

The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

A Surface-Area Study of Cotton Dried From
Liquid Carbon Dioxide at Zero Surface Tension

Raymond A. Sommers

June, 1963

A SURFACE-AREA STUDY OF COTTON DRIED FROM
LIQUID CARBON DIOXIDE AT ZERO SURFACE TENSION

A thesis submitted by

Raymond A. Sommers

B.S. 1953, Wisconsin State College at Stevens Point
M.S. 1959, Lawrence College

in partial fulfillment of the requirements
of The Institute of Paper Chemistry
for the degree of Doctor of Philosophy
from Lawrence College,
Appleton, Wisconsin

June, 1963

TABLE OF CONTENTS

	Page
INTRODUCTION	1
Structure and Surfaces of Cellulose	1
Drying and Surface Tension	2
PRESENTATION OF THE PROBLEM	6
Approach to the Problem	6
DESCRIPTION OF MAJOR APPARATUS AND ITS OPERATION	11
Solvent-Drying and Exchange Apparatus	11
Critical-Point Apparatus	13
Gas-Adsorption Apparatus	18
GENERAL EXPERIMENTAL PROCEDURES	20
Cotton	20
Purification	21
Solvent-Exchange and Drying Procedure	22
Exchanges Using High-Pressure Vessels	22
Exchanges Using Glass Sample Bulbs (WAN-Drying)	24
Unreplaced Solvents	26
Water	26
Methanol	27
Residual Solvents	30
Carbon Dioxide	30
Methanol	31
Water-Vapor Adsorption Isotherms	32
EXPERIMENTAL RESULTS AND DISCUSSION	35
Analysis of Cotton	35
Critical Temperature of Carbon Dioxide	36
Critical Phenomena of Carbon Dioxide Containing Methanol	40

Critical-Point Areas	45
Water-Vapor-Adsorption Isotherms and Areas	49
Solvent-Dried Areas	57
Literature Areas for Solvent-Dried Cotton	59
Isotherms and Pore-Volume Distributions	60
Most Common Pore Size	70
Residual Solvents	71
Unreplaced Solvents	79
Degree of Water Replacement	79
Degree of Methanol Replacement by Liquid Carbon Dioxide	83
Degree of Methanol Replacement by Benzene	85
Discussion	85
Loss of Area of a Dry Sample	94
ANALYSIS OF THE SOLVENT EXCHANGE MECHANISM	98
GENERAL SUMMARY	101
CONCLUSIONS	103
SUGGESTIONS FOR FUTURE WORK	106
ACKNOWLEDGMENT	109
LITERATURE CITED	110
APPENDIX	119
High-Pressure and High-Vacuum Leak Problems	119
Miscellaneous Notes on Experimental Results	120
Water Content of the Two Carbon Dioxide Sources	120
Phosphorus Pentoxide for Drying Liquid Carbon Dioxide	121
Vacuum Leak in Sample C-2HW	122

Flow Stoppage During Passage of Dried Carbon Dioxide	123
Possible Effects of Unreplaced Methanol on the Critical Point and Surface Tension	123
Water-to-Carbon Dioxide Experiment	124
Effect of Pore Size on Critical Phenomena	125
Determination of Pore-Volume Distribution	128
Choice of Method	128
Number of Adsorbed Layers as a Function of Relative Pressure	132
Thickness of an Adsorbed Layer	134
Estimate of Nonpore or External Surface Area	135
Merchant's Critical-Point Attempt	139
Surface Areas and Statistics of Various Samples	141
Summary of Water-Vapor-Adsorption Data	151
Nitrogen-Isotherm Data	154
Pore-Volume-Distribution Data	155

INTRODUCTION

Cellulose is the most abundant organic raw material in the world. This fact, coupled with its unique chemical and physical nature has led to many and various uses as well as to intense study. Despite remarkable advances, however, there still remains much to be learned regarding this complex and interesting material.

STRUCTURE AND SURFACES OF CELLULOSE

Cellulose is a linear high polymer of glucopyranose groups linked together as beta-glucosides through the one and four positions of adjacent glucose units. Particularly important to its properties are the one primary and two secondary hydroxyl groups which are present on each monomeric unit.

The linear polymer chains are arranged essentially parallel to each other, the degree of order varying from the less-ordered amorphous regions to the highly ordered crystalline regions which can be detected by x-ray analysis. Although the exact structure is still not agreed upon, electron microscopy has shown that these linear chains form fibrillar strings which in turn make up the larger and microscopically visible fiber (1). To obtain a crude picture, even though grossly simplified, one might imagine the structure to be made up of ropelike fibers composed of strings, and these in turn made up of smaller strings, etc., down to the polymer molecule itself.

In this type of structure, the surfaces can be divided into two general regions (2), the microscopically visible structure and that within the cell wall which is available only when swollen. In some instances it may be more convenient to refer to the external and internal surfaces, the former being that available for interfiber bonding. The surface being referred to, however, generally is defined by the method of determination and the property or phenomena which are under consideration.

Undried and swollen cellulosic materials generally consist of a structure with a high available surface area possessing an abundance of hydroxyl groups. The dried material retains this structure in varying degrees as will be shown later.

Since the extent, location, and availability of this area is but a manifestation of the microscopic and molecular structure, it is of fundamental importance in studies of chemical reactivity, physical adsorption, retention of dyes and sizing materials, permeability, pulp drainage, fiber-to-fiber bonding, optical properties, and many of the physical properties of cellulosic products.

Various methods have been used to estimate the total available surface area of cellulosic materials (2). Many of these methods fail to measure the total area or else they alter the structure in the process. The nitrogen adsorption method, utilizing the Brunauer, Emmett, and Teller (BET) theory (3), has been shown to be an extremely useful tool in surface area and structure studies. Its application to cellulosic materials has been most recently shown by Haselton (4, 5), Merchant (6, 7), and others (8, 9). This method measures the total surface area available to the small nitrogen molecule and does not noticeably alter the structure. Furthermore, it is capable of giving information concerning the distribution of pore size. It does however require a dry and highly outgassed sample.

DRYING AND SURFACE TENSION

Urquhart (10), as early as 1929, pointed out the irreversibility of cellulose drying as noted by lower water regains in the second water-vapor desorption as compared to the first. It has been shown that predrying of pulp leads to lower tensile strength paper (11-16) and also that the strength decrease is directly related to the degree to which the pulp has been dried (11, 16). It is generally

accepted that this loss of strength is the result of irreversible hydrogen-bonding between hydroxyl-containing elements. Furthermore, Thode, Chase, and Hu (16) have shown that the external surface area, as determined by specific dye adsorption, also decreases with increasing intermediate drying.

In the study of the chemical reactivity of cellulose in nonaqueous solvents it has been found that the rate and degree of reaction is greater when the cellulose has been dried from nonpolar liquids than when dried from water (17-21).

Quite a number of years ago, Campbell (22-24) showed how the surface tension forces of water during drying can create large forces acting to bring the cellulosic elements together for bonding to occur. The largest pressures, probably in the order of 200 atmospheres, occur when the drying is from tiny droplets between adjacent fibers. This compacting pressure may be calculated by application of the fundamental law of capillarity (25) to the vapor interface of a droplet between two parallel plates. These forces of capillary attraction have been discussed by Bikerman (26) and more recently by Swanson (27, 28) and Swanson and Jones (29).

Lyne and Gallay (30) studied the strength of wet webs and found surface tension forces to be important up to about 20 to 25% solids. Decreasing the surface tension of the liquid by surfactants led to decreased strength in this range. Robertson (31), in his recent study of wet web behavior during drying, supported the work of Lyne and Gallay (30) and again pointed out the action of surface tension forces during drying.

Van den Akker (32) and Marchessault, Lodge, and Mason (33) dried wet mats by freezing and sublimation. This reduction in the surface tension effect yielded sheets of very low tensile strength. Merchant (6) found the surface area of freeze-dried pulp to be higher than when water dried. It appeared however that considerable unfrozen water still contributes to the surface tension effect.

Other attempts have been made to eliminate the surface tension effects by replacement of the water by a nonpolar solvent of low surface tension. Some of these attempts with respect to chemical reactivity have already been mentioned. One example of such a procedure is that in which the water is replaced by methanol and then the methanol by a nonpolar liquid such as benzene or n-pentane. The resultant dry surface area has been found to be many times that obtained by water drying (4, 6, 7, 9, 34-36).

It is well known that beating of pulp and wet pressing of the sheet increases the tensile strength of paper presumably through greater bonding. Haselton (4) found that the area of a water-dried sheet decreased with beating or wet pressing, thus indicating greater bonding. Thode, Swanson, and Becher (9) report increasing surface areas of n-pentane-dried pulp with beating, thus indicating that a greater area is available for bonding when a pulp has been beaten.

Merchant (5) dried pulp from water, polar solvents, and various nonpolar solvents. Polar solvents yielded higher areas than water but the nonpolar solvents at the same surface tension gave even higher areas. Drying cellulose over phosphorus pentoxide followed by redispersion in water and drying from n-pentane gave a 60% lower area than when never water-dried.

Broughton and Wang (37) have suggested that strength formation or bonding on drying can be interfered with either by not bringing the fibrils close enough together such as through lowered surface tension, or by lowering or suppressing the orientation of the hydroxyl groups toward the solution by varying the energy density or polarity of the liquid.

It thus has been amply demonstrated that decreasing the surface tension forces during drying by way of solvent exchange or freeze-drying leads to less bonding and to a structure with higher available surface area.

For a more complete review of drying from organic liquids, the reader is referred to Merchant (5, 6). Also, in addition to references already cited, Emerton (38) and Casey (39) have information relative to the above topics.

PRESENTATION OF THE PROBLEM

Merchant (6, 7) conducted an intensive study of the relation of pulp surface area to the drying temperature and the nature of the liquid from which the sample was dried. The most significant and major part of his work involved solvent exchange steps from water (W) to methyl alcohol (A) and then to a nonpolar liquid (N) from which the pulp was dried. He referred to this as WAN--exchange and WAN-drying. It was found that in general an inverse relationship existed between the determined surface area and the surface tension of the final nonpolar liquid. Aliphatic and aromatic hydrocarbons, however, appeared to have separate relationships.

