the above investigation are given in TABLE XII, and represented graphically on page 58 in Graph No. III.

TABLE XII

Data for Degradation of Southern Yellow Pine with Concentrated Sulfuric Acid Followed by Hydrolysis with Dilute Sulfuric Acid for Five Hours

<u>Number of Experiment</u>	<u>Time of Degradation in Hours</u>	<u>Optical Activity in Degrees</u>	<u>Grams of Glucose Obtained</u>	<u>Per Cent Yield (Actual)</u>	<u>Per Cent Yield (Theory)</u>
1	10	0.14	0.56	18.66	35.22
2	15	0.21	0.84	28.00	52.83
3	20	0.32	1.28	42.66	80.50
4	30	0.35	1.40	46.66	88.05
5	40	0.32	1.28	42.66	80.50
6	50	0.28	1.12	37.33	70.44





Degradation of Regenerated Cellulose and of Southern Yellow Pine with Concd.  $H_2SO_4$  Followed by Hydrolysis with Dilute  $H_2SO_4$

Graph No. III

From an investigation of TABLE XII, it can be seen that the degradation of the cellulosic content of Southern Yellow Pine with concentrated sulfuric acid, followed by hydrolysis of the water-soluble product with dilute sulfuric acid, follows a similar course to that of the degradation of regenerated cellulose treated in the same manner. The essential difference being that the optimum time of degradation of the wood is twice that of regenerated cellulose. The greater amount of time required for the degradation of the cellulosic content of the wood is attributed to the following facts:

- 1) Regenerated cellulose has a lower degree of polymerization than does the cellulose found in wood,  
and
- 2) In order to obtain glucose from wood, it is necessary to first free the cellulose from the non-cellulosic materials.

Similar experiments on the degradation of wood pulp with concentrated sulfuric acid showed that an almost theoretical yield of glucose was obtained after a degradation time of 21 hours, as shown in Graph No. III, and in TABLE XIII. This is to be expected in view of the facts that wood pulp is essentially free of all non-cellulosic materials, and that it has a higher degree of polymerization than does regenerated cellulose.

TABLE XIII

Data for Degradation of Wood Pulp with Concentrated Sulfuric Acid  
Followed by Hydrolysis with Dilute Sulfuric Acid for Five Hours.

<u>Number of Experiment</u>	<u>Time of Degradation in Hours</u>	<u>Optical Activity in Degrees</u>	<u>Grams of Glucose Obtained</u>	<u>Per Cent Yield (Theory)</u>
1	21	0.82	3.28	98.43
2	26	0.75	3.00	88.88

Extraction of Cellulose Dextrins with Liquid Ammonia

In the foregoing experiments on the degradation of cellulose with concentrated sulfuric, no attempts were made to isolate either the cellulose dextrins or the glucose. From an examination of the problem, it can be seen that in order to isolate the cellulose dextrins in a pure form it is necessary to first neutralize the sulfuric acid, then separate the dextrins from the sulfate formed. A logical way of separation would be to use a liquid medium in which the dextrins were soluble, and the sulfate insoluble. Franklin (12), in his book on The Nitrogen System of Compounds, reports that practically all sulfates and sulfites are quite insoluble in liquid ammonia. Therefore, liquid ammonia should serve as a good medium for the separation of the cellulose dextrins from sulfuric acid, provided that the dextrins are soluble in this solvent. With this thought in mind the following experiments were carried out:

### Experiment I

Approximately 10 grams of glucose was added to 100 ml. of liquid ammonia. Results showed that glucose was completely soluble in, and apparently unaffected by liquid ammonia.

### Experiment II

The procedure for this experiment was as follows:

- 1) Three gram samples of regenerated cellulose were degraded with concentrated sulfuric acid for 15 hours.
- 2) The degradation mixture from "1" was washed with sulfur dioxide until the sulfur dioxide wash gave no test for the sulfate ion with 10% barium chloride solution.
- 3) Ten ml. of methyl alcohol were added to the degradation mixture in order to break up the very viscous syrup formed.
- 4) The degradation mixture was added cautiously to 200 ml. of liquid ammonia, and the liquid separated from the precipitate of ammonium sulfate and ammonium sulfite by filtering through a fritted-glass, pressure filter.
- 5) The precipitate from "4" was treated with three additional 200 ml. portions of ammonia.
- 6) The combined filtrates from "4" and "5" were subjected to a vacuum until all of the ammonia had been removed.
- 7) The methyl alcohol solution remaining from step "6" was diluted to approximately 200 ml. with distilled water, and refluxed for five hours with dilute sulfuric acid.

8) At the end of five hours, the sulfuric acid was neutralized by the addition of four grams of calcium carbonate, the excess calcium<sup>carbonate</sup> and calcium sulfate filtered off with suction, and the filtrate transferred to a 250 ml. volumetric flask and diluted to the mark with distilled water.

9) The amount of glucose in the sample was determined by means of a polariscope.

The results of Experiment II are given in TABLE XIV.

TABLE XIV

Data for Extraction of Cellulose Dextrins with Liquid Ammonia

<u>Number of Experiment</u>	<u>Opt. Activity of Extracted Sample in °.</u>	<u>Grams of Glucose Extracted</u>	<u>Grams of Glucose that should have been Obtained</u>	<u>Per Cent of Glucose Extracted</u>
1	0.49	1.97	3.24	61.11
2	0.46	1.85	3.24	57.09
3	0.49	1.97	3.24	61.11

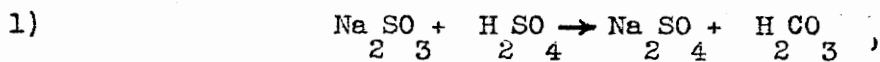
From an inspection of TABLE XIV, it can be seen that an average extraction of 59.77% was obtained by the use of methyl alcohol and liquid ammonia. The low yield is attributed to the fact that on the addition of the methyl alcohol solution of the degradation mixture to liquid ammonia, some of the glucose is charred due to the heat of neutralization of the concentrated sulfuric acid.