On this basis it would appear that further lowering of the surface tension of the final liquid would give even a higher area. The final limit to this increase in area and retention of the water-swollen structure would seem to be the point of zero surface tension.

Therefore, in order to obtain a cellulose sample with maximum retention of the area and structure that is present in a water-swollen state, a way must be found to minimize or ideally eliminate the surface tension of the final liquid. This then is the problem.

APPROACH TO THE PROBLEM

The work of Kistler (40) and that of Anderson (41, 42) suggest the approach to the problem by removal of the final liquid as a gas above its critical point where no liquid-vapor interface or surface-tension forces exist.

Kistler (40) was probably the first one to apply the solvent exchange technique to cellulosic materials. Of particular interest is the fact that he

used liquid propane as the final solvent and removed it as a gas above the critical temperature, thus eliminating the surface tension. He used swollen cellophane with liquid replacements in the order of water, alcohol, ether, petroleum ether, and liquid propane, the latter being removed at 115°C. in an autoclave. The cellophane was found to have retained its swelling and it appeared white by reflected light, but translucent to transmitted light. Rewetting caused it to become transparent and on drying it returned to its original thickness with the appearance of ordinary cellophane. Kistler does not give enough detail for one to determine his method of gas removal. Rapid removal could lead to cooling and subsequent liquefaction and also to literally blowing the structure apart.

More recently Anderson (41, 42), in order to preserve biological specimens in a three-dimensional structure for electron microscope studies, used a solvent-exchange procedure ending with liquid carbon dioxide which he removed as a gas above its critical point. His method of removal involved heating to 35°C. and then gently opening the exhaust valve to allow the gaseous carbon dioxide to expand. Some distortion was still present but he pointed out that this may have been due to extraction of some components by the organic liquids. The solvent-exchange sequence finally used was, water - ethyl alcohol - amyl acetate - liquid carbon dioxide. Other sequences tried (40) were: water - ethanol - amyl acetate - liquid nitrous oxide, water - ethanol - 40% dl-camphor + 60% thymol - liquid CO₂, and water - ethanol - liquid carbon dioxide. Each solvent-exchange sequence except the last one gave good results. Since evidence indicated that ethanol and liquid carbon dioxide were completely miscible, they could offer no reason for the poor results with this sequence.

Anderson (41) has referred to his procedure as the critical-point method. Emerton (43) has also referred to the critical-point method but gave no details or

references. Because of the unique descriptiveness of this term it will be used in this study to refer to that procedure in which the final liquid is removed as a gas above its critical point; or more briefly as the CP-method.

It thus appears that the CP-method will accomplish the desired elimination of surface tension during the final drying.

The final liquefied gas to be used must be unreactive with cellulose, be completely miscible with the liquid which it is to replace, and have a critical temperature slightly above room temperature. This latter requirement will enable the exchange to be carried out at near room temperatures and the removal to be carried out at temperatures which are low enough to prevent any excessive degradation of the cellulose.

A number of liquefied gases appear to fill these requirements, the most likely ones being listed below along with their critical temperatures and pressures:

carbon dioxide	31°C.	1070 p.s.i.a.
nitrous oxide	36.8°C.	1060 p.s.i.a.
ethane	32°C.	710 p.s.i.a.

Carbon dioxide was finally selected because of its high purity at low cost, lack of toxicity and flammability, and because of the availability of solubility data for the liquefied gas (41, 44-46), especially with regard to its complete miscibility with methanol (44).

Methanol was chosen as the intermediate solvent mainly on the basis of Merchant's work (6, 7), where it was found to yield higher areas than other alcohols.

A surface-area study will therefore be made of a cellulose which has been solvent exchanged from water through methanol to liquid carbon dioxide, and the latter removed as a gas above its critical temperature in order to eliminate surface-tension effects. The path of the solvent removal will be similar to the dotted line in Fig. 1. Starting at A the liquid carbon dioxide will be compressed by raising the temperature to 36°C ., the path in Fig. 1 being from A to B. At this point a slow incremental release of the gas will be started, following the dotted line down to some point past C at atmospheric pressure. The reason for the irregular path from B to C is that each incremental release causes a slight cooling after which the temperature is allowed to increase back to the 36°C . isotherm.