### Experiment III

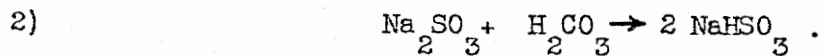
The procedure for this experiment was essentially the same as that for Experiment II with the exception that after the degradation mixture had been washed with sulfur dioxide until the wash sulfur dioxide gave no test for the sulfate ion, 50 ml. of sulfur dioxide were condensed on the degradation mixture and 25 grams of sodium sulfite added. At first the sodium sulfite seemed to dissolve, then on standing a few minutes, a heavy precipitate formed. The excess sulfur dioxide was removed by decantation, and the precipitate transferred to a vacuum desiccator and subjected to a vacuum until the last traces of sulfur dioxide had been removed. The product obtained in this manner did not char when exposed to room temperature, showing that sulfuric acid was not present. The product was extracted with four separate 200 ml. portions of liquid ammonia. Upon allowing the ammonia to evaporate, and drying the residue over phosphorus pentoxide, a light brown, powdery substance was obtained. This light brown powdery substance was dissolved in exactly 250 ml. of distilled water, and the amount of glucose extracted determined as in Experiment II.

The results of the above investigation showed that 3.14 grams of glucose, corresponding to a 96.91% extraction, were extracted by first neutralizing the sulfuric acid with sodium sulfite in a medium of liquid sulfur dioxide followed by the extraction of the product with liquid ammonia.

It is believed that the reactions which take place when sulfuric acid is neutralized with sodium sulfite in a medium of sulfur dioxide are as follows:



and



#### SUMMARY AND CONCLUSIONS

- 1) It appears impossible to nitrate cellulose in a medium of liquid sulfur dioxide either with fuming nitric acid, a mixture of fuming nitric acid and sulfuric acid, a mixture of fuming nitric acid and phosphorus pentoxide, a mixture of fuming nitric acid, phosphorus pentoxide and chlorine gas, or with nitrogen tetroxide. This is attributed to the fact that in each case the primary reaction is that of the formation of the compound  $N_2S_2O_9$ .
- 2) It appears quite probable that a compound having at least 17% sulfur is formed by the action of sulfur dioxide on trisodium cellulosate.
- 3) It was found to be impossible to prepare mixed organic esters of cellulose by first dissolving cellulose acetate in liquid sulfur dioxide, then adding some organic acid with a higher ionization constant than acetic acid.
- 4) Hydrolysis of cellulose to glucose with concentrated sulfuric acid can be carried out in a medium of sulfur dioxide. However the yield of glucose is poor for the times used.
- 5) Liquid sulfur dioxide can be used to remove some of the sulfuric acid from the product obtained by the degradation of cellulose with concentrated sulfuric acid.



6) An almost quantitative yield of glucose can be obtained by the careful degradation of regenerated cellulose, wood pulp, or Southern Yellow Pine sawdust with concentrated sulfuric acid followed by hydrolysis of the water-soluble product with dilute sulfuric acid for five hours.

7) The cellulose dextrins formed by the action of concentrated sulfuric acid on cellulose are soluble in liquid ammonia, and can be separated from the sulfuric acid by first neutralizing the sulfuric acid with sodium sulfite in a medium of liquid sulfur dioxide followed by extracting the residue with liquid ammonia. The dextrins can be obtained in a pure form by merely allowing the ammonia to evaporate.

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## REACTIONS OF CELLULOSE IN LIQUID SULFUR DIOXIDE

by

Philip C. Scherer, Jr. and Lawrence C. Brooks

and following experiment:

Virginia Polytechnic Institute, Blacksburg, Virginia

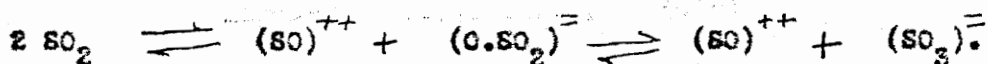
### INTRODUCTION

#### Liquid Sulfur Dioxide as a Solvent and Non-aqueous Reaction Medium

Although many investigations on the use of liquid sulfur dioxide as a solvent and a non-aqueous reaction medium have been carried out since the turn of the last century, it was not until 1936 that Jander and his coworkers (7) pointed out the true nature of this substance as an ionizing medium. Since 1936, Jander and coworkers have made a thorough investigation of the use of liquid sulfur dioxide as a solvent and a non-aqueous reaction medium for both organic and inorganic compounds, and have shown that it resembles to a large extent both liquid ammonia, and water, in its properties as a solvent (8). In brief, it may be said that Jander's work shows that liquid sulfur dioxide serves as a relatively good solvent for a large number of both organic and inorganic compounds,

and that absolutely pure, dry liquid sulfur dioxide is a poor conductor of electricity whereas its solutions are relatively good conductors.

A sulfite system of compounds has been built up in a manner analogous to the aquo in which the sulfur dioxide ionizes according to the following equation:



In this scheme, substances such as thionyl chloride act as acids and metallic sulfites are bases. In addition to neutralizations it is possible to carry out oxidations, reductions, and many other reactions.

The first recorded work involving the use of liquid sulfur dioxide as a solvent medium for cellulose derivatives was that of Clancy (1). Cellulose acetates (2) were prepared in liquid sulfur dioxide in 1927. No other work was found recorded in this field, and in view of the fact that such a meager amount of information was available on the use of liquid sulfur dioxide as a solvent and reaction medium for cellulose, an investigation into this field was carried out. The following typical reactions of cellulose and cellulose derivatives were investigated:

- 1) esterification, 2) etherification, 3) xanthation, and 4) hydrolysis.

#### Materials and Laboratory Procedure

The sulfur dioxide and ammonia used were of the ordinary technical anhydrous grade. The cellulose used was of two varieties. 1) Well-fluffed,

well-dried, spruce sulfite pulp of a high alpha-cellulose content prepared by the Brown Company of Berlin, New Hampshire, and having the following composition for an air dried sample:

Alpha-cellulose .....	95.80%
Moisture .....	3.98%
Lignin .....	0.50%
Ash .....	0.14%

2) Well-dried regenerated cellulose, rayon, prepared in this laboratory from the sulfite pulp by the well-known viscose process.

The wood used in the hydrolysis experiments was well-dried, seasoned, second-growth Southern Yellow Pine sawdust; having the following composition on an air dried sample:

Total cellulose .....	53.0%
CCl <sub>4</sub> extract .....	4.0%
Lignin .....	34.2%
Moisture .....	5.1%
Ash .....	0.4%

The cellulose was determined according to the method of Cross and Bevan (5), and the lignin was determined by the procedure devised by Becker (6).

The trisodium cellulosate used was prepared in this laboratory by the method of Seherer and Hussey (10).

The cellulose acetate used was obtained from the Hercules Powder Company of Parlin, New Jersey, and had an acetyl content of 54.5%.

The nitrogen tetroxide and the nitric acid used in the nitrating experiments were prepared in this laboratory. The former by heating lead nitrate, and the latter by distilling the nitric acid from a mixture of sodium nitrate and concentrated sulfuric acid.

The other chemicals used were of the highest chemically pure grade obtainable.

#### Laboratory Procedure

The laboratory procedure, unless otherwise specified, was as follows: A large test tube, 30 by 300 mm., was immersed in a salt-ice bath and sulfur dioxide condensed in the tube. The material or materials to be investigated were then added to the liquid sulfur dioxide and allowed to remain in contact with it for a specified time with agitation, either with the tube still immersed in the salt-ice bath, or while subjecting the reaction mixture to room temperature by closing the end of the reaction tube with a pressure cap. At the end of a specified time the sulfur dioxide was completely removed by means of a vacuum, and the reaction mixture analyzed to determine what reaction, if any, had taken place.



## EXPERIMENTAL

### Nitration of Cellulose

The experimental work on the nitration of cellulose was divided into two separate series of investigations. In the first series nitric acid was used as the nitrating agent, and involved, 1) the action of nitric acid alone, 2) the action of nitric acid in the presence of phosphorus pentoxide, 3) the action of nitric acid in the presence of concentrated sulfuric acid, and 4) the action of nitric acid in the presence of phosphorus pentoxide and chlorine gas. In the second series attempts were made to use liquid nitrogen tetroxide as the nitrating agent. In each case the nitrating reagents were mixed with the liquid sulfur dioxide and then the cellulose was added. In general, there was no reaction until the addition of cellulose which appeared to initiate a very vigorous reaction. When the reaction appeared to be complete the last trace of sulfur dioxide was removed by a vacuum, and the washed residue tested for nitrates. In no case had any nitrogen been introduced into the cellulose molecule.

During the reaction in sulfur dioxide a white solid formed which was later identified from its properties as probably the anhydro nitrosyl sulfuric acid,  $N_2S_2O_9$ , reported by Manchot and Schmidt (9).

It was concluded that the heat of introduction of cellulose into the liquid solvent was sufficient to initiate the reaction between the nitric acid, or the nitrogen tetroxide, and the sulfur dioxide by which the solvent was oxidized. It should be noted that the above experiments showed that nitric acid, sulfuric acid, nitrogen tetroxide (liquid and gas), and chlorine gas were quite soluble in liquid sulfur dioxide, but that phosphorus pentoxide was not.

#### Esterification of Cellulose

The preparation of cellulose acetates by the action of acetic anhydride with a small amount of concentrated sulfuric acid in liquid sulfur dioxide as a solvent, as described in Brit. P. 501,036 (2) was confirmed. All other attempts at esterification with other organic acids, anhydrides, and catalysts failed as did experiments in which cellulose acetate dissolved in liquid sulfur dioxide was treated with organic acids of higher ionization constants than acetic acid. No mixed esters were formed.

#### Etherification of Cellulose

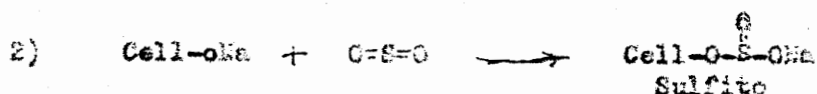
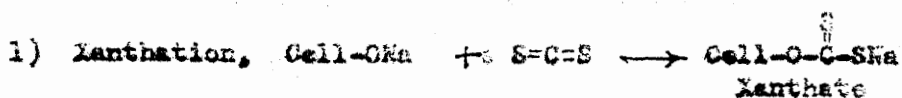
Attempts were made to react on trisodium cellulosate with methyl and ethyl halides and sulfates in order to obtain the corresponding ethers. No ethers were obtained; but it was noted that the trisodium cellulosate lost its fibrous form and became a white amorphous powder. Suspecting a

reaction between the solvent and the cellulosate all free sulfur dioxide was removed from the powder by a vacuum, and the product subjected to analysis.

A weighed sample of the product was oxidized in alkaline hypobromite solution and the average per cent of sulfur was found to be 17.91. This value agrees closely with a theoretical value of 17.87% sulfur for a compound of the formula  $\text{Cell}(\text{ONa}) (\text{OSO}_2\text{Na})_2$ .

A weighed sample of the powder was hydrolyzed with water, the residue filtered off, and the filtrate divided into aliquot portions. On one portion the total sulfite sulfur was determined by titration with iodine and an average value of 17.55% sulfite sulfur was found. The second portion was analyzed for sulfate sulfur by precipitation with barium chloride, and no such sulfur was found present. It was apparent that all of the sulfur in the powder was present as the sulfite form.

It is suggested that no etherification of trisodium cellulosate occurred in liquid sulfur dioxide owing to a reaction between the solvent and cellulosate producing a compound which was no longer susceptible to etherification. The reaction may proceed in a manner similar to the reaction between soda cellulose and carbon disulfide to give the sulfite product.