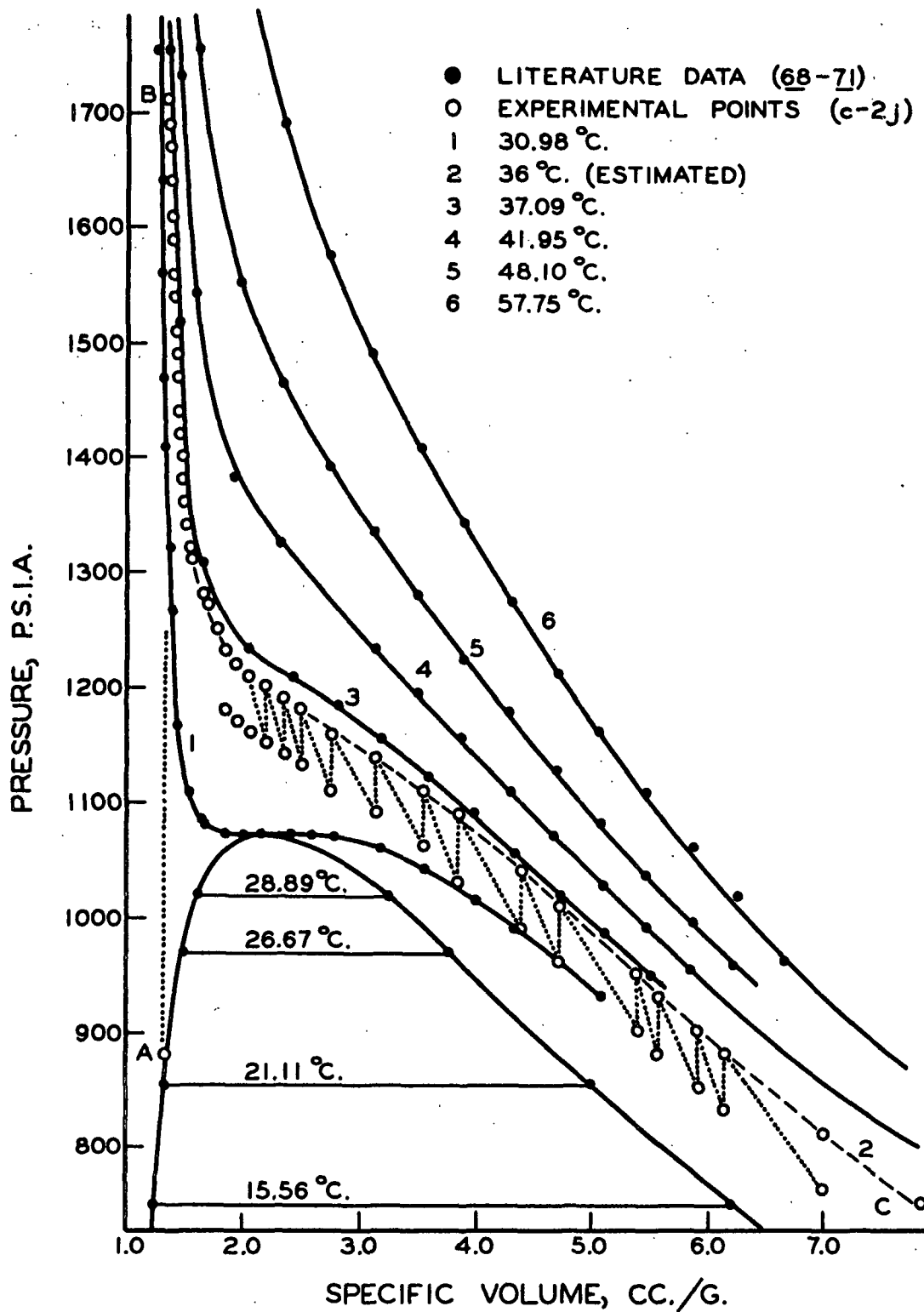


Figure 1. Solvent Removal Path on CO₂ P-V-T Diagram

DESCRIPTION OF MAJOR APPARATUS AND ITS OPERATION

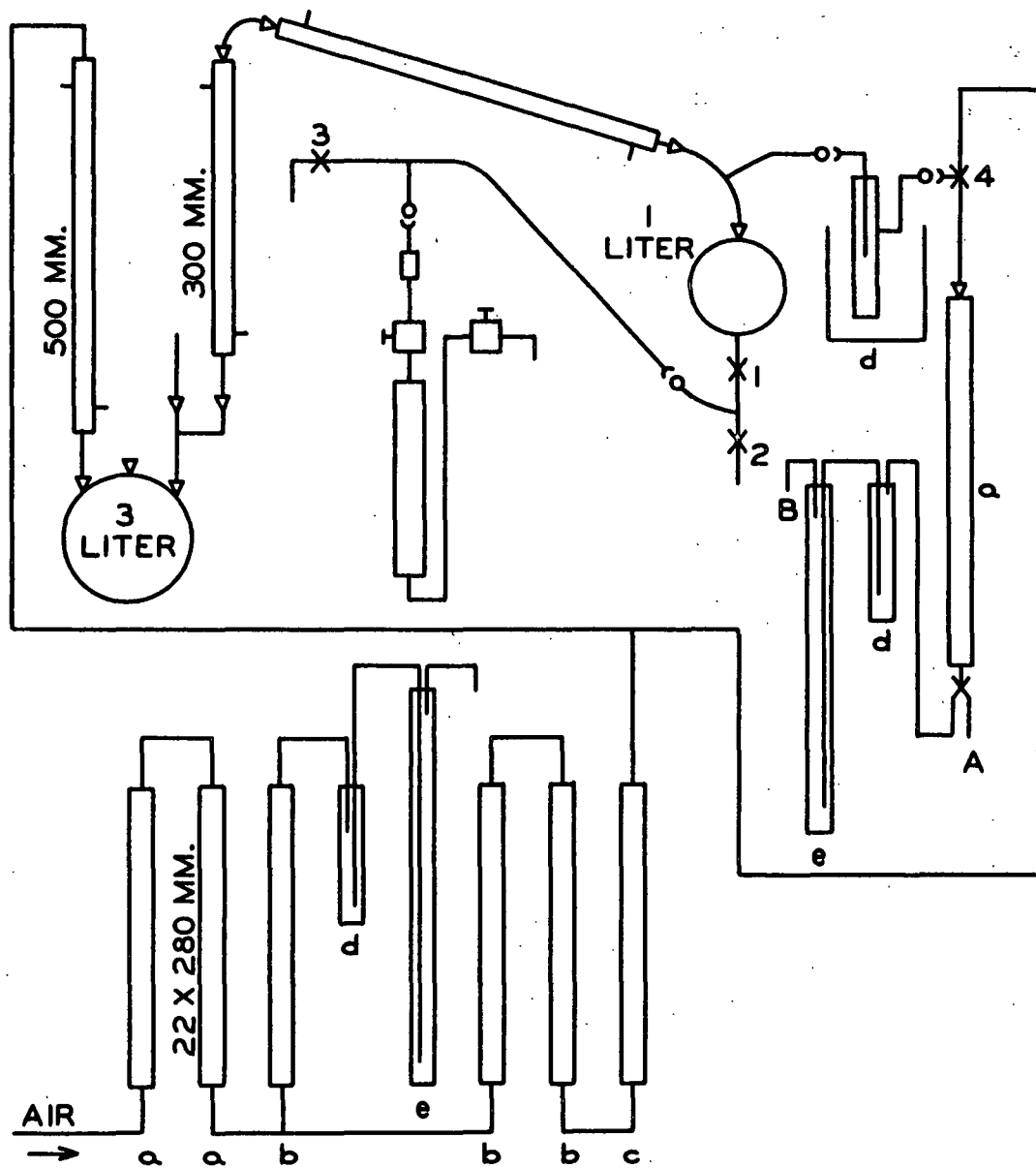
Only three pieces of apparatus will be described here; namely, the solvent-drying and exchange apparatus, the critical-point apparatus, and the gas adsorption apparatus. Other equipment and apparatus which were used are in most cases commercially available. These will be described briefly along with the presentation of the results.

SOLVENT-DRYING AND EXCHANGE APPARATUS

The solvent-drying and exchange apparatus was constructed out of pyrex glass by means of ground glass-, ball and socket-, and glass blown-joints. All parts which solvent was likely to contact were made of glass. Tygon tubing and rubber stoppers were used however in the air-drying and exit sections. The apparatus in its final form is shown in Fig. 2. The arrangement was such that solvent could be dried, stored and used in exchange, without contact with atmospheric moisture.

The method for drying methanol was essentially that of Lund and Bjerrum (47). Two hundred cc. of methanol, 12 g. of magnesium turnings, and 1.2 g. of iodine are added to the 3-liter reaction flask. Generally, the reaction starts within a short time, but if not, some heating may be necessary. This part of the operation evolves considerable hydrogen which escapes through the bubbler at B under 6 inches of water pressure.

When the magnesium turnings are no longer visible and the pressure drops off, an additional 2200 cc. of methanol are added. The pressure inside the system is then maintained at 6 inches of water by means of dried air entering the flask and flowing out of the system through the exit bubbler.



O) BALL AND SOCKET JOINT
 ▷ GROUND GLASS JOINT
 a DRIERITE
 b ANHYDRONE

c PHOSPHORUS PENTOXIDE
 d TRAP
 e BUBBLER
 X STOPCOCKS

Figure 2. Solvent-Drying and Exchange Apparatus

As the reaction slows down, the flask is heated until after about 30 minutes the alcohol begins to reflux. This refluxing is then continued for 30 minutes, at which time distillation is started.

Stopcocks 2 and 3 are used for removing the first part of the distillate and for flushing the line to the sample. Once the solvent exchange is started, 12 to 18 inches of water pressure is maintained. After stopping the distillation Stopcock 4 is turned to connect the trap to the dry air line. Exchange is normally started during the distillation.

The initial exchange with undried reagent-grade methanol utilizes a 1-liter separatory funnel with a ball and socket joint at the bottom and a drying tube containing Anhydron at the top.

During the first two runs (c-1a and c-1b) Stopcocks 2 and 3 were very lightly greased with silicone high-vacuum grease. Before any other runs, the complete apparatus, including the above-mentioned stopcocks, was degreased with hot alcoholic potassium hydroxide followed by dichromate cleaning solution and distilled water. The stopcocks were left ungreaed, even though a slight leakage occurred.

The stainless-steel sample vessel was connected to the ball and socket joint through a Central Scientific Co. high-vacuum glass-to-metal seal. This seal employs a neoprene "O" ring which was left ungreaed.

CRITICAL-POINT APPARATUS

The critical-point apparatus was constructed of stainless steel superpressure components from the Superpressure Division of the American Instrument Co. The vessels, valves, and fittings were made of 316-stainless steel with the maximum

working pressure for the vessels being 11,250 p.s.i. All other components had higher maximum working pressures. The tubing was 0.25 inch and made of 304-stainless steel. The vessels have an outside diameter of 2 inches and an inside diameter of 1 inch and contain a volume of approximately 100 ml. They are classified as "preliminary reaction vessels" and have a threaded head which bears against a flat gasket when closed to make a seal.

Several modifications were made in the apparatus as first constructed; most of them resulting in simplification. The apparatus in final form is sketched in Fig. 3.

The temperature of the water bath is maintained through the use of a Powers Fotoguard, a thermostatic control using hot and cold water to give a water flow of constant temperature. The temperature of the bath was generally held to within 0.5°C. Because of the high heat capacity of the stainless steel vessel the temperature control therein was probably much better. The constant-temperature water was directed to the bottom of the Plexiglas container and removed from the top by means of a plain siphon and a siphon-type level controller (48).

All vessels were sealed with copper gaskets except Vessels B and C which comprised the mercury reservoir. These were sealed with Teflon gaskets.

As a safety precaution, a piece of 0.5-inch plywood was mounted behind the apparatus and a piece of 0.5-inch Plexiglas was mounted in front. The stems of all valves except 1, 6, and 7 extended through the Plexiglas. To facilitate operation the closed positions of all valves were marked on the Plexiglas sheet with a wax pencil. A checklist of the manipulations was also placed behind the Plexiglas, and each operation was checked off as performed.

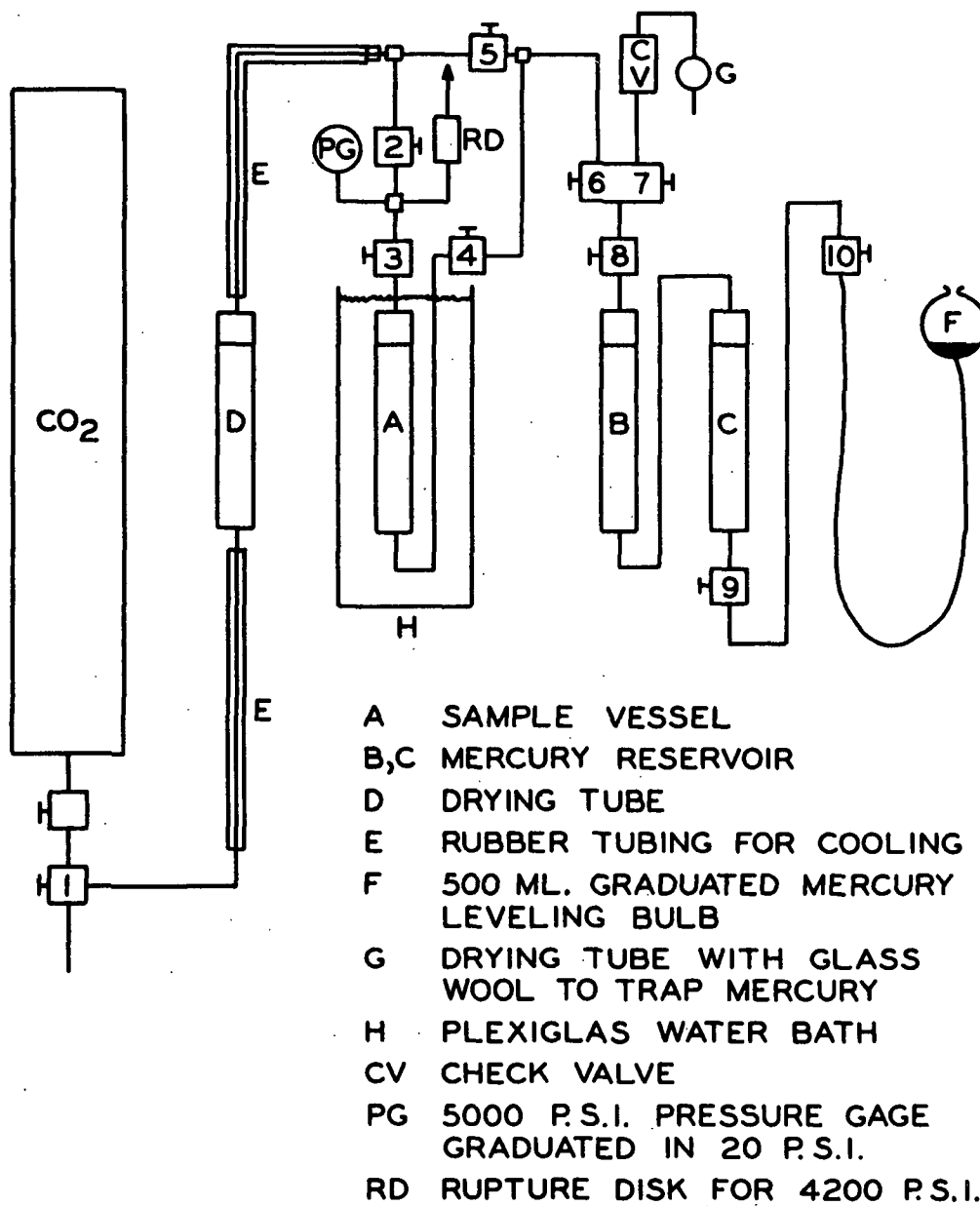


Figure 3. Carbon Dioxide Exchange Apparatus

At first, flushing of the air from the apparatus was accomplished by evacuation and filling with carbon dioxide. This was found to cause mercury from the reservoir to become distributed in other parts of the system and was therefore discontinued. The procedure for flushing finally consisted in passing phosphorus pentoxide-dried carbon dioxide at about 5 p.s.i.g. through the connection to Valve 3 for about 15 minutes before connecting and then for another 15 minutes through the connection to Valve 4 before connecting. This was followed by passage through the check valve for another 15 minutes.