### Hydrolysis of Cellulose

During the course of this investigation it was found that concentrated sulfuric acid is miscible with sulfur dioxide in all proportions, and that glucose is insoluble in, and apparently unaffected by sulfur dioxide. It appeared, therefore, that it might be possible to first degrade cellulose in liquid sulfur dioxide with concentrated sulfuric acid, then remove the sulfuric acid by washing with sulfur dioxide. It should be possible to obtain the glucose in a pure form by using this simple extraction method. With this thought in mind, a thorough investigation of the problem was carried out.

Preliminary experiments, in which cellulose was degraded all the way to a brown, viscous syrup in a solution of concentrated sulfuric acid in sulfur dioxide, showed that although some of the sulfuric acid could be removed from the degradation mixture by washing with sulfur dioxide, that the product charred to a black mass when allowed to stand at room temperature, showing that sulfuric acid was still present. It was also shown that a mixture of liquid sulfur dioxide and ether of the right proportions could disperse the brown, viscous syrup into a homogeneous solution, and that on the addition of an excess of either sulfur dioxide, or ether, the brown, viscous syrup again settled out. On repeated solution and precipitation by the use of ether it was found to

be impossible to remove all of the sulfuric acid from the degradation mixture. All of the free sulfuric acid was removed as shown by a barium chloride test on the wash sulfur dioxide and the sulfuric acid remaining was either chemically bound or very strongly adsorbed on the reaction product.

Degradation of Cellulose with Concentrated Sulfuric Acid Dissolved in Sulfur Dioxide

In order to determine the amount of glucose formed by the action of concentrated sulfuric acid dissolved in sulfur dioxide on cellulose, a series of experiments were carried out in which a known volume of sulfuric acid dissolved in a known volume of sulfur dioxide was allowed to act on cellulose for various periods of time.

The procedure for each of the experiments was as follows:

- 1) Exactly three grams of regenerated cellulose (rayon) were added to a solution of 10ml. of concentrated sulfuric acid and 50 ml. of sulfur dioxide, and allowed to remain in contact with it at  $-15^{\circ}\text{C}$ . for a specified time, with intermittent stirring.
- 2) At the end of the reaction time, the sulfur dioxide-sulfuric acid solution was decanted, and the product washed with sulfur dioxide until the wash sulfur dioxide gave no test for the sulfate ion.
- 3) The sulfuric acid remaining in the product was neutralized by the care-

ful addition of a suspension of 20 grams of calcium carbonate in 100 ml. of water. The contents of the reaction tube were kept at  $-15^{\circ}\text{C}.$ , by means of a salt-ice bath, throughout the neutralisation of the sulfuric acid.

- 4) The excess calcium carbonate and calcium sulfate was removed by filtering under suction. The precipitate was washed with five separate 10 ml. portions of cold distilled water.
- 5) The filtrate was transferred to a 250 ml. volumetric flask and diluted to the mark with distilled water.
- 6) The amount of glucose in the sample was determined by means of a polariscope which had been calibrated with a standard glucose solution.

The results of the investigation of the action of concentrated sulfuric acid dissolved in sulfur dioxide on cellulose are given in TABLE I, and represented graphically in Graph No. I.

TABLE I

Data for Degradation of Regenerated Cellulose in Liquid Sulfur Dioxide with Concentrated Sulfuric Acid

<u>Number of Experiment</u>	<u>Time of Degradation in Hours</u>	<u>Optical Activity in Degrees</u>	<u>Grams of Glucose Obtained</u>	<u>Per Cent Yield (Actual)</u>	<u>Per Cent Yield (Theory)</u>
1	6	-0.17	...	...	...
2	10	-0.21	...	...	...
3	15	-0.10	...	...	...
4	20	0.10	0.40	13.33	12.01
5	30	0.25	1.00	33.33	30.03
6	40	0.28	1.12	37.33	33.63
7	50	0.32	1.28	42.66	36.43

From an examination of TABLE I, it can be seen that the optical activity of the product was at first negative, then passed through zero and became positive, and increased rapidly up to a degradation time of 25 hours. After this time, only a small increase in the optical activity of the product was shown with an increased time of degradation. These results seem to be contradictory to the fact that cellulose is made up of beta-glucose units. However, Honig and Schubert (4) have shown that on the hydrolysis of cellulose with concentrated sulfuric acid at low temperatures, sulfuric acid esters of cellulose, which have a negative

optical activity, are first formed. Monig and Schubert have shown further that on prolonged hydrolysis, these sulfuric acid esters of cellulose are broken down with the formation of glucose. Therefore, in view of the fact that the investigation was carried out at  $-15^{\circ}\text{C.}$ , it is not surprising that the product has a negative optical activity for the first few hours of degradation.

Stern (11) has shown that the sulfuric acid esters of cellulose, which are formed at low temperatures by the action of concentrated sulfuric acid on cellulose, can be hydrolyzed to glucose by boiling with dilute sulfuric acid.

In order to see if the water soluble product obtained from the action of concentrated sulfuric acid dissolved in sulfur dioxide on regenerated cellulose could be hydrolyzed to glucose by boiling with dilute sulfuric acid, a series of experiments were carried out in which the procedure was identical with that for the degradation of cellulose with concentrated sulfuric acid dissolved in sulfur dioxide with the exception that the filtrate from step 4 was diluted to approximately 200 ml., and refluxed for five hours with 2 ml. of concentrated sulfuric acid. At the end of this time, the solution was neutralized by the careful addition of four grams of calcium carbonate, clarified by the addition of one gram of activated charcoal, filtered, transferred to a 250 ml. volumetric flask, and diluted to the mark with distilled water. The amount of glucose obtained was determined by means of a polariscope.



The results of the degradation of cellulose with concentrated sulfuric acid dissolved in sulfur dioxide followed by the hydrolysis of the water soluble product with dilute sulfuric acid are given in

TABLE II, and represented graphically in Graph No. I and No. III.

1) Regenerated Cellulose, 2) Wood pulp, and 3) Southern Yellow Pine

EXTRACTS. THE EXPERIMENT FOR TABLE II WAS CONDUCTED WITH REGEN-

ERATED CELLULOSE, AND THE DATA ARE GIVEN FOR THE DEGRADATION OF CELLULOSE

Data for Degradation of Regenerated Cellulose in Liquid Sulfur Dioxide with Concentrated Sulfuric Acid Followed by Hydrolysis with Dilute Sulfuric Acid for Five Hours.

THE TABLE WAS PREPARED BY THE BUREAU OF CHEMISTRY

Number of Experiment	Time of Degradation in Hours	Optical Activity in Degrees	Grams of Glucose Obtained	Per Cent Yield (Actual)	Per Cent Yield (Theory)
1	6	0.14	0.56	18.66	16.81
2	10	0.18	0.72	24.00	21.62
3	15	0.21	0.84	28.00	25.22
4	20	0.25	1.00	33.33	30.03
5	30	0.25	1.00	33.33	30.03
6	40	0.32	1.28	42.66	38.43
7	50	0.32	1.28	42.66	38.43

From an examination of TABLE II, it can be seen that although all of the water-soluble product appears to be hydrolyzed to glucose, the yield obtained was not sufficient to warrant further study of the problem.

A series of experiments identical with those of the degradation of regenerated cellulose with concentrated sulfuric acid dissolved in sulfur dioxide, with the exception that the original degradation was carried out with concentrated sulfuric acid alone, were conducted with 1) regenerated cellulose, 2) wood pulp, and 3) Southern Yellow Pine sawdust. The procedure for each of the experiments, both before and after hydrolysis, was the same as that for the degradation of cellulose in the previous series with the exception that the actual degradation was carried out at 0°C. instead of at -15°C.

The results of the above investigations are listed separately in TABLES III to VI inclusive, and represented graphically in Graphs No. II and No. III.

**TABLE III**

**Data for Degradation of Regenerated Cellulose with Concentrated Sulfuric Acid**

<u>Number of Experiment</u>	<u>Time of Degradation in Hours</u>	<u>Optical Activity in Degrees</u>	<u>Grams of Glucose Obtained</u>	<u>Per Cent Yield (Actual)</u>	<u>Per Cent Yield (Theory)</u>
1	2	0.14	0.55	18.66	16.81
2	6	0.81	3.24	108.00	97.26
3	10	1.28	5.12	170.06	153.75
4	15	1.42	5.68	189.33	170.57
5	20	1.49	5.96	198.66	178.98
6	30	1.56	6.24	208.00	187.38
7	40	0.68	2.72	90.66	81.68
8	57	1.28	5.12	170.06	153.75

**TABLE IV**

**Data for Degradation of Regenerated Cellulose with Concentrated Sulfuric Acid Followed by Hydrolysis with Dilute Sulfuric Acid for Five Hours**

**Data for Degradation of Regenerated Cellulose with Concentrated Sulfuric Acid Followed by Hydrolysis with Dilute Sulfuric Acid for Five Hours**

<u>Number of Experiment</u>	<u>Time of Degradation in Hours</u>	<u>Optical Activity in Degrees</u>	<u>Grams of Glucose Obtained</u>	<u>Per Cent Yield (Actual)</u>	<u>Per Cent Yield (Theory)</u>
1	2	0.25	1.00	33.33	30.03
2	6	0.64	2.56	85.33	76.87
3	10	0.78	3.12	104.00	93.69
4	15	0.81	3.24	108.00	97.26
5	20	0.81	3.24	108.00	97.26
6	30	0.78	3.12	104.00	93.69
7	40	0.71	2.84	94.66	85.28
8	50	0.64	2.56	85.33	76.87

**TABLE V**

**Data for Degradation of Southern Yellow Pine with Concentrated Sulfuric Acid Followed by Hydrolysis with Dilute Sulfuric Acid for Five Hours**

<u>Number of Experiment</u>	<u>Time of Degradation in Hours</u>	<u>Optical Activity in Degrees</u>	<u>Grams of Glucose Obtained</u>	<u>Per Cent Yield (Actual)</u>	<u>Per Cent Yield (Theory)</u>
1	10	0.14	0.56	18.66	35.22
2	15	0.21	0.84	28.00	52.83
3	20	0.32	1.28	42.66	80.50
4	30	0.35	1.40	46.66	88.05
5	40	0.32	1.28	42.66	80.50
6	50	0.28	1.12	37.33	70.44

**TABLE VI**

**Data for Degradation of Wood Pulp with Concentrated Sulfuric Acid Followed by Hydrolysis with Dilute Sulfuric Acid for Five Hours**

<u>Number of Experiment</u>	<u>Time of Degradation in Hours</u>	<u>Optical Activity in Degrees</u>	<u>Grams of Glucose Obtained</u>	<u>Per Cent Yield (Actual)</u>
1	21	0.82	3.28	98.43
2	26	0.75	3.00	88.88

From an examination of Graph No. III, it can be seen that the essential difference in the results of the degradation of regenerated cellulose, wood pulp, and wood with concentrated sulfuric acid followed by hydrolysis of the water-soluble product for five hours with dilute sulfuric acid is the optimum time of degradation; that for regenerated cellulose being 16 hours, that for wood pulp being 21 hours, and that for wood being 30 hours. This difference in the optimum times of degradation is attributed to the following facts: 1) Regenerated cellulose has a much lower degree of polymerization than does wood pulp, or the cellulose found in wood. 2) In order to obtain glucose from the cellulose in wood, it is necessary to first free the cellulose from the non-cellulosic materials.

#### Extraction of Cellulose Dextrins with Liquid Ammonia

In the foregoing experiments on the degradation of cellulose with concentrated sulfuric acid, no attempts were made to isolate either the cellulose dextrins, or the glucose. From an examination of the problem, it can be seen that in order to isolate the cellulose dextrins in a pure form it is necessary to first neutralize the sulfuric acid, then separate the dextrins from the sulfate formed. A logical means of separation would be to use a liquid medium in which the dextrins were soluble, and the sulfate insoluble. Franklin (3) reports that practically all sulfates and sulfites are quite insoluble in liquid ammonia. Therefore,

liquid ammonia should serve as a good medium for the separation of the cellulose dextrins from sulfuric acid, provided that the dextrins are soluble in this solvent. With this thought in mind the following experiments were carried out: 1. With distilled water, and 2. With liquid ammonia.