The solvent-exchange operation has been classified into five operations; initiation, displacement, exhaust, mercury leveling, and predisplacement. The first operation is performed only once whereas the other four are performed once for each liquid displacement. These operations and the corresponding valve manipulations are given below:

Initiation:

3, 4, 7, 9, 10 closed (others are open).
Carbon dioxide cylinder valve opened.
5 closed.
3, 4, opened.
9 opened.

Displacement:

10 cracked to displace 145 cc. of mercury
in about 4 minutes.
10 closed.

Exhaust:

6, 8, closed.
7 opened.
8 cracked; opened.

Mercury Leveling:

10 opened and mercury leveled.

Predisplacement:

7, 8, 10 closed.

6 opened.

8 opened slowly

To ensure that the carbon dioxide was a liquid in the sample section the supply line was cooled with cold tap water and the exchanges were run at 15°C., with the exception of the first run at 20°C. which was the minimum temperature of the tap water.

The time that a given quantity of liquid carbon dioxide was in contact with the cotton sample was generally about 10 minutes.

Following the last displacement, the temperature of the bath was increased to 36°C. (45°C. in the case of Samples c-2e and c-2f), and after one hour for thermal equilibrium, the removal step was started.

The removal is similar to a displacement sequence except that the amount of mercury displaced was that which corresponded to a pressure drop of 50 to 70 p.s.i. Five minutes were allowed between each such incremental displacement during which time the pressure was found to increase 30 to 40 p.s.i. This was taken as an indication of cooling during expansion and the subsequent rewarming. This

pressure increase did not occur, however, when the system had reached the lower pressures. The incremental displacements were continued until the total mercury displaced was about 200 cc. at which time the sequence for exhaust, leveling, and predisplacement was performed. In the final stages, 200 cc. of mercury were displaced with only a small decrease in pressure. The total time for the removal was five hours or less. The course of removal for Sample c-2j is shown in Fig. 1, the dashed line being the estimated 36°C . isotherm. Since the over-all specific volumes for the system were not accurately known the path is plotted accordingly where one might expect the 36°C . isotherm to fall. The important thing to note however is that the removal path avoids the two-phase region by a comfortable distance.

Anderson's (41) apparatus consisted of a vessel, two valves, and a pressure gage, with removal being merely an opening of the exit valve. The evaporative cooling in such a case could very easily result in a 2-phase system.

It should be pointed out that considerable time was expended in attempts to locate and eliminate leaks in the high-pressure system. A discussion of this problem is given in the Appendix, on p. 119-20.

GAS-ADSORPTION APPARATUS

The gas-adsorption apparatus used is that of Haselton (4, 5) with some slight modifications. Since he has adequately described the apparatus and its operation this will not be repeated here, but a description will be given of the main changes.

Haselton's (4, 5) apparatus was similar to that of Harkins and Jura (49), being a volumetric type based upon measurements of pressure for known volumes.

Merchant's (6) main modification was to substitute a joint for connecting the sample instead of making glass-blown seals. Recently, a seven-bulb buret was substituted for the three-bulb buret used by Haselton. This seven-bulb buret is similar to that used by Harkins and Jura (49) and enables one to obtain a check of each measurement as well as the determination of several points before more nitrogen must be added.

As mentioned in an earlier section, a Central Scientific Co. glass-to-metal seal was used in the connection of the stainless-steel sample vessel to the methanol exchange apparatus. A similar connection was used to connect the vessel to the gas-adsorption apparatus. In this case however the "O" ring was coated with Dow Corning silicone high-vacuum grease and/or Dow Corning silicone diffusion-pump oil. In addition, a certain degree of flexibility in making the connection was permitted by use of the arrangement shown in Fig. 4.

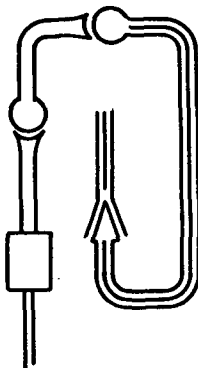


Figure 4. Connection of Pressure Vessel to Adsorption Apparatus

GENERAL EXPERIMENTAL PROCEDURES

COTTON

After considering three broad sources of cellulose, an unpurified cotton was selected in preference to either a commercial wood pulp or a high alpha-cellulose pulp. The cotton does not have hemicelluloses, uronic acids, or residual lignin which might strongly absorb carbon dioxide (4) or affect the degree of swelling (50). It does contain certain waxes and pectic substances, but these are practically all removed during mild purification.

The cellulose in cotton, unlike wood pulp, is fairly evenly distributed across the cell wall. Also it can be stored dry with little worry of degradation and its previous history regarding mechanical action and exposure to heat is better known.

It does entail more work, however, because it must be purified in the laboratory as needed.

Nine pounds of cotton were obtained from the United States Department of Agriculture, Agricultural Research Service, Southern Utilization Research and Development Division, New Orleans 19, Louisiana, through the courtesy of R. J. Cheatham, Chief, Cotton Mechanical Laboratory. The description of the cotton is as follows: "...Empire cotton, a strain developed from Stoneville 2B cotton, which was processed through our regular opening, cleaning, and picking processes and then double carded and placed on ribbon laps. This cotton has had no chemical treatment and has been stored in large cans away from light for a number of years." The cotton arrived in a corrugated box and was then stored in a double polyethylene bag in a cold room at 40°F.

PURIFICATION

The recommended purification procedure of Conrad (51) which should remove practically all of the noncellulosic material (52) is essentially that used. Four separate batches of cotton were purified. The initial batch was used for analysis, Batches c-1 and c-2 were used for the solvent-exchange and surface-area study, and Batch c-3 was used for the water-vapor-adsorption experiment.

The apparatus consisted of a 2-liter Erlenmeyer flask, a 2-liter beaker, another beaker, 2 Meker blast burners, a basket made from 28-mesh stainless-steel wire gauze, and a series of siphons.

The cotton was placed in the two-liter beaker under the inverted wire basket. The basket was kept off the bottom of the beaker by wires and was prevented from rising during boiling by a glass weight.

In the case where boiling solutions were used, the solution from a stock bottle was run into the stoppered Erlenmeyer where it was preheated and then passed to the bottom of the beaker, where heating was continued. Flow was regulated by an air inlet in the stoppered Erlenmeyer, a series of pinch clamps, and the level controller which removed the solution from above the basket and emptied it in a measuring container. Unheated liquids were passed directly to the bottom of the beaker.

In general the cotton was:

1. Initially purified by tediously removing with a forceps nearly all visible extraneous and nonfibrous material.
2. Extracted with 95% ethanol in a Soxhlet extractor for at least 3 hours.
3. Washed in two successive 500-ml. quantities of distilled water, being allowed to sit 30 minutes in the second wash.

4. Placed under the basket in the 2-liter beaker in about 1500 cc. of water, heated to boiling, and boiled for 20 minutes.
5. Placed in 1500 cc. of 1+0.05% sodium hydroxide and heated to boiling.
6. Boiling was continued with 6000 cc. of fresh boiling sodium hydroxide passed through the cotton continuously over a period of about 45 minutes.
7. Then, 6000 cc. of boiling distilled water in about 45 minutes.
8. 4500 cc. of cold distilled water in about 30 minutes.
9. 1500 cc. of 0.5% acetic acid in about 15 minutes.
10. 9000 cc. of cold distilled water in about 45 minutes. The displaced water at this point tested neutral to litmus paper.

All quantities in the initial purification were proportionately smaller and the wire basket was not used, but a stirring rod was used in an attempt to keep the cotton below the boiling liquids. The initial batch as well as Batch c-1 used a level controller for admitting the solutions to the sample. This was discontinued since it tended to mix air into the liquid and a straight siphon was then used.

Batch c-1 was stored under water and Batch c-2 under methanol, both in a refrigerator at near 0°C.

SOLVENT-EXCHANGE AND DRYING PROCEDURE

EXCHANGES USING HIGH-PRESSURE VESSELS

In order to facilitate addition and removal of cotton samples to the stainless-steel vessels, glass liners were made out of 25-mm. test tubes. Only those tubes which gave a very close fit inside the vessels were selected. They were cut off at both ends and necked down at the bottom to hold a small disk of 100-mesh stainless steel wire gauze.

For Runs c-1a and c-1b the cotton was taken from the water in which it had been stored and placed in methanol. A partial vacuum was applied to remove some of the dissolved or entrapped air. This procedure was then repeated with fresh methanol. For the other runs the cotton had been given this treatment before storage under methanol.

A liner was placed in a test tube of methanol and the cotton was transferred to it by means of a forceps. After transfer of a small quantity of cotton a small stirring rod was used to work out as much air as possible. The procedure was continued until the liner was filled.

The liner holding the cotton and methanol was stoppered on the top and transferred to a stainless-steel vessel which was about half-full of methanol. The closing surface of the vessel was carefully dried, the vessel head tightened, and methanol was passed into the vessel at the bottom in order to displace any air at the top.

The sample was connected to the solvent-exchange apparatus and the exchange was started. For Samples c-1a and c-1b the alcohol passed through the sample from top to bottom. For the other exchanges flow was from the bottom to the top as discussed below.

The number of exchanges and the time of contact between the cotton and alcohol varied and is summarized in the Appendix on p. 145-50. A single exchange step, or displacement, involves passage of a given quantity of solvent, the contact time referring to the time since the prior displacement.

The exchange to liquid carbon dioxide and its removal have already been described on p. 16-18.