Five samples were analyzed with sulfuric acid.

#### Experiment I

1. 100 ml. of five samples, which were degraded with concentrated sulfuric acid, were analyzed. Approximately 10 grams of glucose was added to 100 ml. of liquid ammonia. Results showed that glucose was completely soluble in, and apparently unaffected by liquid ammonia.

#### Experiment II

The procedure for this experiment was as follows:

1. Three gram samples of regenerated cellulose were degraded with concentrated sulfuric acid for 15 hours.

2. The degradation mixture from (1) was washed with sulfur dioxide until the sulfur dioxide wash gave no test for the sulfate ion with 10% barium chloride solution.

3. 100 ml. of methyl alcohol were added to the degradation mixture in order to break up the very viscous syrup formed.

4. The degradation mixture was added cautiously to 200 ml. of liquid ammonia, and the liquid separated from the precipitate of ammonium sulfate and ammonium sulfite by filtering through a fritted-glass, pressure filter.

5. The precipitate from (4) was treated with three additional 200 ml. portions of ammonia.

6. The combined filtrates from (4) and (5) were subjected to a vacuum until all of the ammonia had been removed.

7. The methyl alcohol solution remaining from step (6) was diluted to approximately 200 ml. with distilled water, and refluxed for five hours with dilute sulfuric acid.

8. At the end of five hours, the sulfuric acid was neutralized by the addition of four grams of calcium carbonate, the excess calcium carbonate and calcium sulfate filtered off with suction, and the filtrate transferred to a 250 ml. volumetric flask and diluted to the mark with distilled water.

9. The amount of glucose in the sample was determined by means of a polariscopc.

The results of Experiment II are given in TABLE VII

TABLE VII

Data for Extraction of Cellulose Dextrins with Liquid Ammonia

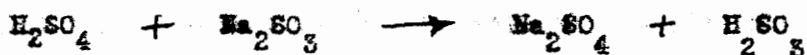
<u>Number of Experiment</u>	<u>Opt. Activity of Extracted Sample in °.</u>	<u>Grams of Glucose Extracted</u>	<u>Grams of Glucose that should have been obtained</u>	<u>Per Cent of Glucose Extracted</u>
1	0.48	1.97	3.24	61.11
2	0.46	1.85	3.24	57.09
3	0.49	1.97	3.24	61.11

From an inspection of TABLE VII, it can be seen that an average extraction of 59.77% was obtained by the use of methyl alcohol and liquid

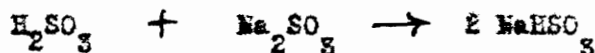
ammonia. The low yield is attributed to the fact that on the addition of the methyl alcohol solution of the degradation mixture to liquid ammonia, some of the glucose was charred due to the heat of neutralization of the concentrated sulfuric acid.

### Experiment III

The procedure for this experiment was essentially the same as that for Experiment II with the exception that after the degradation mixture had been washed with sulfur dioxide until the wash sulfur dioxide gave no test for the sulfate ion, 50 ml. of sulfur dioxide were condensed on the degradation mixture and 25 grams of sodium sulfite added. At first the sodium sulfite seemed to dissolve, then on standing a few minutes, a heavy white precipitate formed. It is believed that the following reactions took place when the sodium sulfite was added to sulfuric acid dissolved in liquid sulfur dioxide:



and



The excess sulfur dioxide was removed from the above reaction mixture by decantation, and the precipitate transferred to a vacuum dessicator and subjected to a vacuum until the last traces of sulfur dioxide had been



had been removed. The product obtained in this manner did not char when exposed to room temperature, showing that sulfuric acid was not present. The product was extracted with four separate 200 ml. portions of liquid ammonia. Upon allowing the ammonia to evaporate, and drying the residue over phosphorus pentoxide, a light brown, powdery substance was obtained. This light brown, powdery substance was dissolved in exactly 250 ml. of distilled water, and the amount of glucose extracted determined as in Experiment II.

The results of the above investigation showed that 3.14 grams of glucose, corresponding to a 96.91% extraction, were extracted by first neutralizing the sulfuric acid with sodium sulfite in a medium of liquid sulfur dioxide followed by the extraction of the product with liquid ammonia.

### SUMMARY

1. It appears impossible to nitrate cellulose in liquid sulfur dioxide owing to a probable reaction between the solvent and nitrating agent producing a nitrosyl sulfuric anhydride.
2. Mixed esters could not be prepared in liquid sulfur dioxide by the action of strong acids on cellulose acetate.
3. Etherification of trisodium cellulosate did not take place in liquid sulfur dioxide probably owing to the formation of a sodium sulfite cellulose by a reaction analogous to the formation of sodium cellulose xanthate.
4. Hydrolysis of cellulose to reducing sugars can be carried out by sulfuric acid dissolved in liquid sulfur dioxide. The rate of reaction is very slow.
5. The optimum times for the hydrolysis of cellulose to dextrans was determined for wood, wood pulp, and viscose regenerated cellulose.
6. A procedure for the isolation of cellulose dextrans from the acid reaction mixture was devised by which 97% of the theoretical yield could be obtained. The steps are as follows:
  - a. Hydrolysis of cellulose with concentrated sulfuric acid at 0° C. for 15 hours for regenerated, 20 hours for wood pulp, or

30 hours for wood.

b. Extraction of excess acid by washing with liquid sulfur dioxide.

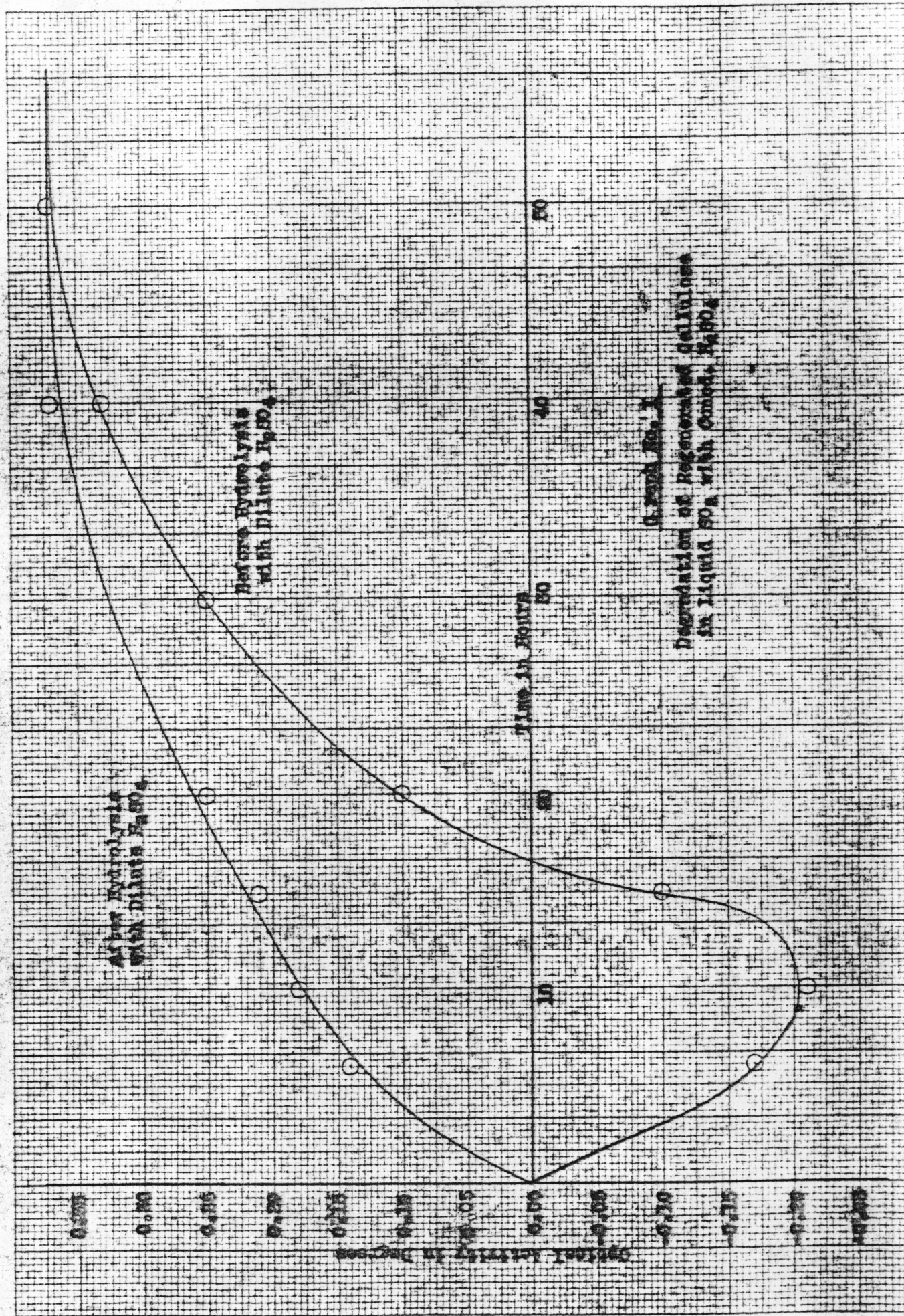
c. Neutralization of remaining acid by a solution of sodium sulfite in liquid sulfur dioxide.

d. Extraction of the soluble dextrans from the sulfates and sulfites by liquid ammonia.

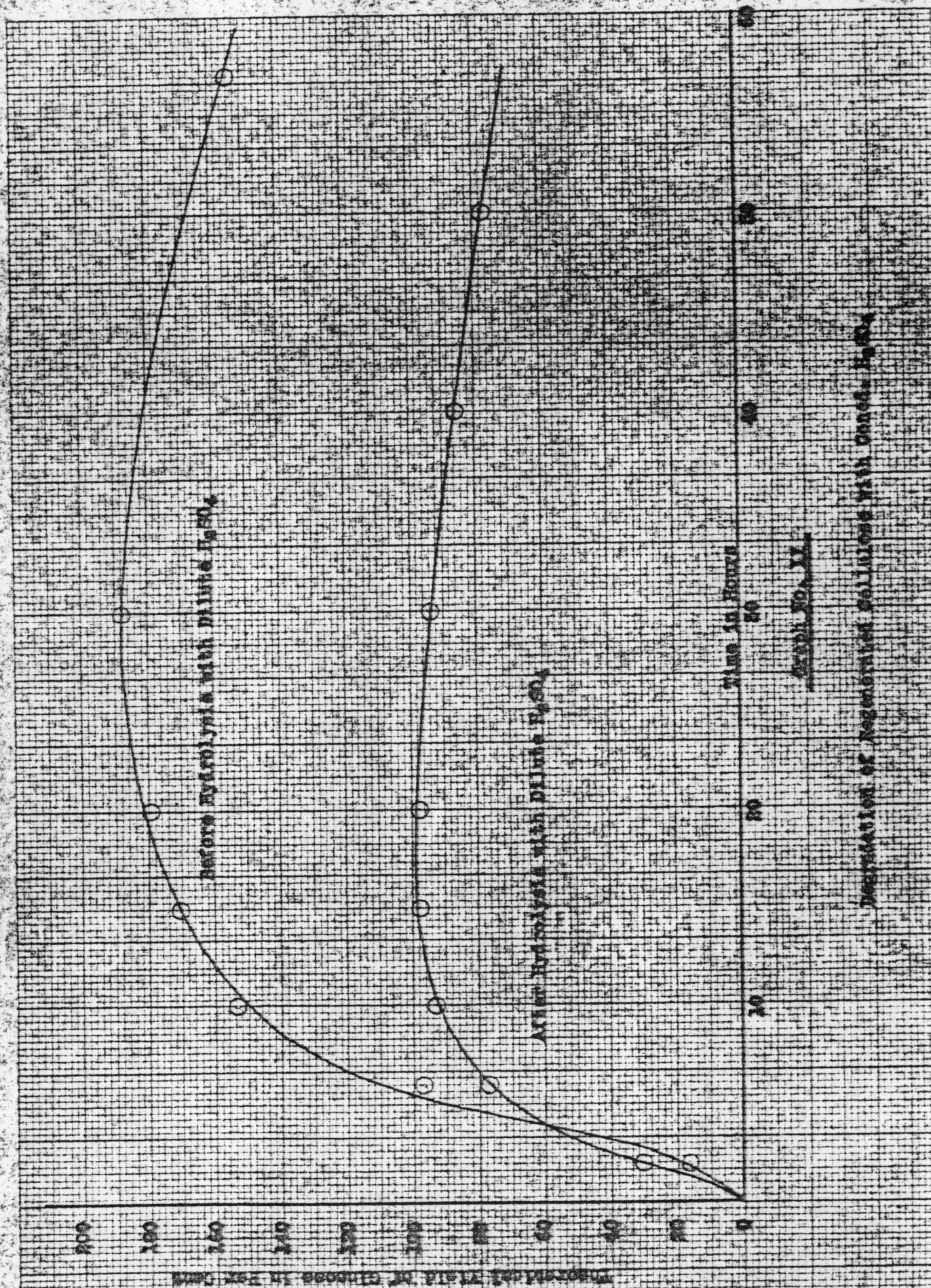
e. Evaporation of liquid ammonia to give dry powdery dextrin product.