EXCHANGES USING GLASS SAMPLE BULBS (WAN-DRYING)

The dimensions and method of construction of the glass sample bulbs were quite similar to those described by Merchant (6, 7). They were in general made from 25-mm. test tubes, 2-mm. capillary tubing, 2-mm. capillary stopcocks and 2-mm. 10/30 ground-glass joints. The bulb for Sample c-2bw was constructed with stopcocks on top and bottom and solvent flow was from top to bottom. During the solvent exchanges with distilled solvents using this type of bulb, it was found that a considerable quantity of vapor or air was evolved when the solvent passed through the sample. This air or vapor collected above the cotton and in several cases a backflushing with freshly displaced solvent was required to remove this air and prevent it from reaching the cotton. It is believed that this was air from a saturated or supersaturated solvent being released due to a slight reduction in pressure.

In subsequent runs the direction of flow was reversed, thus causing it to flow up through the cotton sample and remove the evolved air. The sample-bulb assembly used for this purpose is shown in Fig. 5 and was found to work quite well. It was also possible to immerse this bulb assembly in a water bath during drying.

Since the cotton had been stored under methanol it was thoroughly rinsed in distilled water before being loaded into the glass bulb. The cotton and the bulb were immersed in a tray of distilled water where the bulb was loaded by means of a forceps and small stirring rod through the approximately 6-mm. hole which remained prior to the final sealing to the upper stopcock in Fig. 5. During the final flame sealing wet towels were wrapped around the bulb at the level of the cotton, which was several centimeters from the place of the seal, and the water level was maintained above the cotton by means of a leveling bulb.

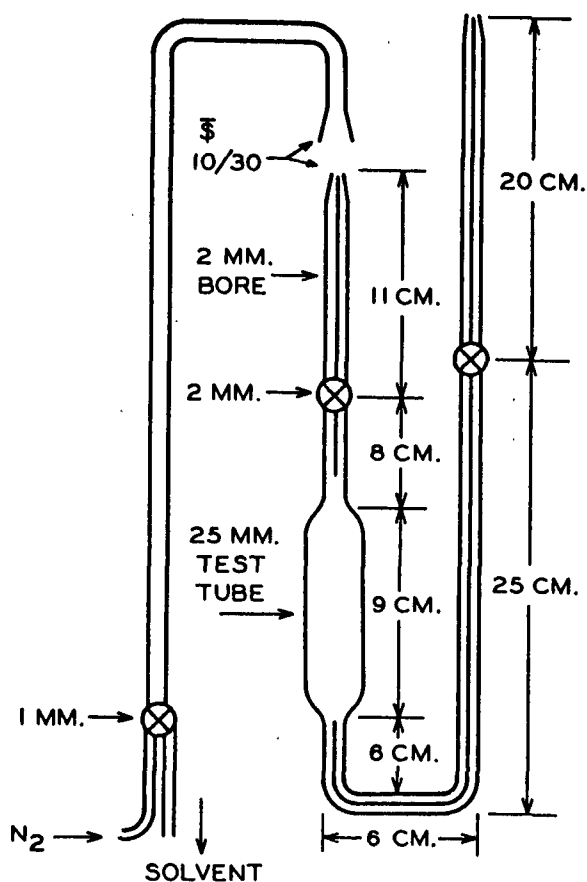


Figure 5. Sample-Bulb Assembly for C-2cw

The methanol drying and exchange has already been described on p. 11-13. The n-pentane, Phillips 99 mole % minimum purity, and the benzene, Mallinckrodt purified, were dried by refluxing over freshly extruded sodium for about 3 hours and then distilling until an increase in the distillation temperature was noted. The pentane exchanges for the pentane-dried samples were conducted on the solvent-exchange apparatus of the Physical Chemistry Department. This apparatus differs only in minor detail from that described before. When pentane or benzene was processed in the solvent-exchange apparatus of this worker, a cold trap was used after the last bubbler in order to condense the vapors.

The samples were dried by passing phosphorus pentoxide-dried prepurified nitrogen through the bulb from top to bottom at 50 ml./min. Sample c-2bw was dried without removal from the solvent-exchange apparatus. Since a cooling of the bulb was noted, all other dryings involved placing the sample bulb in a bath of water initially at 25°C. Drying from pentane was done for 38 and 39 hours, respectively, for c-2bw and c-2cw, whereas from benzene the time was 61 and 66 hours, respectively, for c-2hw and c-2gw.

Prior to drying, the top stopcock plug was removed and greased. During this operation the nitrogen flow was maintained out of the openings. After completion of drying and before stopping the nitrogen flow, the lower stopcock plug was removed and greased. This lower stopcock was then removed, except for Sample c-2cw, under partial evacuation by use of a torch.

UNREPLACED SOLVENTS

The term unreplaced solvent will be used with reference to a liquid which remains in the cellulose after attempts have been made to replace it with another liquid.

WATER

A Beckman KF-2 Aquameter (53) employing automatic titration with the Karl-Fischer reagent was used to determine the water content of methanol. The Karl-Fischer reagent was prepared according to Mitchell and Smith (54).

The water contents of the dried methanol and of the methanol which was displaced after contact with the sample were determined. The difference of these concentrations is taken as a measure of unreplaced water which is still being

removed. When no more water can be replaced the concentration of the incoming dried alcohol and the displaced alcohol should be the same.

Poor reproducibility was at first encountered, and was finally traced to water pickup during the transfer of the alcohol sample to the Aquameter.

The method which was finally used and which appeared to minimize this problem consisted in passing either the dried or the displaced methanol directly into a buret. This buret was fitted with a Drierite tube at the top and was filled by means of a side-arm stopcock at the bottom. The buret tip passed through a rubber stopper which fitted the sample port in the neoprene cover of the titration vessel. The solution in the titration vessel was brought to the end point immediately preceding the addition of the alcohol sample. All determinations were made in triplicate and average values are reported.

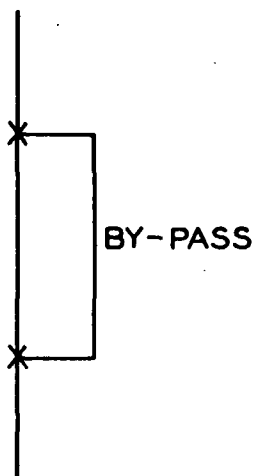
METHANOL

Let us consider first the methanol-to-carbon dioxide exchange.

Several attempts were made to recover the methanol in a known-concentration methanol-liquid carbon dioxide mixture by absorption of the gas in water or by condensation in a Dry Ice-acetone cold trap. These attempts showed only partial recovery of the alcohol.

The gas chromatograph, an Aerograph Chromatographic Instrument equipped with a Brown Elektronik Recorder and a Disc Integrator, was calibrated for known-concentration methanol-carbon dioxide gas samples and was then used for analysis of several samples of carbon dioxide from displacement and removal steps of an exchange.

The gas-sampling device was made from two 3-way stopcocks and a length of 6-mm. glass tubing and had a volume of about 5 ml. A sketch is shown below:



In operation, the carrier gas was directed along the by-pass and after momentarily equilibrating the pressure in the sample section the stopcocks were turned so that the carrier gas took the sample into the instrument.

The operating conditions of the gas chromatograph were:

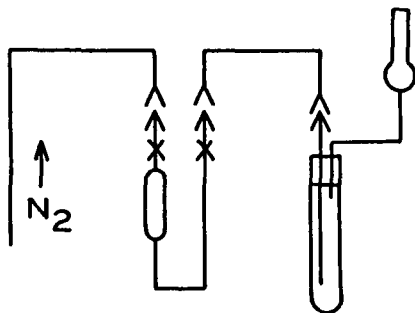
Carrier gas	Helium
Flow rate, ml./min.	30
Inlet gas pressure, p.s.i.g.	5
Column	20% Carbowax on acid-washed Chromosorb W
Furnace temp., °C.	38
Injector and collector temp., °C.	40
Filament current, ma.	186

Two known-concentration gas samples were prepared by bubbling carbon dioxide through five tubes of methanol immersed in an ice bath (4.0 mole % methanol in carbon dioxide) and in a carbon tetrachloride-Dry Ice bath (0.83 mole % methanol in carbon dioxide).

After trying several different methods for standardization, the one using the quantity, (retention time) x (peak height), was selected. The sum of this quantity for the methanol and for the carbon dioxide is determined and the percentage of the summation due to methanol is taken as the mole per cent of methanol. Best results were obtained when the carbon dioxide quantity had been multiplied by a factor directly related to the methanol peak height.

Another method of determining unreplaced methanol was the passage of the displaced or removed carbon dioxide gas through a phosphorus pentoxide tube. The increase in weight is attributed mainly to methanol.

The unreplaced methanol in one of the benzene-dried samples, c-2gw, was determined during its drying by passing the phosphorus pentoxide-dried nitrogen through the sample, a trap, and then a phosphorus pentoxide tube. The increase in weight of the latter was taken as due to unreplaced methanol although part may have been due to small amounts of unreplaced water. A trap was used to prevent any liquid benzene from entering the drying tube as shown below.



RESIDUAL SOLVENTS

The term residual solvents will be used with reference to those liquids which remain after the surface area determination and the outgassing under high vacuum which accompanies it.

After the outgassed weight was determined the cotton was soaked in a stoppered flask of distilled water in order to reswell it and allow residual solvents to be washed out. It was soaked in 35 to 80 cc. of water and generally for 2 days or longer. Sample c-1a was the exception and was soaked overnight in 350 cc. of water. The cotton was then oven dried at 105°C. to constant weight and the total residual was determined as the loss in weight.

The excess water was separated from the cotton by filtration through a fritted-glass funnel using a positive pressure of air to speed the operation. This water will be referred to as the water extract in the subsequent analyses to be described below.

In several cases, the water which could not be removed by filtration was removed by evacuation through a Dry Ice-methanol trap. While under vacuum the sample was heated in a steam bath for about an hour. The material which collected in the cold trap will be referred to as the condensate in the analyses to be discussed below.