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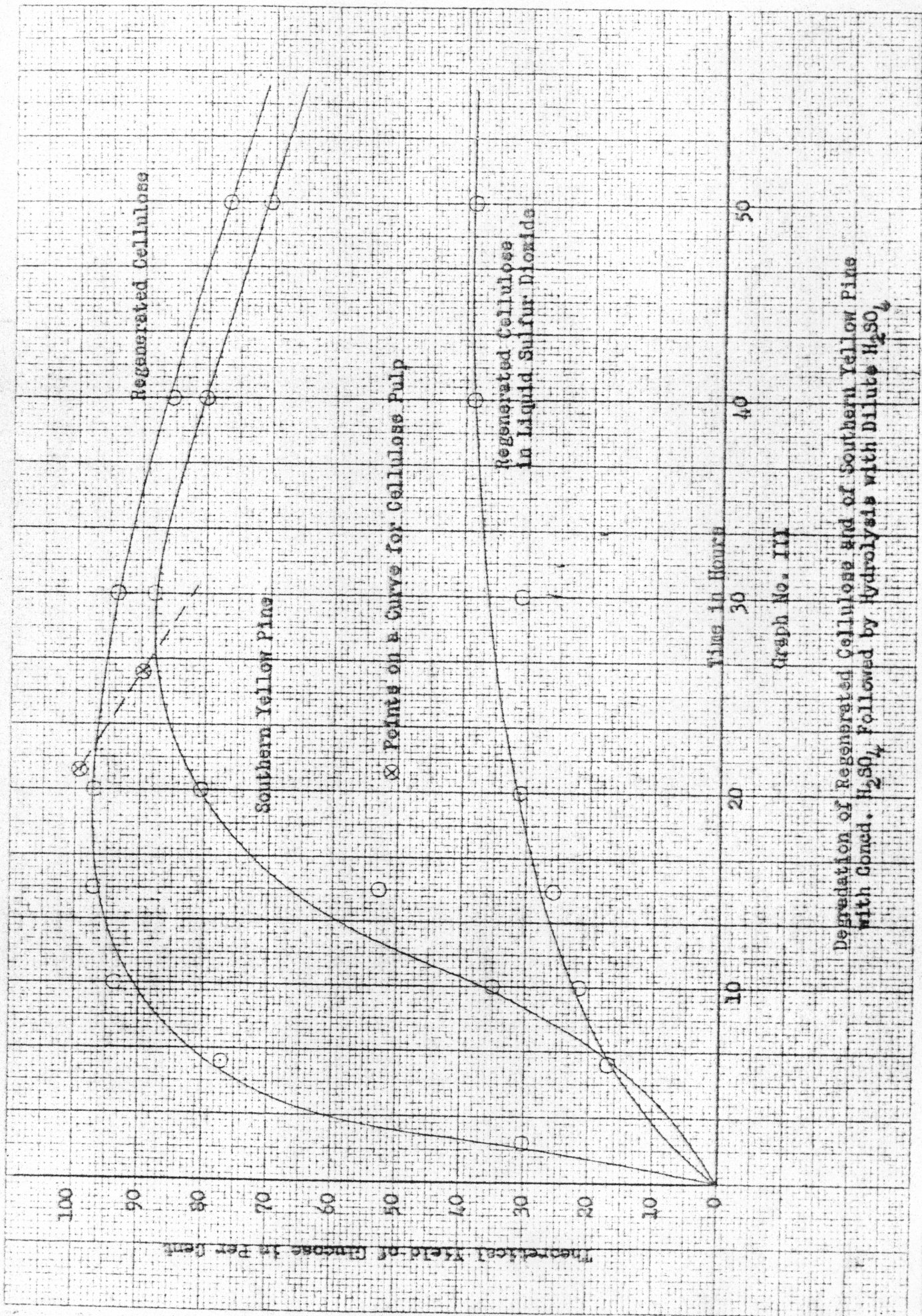




DEGRADATION OF AGARIC ACID POLYMER WITH DILUTE  $H_2SO_4$

Graph No. VI





Graph No. III

Degradation of Regenerated Cellulose and of Southern Yellow Pine with Concd.  $H_2SO_4$  Followed by Hydrolysis with Dilute  $H_2SO_4$