CARBON DIOXIDE

Part of the water extract from Sample c-1a (200 cc.) was gravimetrically analyzed for carbon dioxide. The procedure (55, 56) in general consisted of addition of hydrochloric acid to the aqueous sample, boiling, and passage of carbon dioxide-free air through the solution and then through a series of

Drierite, anhydrous cupric sulfate, and Ascarite absorption tubes. Initially, a blank was determined by making a run under identical conditions with carbon dioxide-free distilled water. The increase in weight of a tube containing Ascarite followed by Drierite and which has been corrected for the blank, gives the amount of carbon dioxide evolved.

METHANOL

The spectrophotometric method of Reid and Truelove (57) and Reid and Salmon (58) for the determination of methanol in water was standardized and used for a considerable number of determinations before it was finally abandoned. It was not sensitive enough for the small amounts involved.

The gas chromatograph which has already been described was used for all methanol determinations reported. Operating conditions were:

Carrier gas	helium
Flow rate, cc./min.	45
Inlet gas pressure, p.s.i.g.	9
Column	Carbowax
Furnace temp., °C.	90
Injector and collector temp., °C.	105
Filament current, ma.	180

The various water solutions were injected into the apparatus in 50-microliter quantities by way of a graduated microsyringe. A series of known-concentration methanol solutions were used for the calibration which involved a plot of methanol concentration against the methanol peak height. The relationship was essentially linear above about 1.5 units or the corresponding 0.008% methanol by weight. All

determinations in which a measurable amount was found were run in triplicate; others were run in duplicate.

WATER-VAPOR ADSORPTION ISOTHERMS

Thirteen cotton samples of about 2 g. each were used. These samples were conditioned from the water-wet state to equilibrium over various salt solutions at 73°F. The dishes used have been described by Wink (59), and the relative humidities of the saturated salt solutions used have been determined by Wink and Sears (60) and are given in Table I.

TABLE I
RELATIVE HUMIDITIES OF SATURATED SALT SOLUTIONS (60)

Chemical	Formula	R.H. at 73°F.
Lithium chloride	LiCl	0.111
Potassium acetate	$KC_2H_3O_2$	0.229
Magnesium chloride	$MgCl_2 \cdot 6H_2O$	0.329
Chromium trioxide	CrO_3	0.392
Potassium carbonate	K_2CO_3	0.439
Sodium dichromate	$Na_2Cr_2O_7 \cdot 2 H_2O$	0.541
Sodium nitrite	$NaNO_2$	0.648
Sodium chloride	NaCl	0.755
Potassium chromate	K_2CrO_4	0.865
Ammonium monophosphate	$NH_4H_2PO_4$	0.929

The samples were weighed every 3 to 7 days until the conditions of "equilibrium" set forth below were met; the time to reach this point being from 3 to 83 days. The initial desorptions at the higher relative humidities required the

longest periods of time. Generally, equilibrium was attained faster for adsorption than for desorption, but the magnitude of the relative humidity change was also important. The samples, after reaching equilibrium, were transferred to different relative humidities. The total experiment required over 4 months, during which time 50 experimental points were obtained for initial desorption from a water-wet state, subsequent adsorption, and a second desorption.

Generally, when the calculated change in weight per day was 0.0001 g. or less, this was accepted as the equilibrium point. In desorption if the sample gained weight, or in adsorption if the sample lost weight, this was considered equally valid as the equilibrium point. These conditions will be referred to as the basic criteria.

In some cases additional data were collected after the conditions of the basic criteria were met. If the sample was being equilibrated over phosphorus pentoxide, the minimum value was taken as the equilibrium point. If the sample was adsorbing vapor, the maximum value was taken, as long as it did not greatly differ from the other values.

In desorption, it was found that the sample continually lost weight. It is believed that this was due to a cyclic variation in relative humidity caused by small temperature changes. Although the experiment was conducted in a room with a controlled atmosphere at 50% relative humidity and 73°F. the temperature control is generally $\pm 1^\circ\text{F}$. This change in temperature does affect the relative humidity to a small degree (60), some solutions being affected more than others.

Wink (61) showed this effect to continually decrease the equilibrium water content of cellulosic materials dried under carefully controlled conditions of relative humidity cycling between 0.48 and 0.52. The reason for the continual

decrease is that once a slightly lower relative humidity has been reached a new equilibrium moisture content is obtained when the higher relative humidity is again reached. Thus, a continued cycling over a small relative humidity range should eventually bring the desorption equilibrium value down to that of adsorption. This is especially important at the higher relative humidities where a small change in relative humidity greatly affects the amount of water adsorbed.

It is for this reason that the basic criteria were rigidly applied for the desorption equilibrium point. It should be pointed out that the choice of the value of 0.0001 g. per day was rather arbitrary. At the higher relative humidities, since there is an appreciable water content at equilibrium, small changes are relatively insignificant.

EXPERIMENTAL RESULTS AND DISCUSSION

ANALYSIS OF COTTON

The initial batch of purified cotton, which had a yield of 95%, was used for analysis. The results, in duplicate, are given in Table II, those samples for the alpha-cellulose and copper number determinations having been first passed through an Abbé mill.

TABLE II

COTTON ANALYSIS

Alpha Cellulose ^a , %	Copper Number ^b	Ash ^c , %
92.6	0.40	0.2
92.2	0.33	0.1

^aInstitute Method 421, Jan., 1951.

^bTAPPI Standard 215, m-50; weight of copper reduced per 100 g. of pulp.

^cInstitute Method 422, Jan., 1951; at 575 \pm 25°C.

Viscosities of four different concentration cellulose solutions in cupri-ethylenediamine (cuene) were determined at 25°C. using No. 100 Cannon-Fenske viscometers and 7.0 ml. of solution. The dissolution of the cellulose and the method for maintaining the solutions under nitrogen was essentially that of Browning, Sell, and Abel (62). It was found that in order to effect dissolution of the cellulose it first had to be shaken in water and then in dilute cuene solution before the final cuene addition to give a 0.5M copper concentration.

Realizing that in this viscosity range there is apparently an effect of rate of shear (63) and variation in the Martin constant (64, 65) it was decided

to estimate the intrinsic viscosity, i.e., $[\eta] = \lim_{c \rightarrow 0} (\eta_{rel} - 1)/c$, from that determination where $[\eta]_c = 3.0 \pm 0.5$ (66, 67). The relative viscosity, η_{rel} is equal to t/t_0 , where t and t_0 are the efflux times for solution and solvent, respectively, and c is the concentration of the cellulose-cuene solution in g./100 ml. A recently published table for determining $[\eta]_c$ from η_{rel} (66), in which the Martin constant has a value of 0.13, was utilized. The results are shown in Table III.

TABLE III
VISCOSITY RESULTS

Viscometer no.	27	A190	BL26	J244
Concentration, c , g./100 ml.	0.209	0.300	0.101	0.0676
Time, t , sec.	1041.7	1503.9	269.4	175.8
Time of solvent, t_0 , sec.	99.9	76.3	65.6	76.5
Relative viscosity, $\eta_{rel} = t/t_0$	10.42	19.68	4.11	2.30
Specific viscosity, $\eta_{sp} = (t - t_0)/t_0$	9.42	18.68	3.11	1.30
Reduced viscosity, $\eta_{red} = \eta_{sp}/c$	45.1	62.2	30.8	19.2
Intrinsic viscosity, $[\eta] = \lim_{c \rightarrow 0} (\eta_{sp}/c)$	16.2	--	--	--

It should be pointed out that originally it was planned to determine the above quantities for each batch of purified cotton in order to estimate any batch-to-batch variation. To conserve the purified cotton it had been planned to make such analyses after surface area determinations. Because of a lack of time and the possibility of changes due to different times of oven drying these analyses were not performed.

CRITICAL TEMPERATURE OF CARBON DIOXIDE

The critical temperature is sometimes defined as that temperature above which a pure gas cannot be liquefied regardless of the magnitude of the applied

pressure. More generally, however, the critical point is the temperature and pressure where the liquid and vapor phases coincide and are indistinguishable. On a pressure-volume diagram this is the point where the liquid and vapor lines meet.

The literature is quite abundant with critical-point data for carbon dioxide and in general the data agree quite closely. According to several sources (68-73) the critical temperature can be taken as 31.0°C . and the critical pressure as 1070 p.s.i.a.

It was decided to determine the critical temperature experimentally for two reasons: (1) in order to be confident that the critical point of the carbon dioxide being used is essentially the same as the literature value, and (2) in order to examine the precision of the method since it may be desirable to study the critical points of carbon dioxide-methanol solutions.

Two methods which are based on pressure-temperature measurements were used. One is the method of Cailletet and Colardeau (1888) as described by Glasstone (74). The pressure is determined as a function of temperature at different over-all specific volumes for the system. The specific volumes are ideally bracketed around the critical specific volume, but the exact numerical values are not required. At a given temperature the pressure remains independent of specific volume as long as there is a 2-phase system; i.e., liquid and vapor. Above the critical temperature there will be no such independence.

To collect such data, the stainless-steel vessel was cooled to 10°C . and allowed to fill with liquid carbon dioxide by opening it to the supply cylinder. The vessel was then isolated and the over-all specific volume was increased by removal of some of the carbon dioxide. The approximate volumes of various

sections of the apparatus were previously determined by linear measurement of the lines and valves and by volumetric measurement of a vessel assembly using water. An auxiliary vessel assembly was included in these determinations and will be referred to later as Vessel 2. From a knowledge of these volumes and an approximation regarding the gas temperature therein the specific volumes in Vessel 1 were varied and calculated. Two runs were made in this manner, each run involving temperature-pressure measurements for several over-all specific volumes.

A third run used 1 g. of methanol in the carbon dioxide but since it is believed that the methanol was removed before the data were collected and since the data are in agreement with the two earlier runs using just carbon dioxide results of these three runs are plotted together in Fig. 6.

In this plot the specific volumes were selected by noting the literature value for the pressure of the 34° isotherm. These specific volumes were in general agreement with the calculated values, and by using the latter the same critical temperature was indicated but there was more scatter. From this plot the critical temperature seems to be between 30 and 34°C . and quite likely in the region of 32°C . Considering the fact that the pressure gage is graduated in 20-pound intervals and that readings were made to the nearest 5, this agreement is very good.

The liquid-vapor boundary in Fig. 6 is the same as in Fig. 1 on p. 10 and along with the isotherms in Fig. 1 was determined from the data of several sources (68-71).

Another method for the analysis of the pressure-temperature data has been described by Ipatieff and Monroe (75) who used it for critical-temperature determinations of propane, n-hexane, cyclohexane, and benzene as well as for

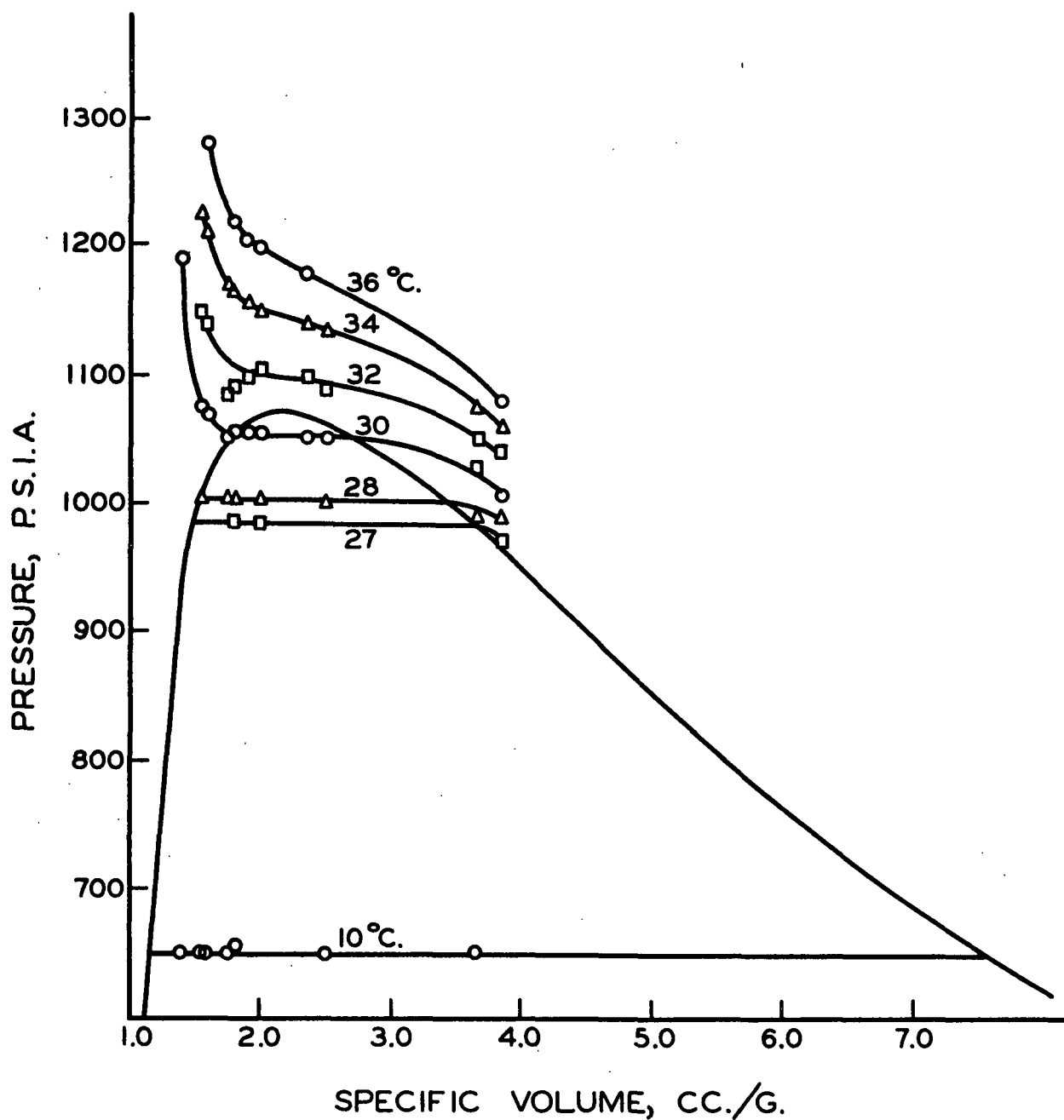


Figure 6. Critical Point Determination for Carbon Dioxide

several binary mixtures. They found that their values for the former agreed well with literature values and although they did not have such values to compare the binary solutions with, they believed that the experimental evidence indicated the critical temperatures. The method consists of plotting the pressure versus temperature for a constant volume system. Up to the critical temperature the relationship is convex to the temperature axis, but above this, the relationship is linear. Intersection of these two lines gives the critical temperature with an accuracy which they estimate to be $\pm 2^{\circ}\text{C}$. They found that the amount of material charged to their bomb could vary from 20 to 50% of the total capacity without there being a shift in the discontinuity.

Plotting the pressure-temperature data for the first 2 runs indicated a critical temperature of 31 or 32°C .

It should be mentioned that on a pressure-temperature plot for a pure compound the two-phase region is indicated by a line. Increasing the temperature of a liquid-vapor system at constant volume will cause a path to be traced along this two-phase line. Depending upon the relative amounts of liquid and vapor initially present the amount of liquid phase will either increase or decrease as the temperature is raised, unless the over-all specific volume corresponds to the critical volume (2.24 cc./g. for carbon dioxide). At a point where only liquid or only vapor is present, the curve will branch out from the liquid-vapor line linearly in the appropriate direction. The method of Ipatieff and Monroe (75) apparently utilizes this principle.

CRITICAL PHENOMENA OF CARBON DIOXIDE CONTAINING METHANOL

Since there appears a possibility that there will be some methanol in the final liquid carbon dioxide it might be well to look briefly at what this may mean in terms of the critical point.

The pressure-volume and pressure-temperature plots discussed in the above section are merely projections of the three-dimensional P-V-T-surface. In the case of a binary system we have such a surface for each particular composition of the binary solution.

Probably the most widely used data in the discussion of critical phenomena for binary solutions are those of Kay (76) for the ethane--n-heptane system. Figures from Kay or from his data are found in numerous discussions (77-81), several of which (77, 78, 80) give three-dimensional representations of the vapor pressure-temperature-composition surface.

To see how the critical phenomena of a binary solution differ from those of the pure components it is instructive to examine the pressure-temperature projections such as shown in Fig. 7 and 8. In Fig. 7 A C_A is the vapor pressure line for pure ethane and B C_B is for pure n-heptane, C_A and C_B being the respective critical points. The other curves are border curves for different compositions of ethane--n-heptane mixtures, the critical points being C₁, C₂, and C₃. The fact that the critical point, i.e., the point where the bubble- and dew-point lines meet is not necessarily at the maximum temperature and pressure where the liquid phase can exist leads to what are called retrograde phenomena. In Fig. 8, for instance, following paths 3-2 or 1-2 we see two different cases of retrograde phenomena. Path 3-2 results in the formation of a vapor phase at D and then with increased temperature it disappears at L. In path 1-2 a liquid phase appears at G but disappears at M.

Therefore, if there should remain a two-component mixture of carbon dioxide and methanol at the solvent removal step, it is not necessarily the critical temperature which must be exceeded, but rather the maximum temperature at which the liquid can exist.

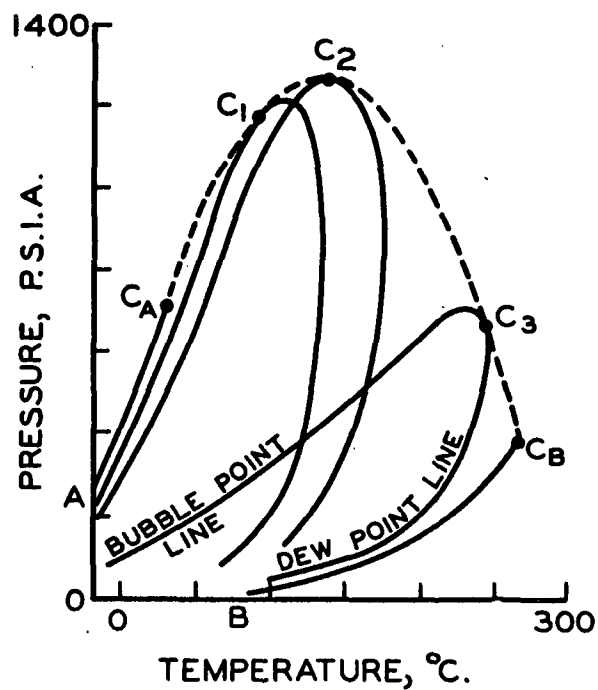


Figure.7.. P-T Relationship for Ethane--n-Heptane Mixtures (76)

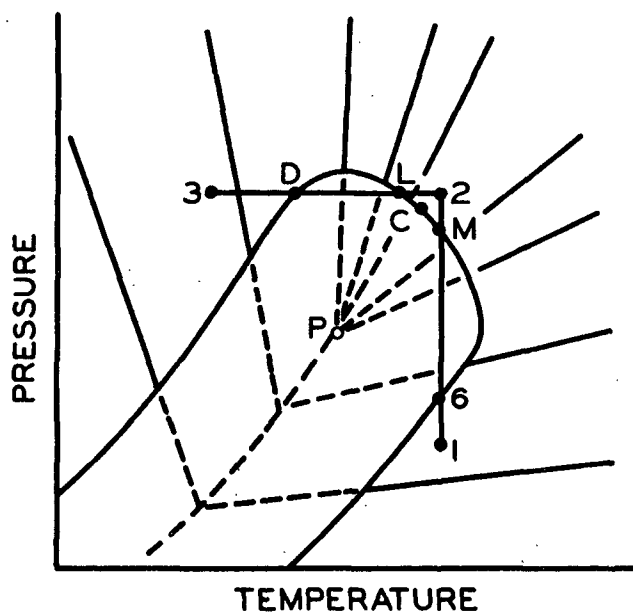


Figure.8. P-T Diagram for One Composition of a Binary System

In the case of "normal liquids" the critical temperature (and also the maximum temperature at which liquid exists) lies between that of the higher-boiling component and the lower-boiling one. Furthermore, the higher the concentration of the high-boiling component, the higher the critical temperature of the mixture (82).

A total of six runs was made in collection of pressure-temperature data for dilute solutions of methanol in liquid carbon dioxide, the concentrations of methanol varying from 1 to 5% by weight and the amount of liquid from 30 to 50% of the vessel capacity at 10°C. Difficulty was encountered in the preparation of the solutions. Methanol was added to the evacuated vessel by way of an eyedropper and then liquid carbon dioxide was either distilled in directly and the volume of liquid changed by removal of vapor or else an auxiliary vessel of a predetermined available volume was filled and then allowed to distill back to the vessel containing the methanol. Calculations were only approximate by virtue of the uncertainties involved. All data were plotted as pressure-temperature relations in order to determine the critical point at the discontinuity according to Ipatieff and Monroe (75).

Such discontinuities generally occurred with the corresponding temperature varying from 27 to 36°C. There was no consistency however from run to run and hence these values cannot be taken as the critical points.

Just from experimental considerations it is not difficult to see that the experimental determinations with existing equipment are not likely to yield good results. There is no assurance that the methanol has ever been completely dispersed in the liquid carbon dioxide since shaking or mixing was not feasible. There is also a question regarding the disturbance of the composition by removing

any material, since the composition of the two phases will be different. There is also a mass equilibrium which must be attained in addition to thermal equilibrium.

The only significant information appears to be the fact that in most cases the pressure of the solutions at 30°C. were lower than for a pure liquid-vapor system. As in Fig. 7, this would be consistent with the formation of a solution of a higher critical temperature.

Going back to Fig. 8, it should be pointed out that the isochores outside of the two-phase region are nearly linear and follow the same pattern as for a pure substance but inside they reportedly exhibit appreciable curvature without showing rapid change in this curvature even near the critical point (82).

The dotted lines are merely extensions of the true isochores showing the pseudocritical point which is useful in generalized compressibility curves (79). Again, this appears to be the basis for Ipatieff and Monroe's (75) method but in the case of binary solutions it would seem that the point they determine is somewhere on the boundary curve and probably farther from the critical point than in the case of a pure compound.

It has been pointed out (78) that for dilute solutions of a nonvolatile component the elevation of the critical point is proportional to the molar concentration of the solute. More specifically, Booth and Bidwell (83) found an increase of 8.8°C. in the critical temperature per mole per cent of a solute with no apparent restriction on its volatility. However, it has been shown by Thiele and Kay (77) that carbon dioxide and ethane which individually have nearly the same critical temperature, form a mixture of lower critical temperature. Thus, the statement (77) that in general there is no way of predicting the critical behavior of a mixture from that of its components, must be considered.

Because of the above difficulties, attempts to determine the critical temperatures for methanol-carbon dioxide mixtures were discontinued in favor of studying a method to find out whether or not methanol actually is present in the final carbon dioxide. As will be shown in a later section initial indications showed no detectable methanol in the final carbon dioxide.

CRITICAL-POINT AREAS

A total of five samples were carried through the complete CP-drying procedure and surface-area determinations. Three other samples were started, two of which went as far as the outgassing step where they finally had to be discontinued because of vacuum leaks.

The treatment of each sample varied somewhat from the others for several reasons. (1) Attempts were being made to improve the efficiency of the procedure. (2) Secondary information was being obtained. (3) Several days were generally required and hence time schedules had to be kept somewhat flexible. (4) The amount of dried methanol per batch determined somewhat the number of exchanges.

Previous workers (4, 6) have outgassed samples for surface-area determination overnight. Since there was the possibility of leaks in the metal system the pressure buildup in the system was noted after various outgassing times. This was done by isolating the gas-adsorption apparatus from the pumps and noting the pressure on the McLeod gage as a function of time, generally over a period of several hours or more. It was found that considerably longer outgassing than just overnight was required. The question arose as to what rate of pressure buildup is tolerable. Examination of the gas adsorption apparatus itself without any sample present seemed to indicate that a maximum pressure

of about 0.04 to 0.05 micron of mercury would result on pump isolation. Somewhat arbitrarily the rate of pressure buildup which was tolerable was set at about 0.01 micron per hour, starting of course at essentially the zero reading. Some variability is present in this rate since the McLeod gage has a logarithmic scale, graduations being at 0, 0.005, 0.01, 0.05, 0.10, 0.2, 0.3 microns, etc. The minimum outgassing period allowed for the CP-samples was about 5 days.

Because of the long time required to bring a sample to the point for a surface area determination at least two such determinations were made for each sample. Extreme care was also taken to ensure maximum precision. Only experimental points in the relative pressure range of 0.05 to 0.30 were used and all determinations of slopes and intercepts of the BET plots were made by the method of least squares. The cross-sectional area of the nitrogen molecule was taken to be 16.2 sq. A. These comments are also applicable to the surface areas of solvent-dried samples.

The three CP-samples which used liquid carbon dioxide directly from the cylinder gave the following average surface areas:

51.8 sq. m./g. for Sample c-1a,
52.8 sq. m./g. for Sample c-1b, and
39.4 sq. m./g. for Sample c-2j.*

Complete details of the exchanges and results of all CP-samples are given in the Appendix in Tables XIII to XVIII on p.145-50. Note that the word "Displacement"

*The sample designation consists of the batch designation, c-1 or c-2, followed by a small letter to designate a particular portion of the batch. In the case of solvent-dried samples, an additional letter, w, is used, for example, c-2bw.

or the letter "D" followed by a number refers both to the act of flowing a given quantity of liquid through the sample and also to that material which is removed or displaced. The contact time refers to the contact between the displaced liquid and the sample.

Two different batches of cotton, c-1 and c-2, were used in the CP-studies. Also, two different cylinders of carbon dioxide were used respectively for these batches. The difference between the above areas for Batches c-1 and c-2 thus may be due to either a difference in the samples or in the carbon dioxide used. Since a difference in the water content of the carbon dioxide could be a highly important factor the water contents in the two cylinders were determined (the details being given in the Appendix on p. 119-20), and were found to be 0.0622 and 0.0647 mg./g. the latter being for the carbon dioxide used for Batch c-2. It is not known whether this 4% greater water concentration could account for a 25% lower surface area or not.

The carbon dioxide used was the Matheson Company's Bone Dry grade, which according to their literature has a minimum purity of 99.8 mole %, or a typical analysis as follows; 99.95% carbon dioxide, 0.05% nitrogen and oxygen, a dew point of -30°F., and less than 5 p.p.m. of oil. This dew point corresponds to about .095 mg. water per g. carbon dioxide; however, it has been pointed out (84) that a more typical value is .038 mg./g. As can be seen, the determined value falls within this range and is therefore a reasonable estimate. This value may be compared with the solubility of water in liquid carbon dioxide of 0.9 mg./g. (46) and the generally attained water content of dried methanol of less than 0.01 mg./g. Since the supplier does not have the facilities to furnish carbon dioxide with a lower water content (85) it was decided to dry the liquid carbon dioxide by passage through a drying tube before entering the sample.

This drying tube was a stainless-steel vessel filled while hot with about 3 inches of activated coconut charcoal, 3 inches of phosphorus pentoxide, and 2 inches of oven-dried absorbent cotton. A plug of oven-dried glass wool was placed between each component. The activated coconut charcoal was included, as suggested (85), in order to remove any oil in the liquid carbon dioxide.

Drying the carbon dioxide in this manner gave an average surface area of 49.5 sq. m./g. for Sample c-2e. This is a definite improvement over the 39.4 sq. m./g. and is quite close to the other values.

After soaking the sample in water and oven drying it was found to have charred severely in several places. Although no solubility data could be found for phosphoric acid in liquid carbon dioxide, that for 95% sulfuric acid is very nearly that of water (44). It appears that the water in the liquid carbon dioxide was merely converted to phosphoric acid in the drying tube and some of this was carried into the cotton sample. This may be the reason that a still higher area was not obtained.

Since cellulose itself is very hygroscopic it appeared that carefully oven-dried cotton may be able to remove some water from the liquid carbon dioxide. Absorbent cotton and glass wool were oven-dried at 105°C. for 24 hours, followed by 12 hours in a vacuum oven at the same temperature. Evacuation was continuous through a methanol Dry Ice trap except when the oven was flushed six times with hot phosphorus pentoxide-dried air. The hot stainless steel vessel was loaded as rapidly as possible in order to minimize the adsorption of water vapor. Three plugs of the hot cotton separated from each other by glass wool were used. The vessel was fitted with a rubber stopper and outgassed through the cold trap until it cooled. Dried air was then added to the vessel and it was sealed and installed in the apparatus.

Drying the liquid carbon dioxide by means of the oven-dried cotton yielded an average surface area of 23.8 sq. m./g. for Sample c-2f. It would appear that enough moisture was present in the cotton so that the carbon dioxide probably increased in water content.

It becomes quite evident at this point that the water content of the liquid carbon dioxide is an extremely important factor in determining the final surface area of a CP-dried sample, and that a small difference in this water content is likely to have a considerable effect on the area.

It should be noted that the 49.5 and 23.8 sq. m./g. were obtained with a 45°C. removal temperature compared to 36°C. for the other areas. Although other variables were involved it is concluded from this that there is no evident change in results by increasing the removal temperature.

WATER-VAPOR-ADSORPTION ISOTHERMS AND AREAS

The procedure for the determination of the water-vapor adsorption isotherms has already been given on p. 32-4. The results are shown in Fig. 9 where W_{ads} is the weight of equilibrium moisture per gram of the phosphorus pentoxide-dried cotton, P is the vapor pressure over the saturated salt solution, and P_0 is that over pure water at the same temperature. Numerical data are given in the Appendix in Tables XIX to XX on p. 151-3, where the initial desorption, adsorption, and second desorption are designated respectively by D_1 , A , and D_2 . In Table XX, p. 153, the adsorption values are listed in the same order as the sample letters.

It has already been pointed out that from 3 to 83 days were required for an acceptable "equilibrium". This long time has also been noted by other workers using salt or sulfuric acid solutions, who report 6 to 60 days for somewhat less severe "equilibrium" criteria (86, 87).

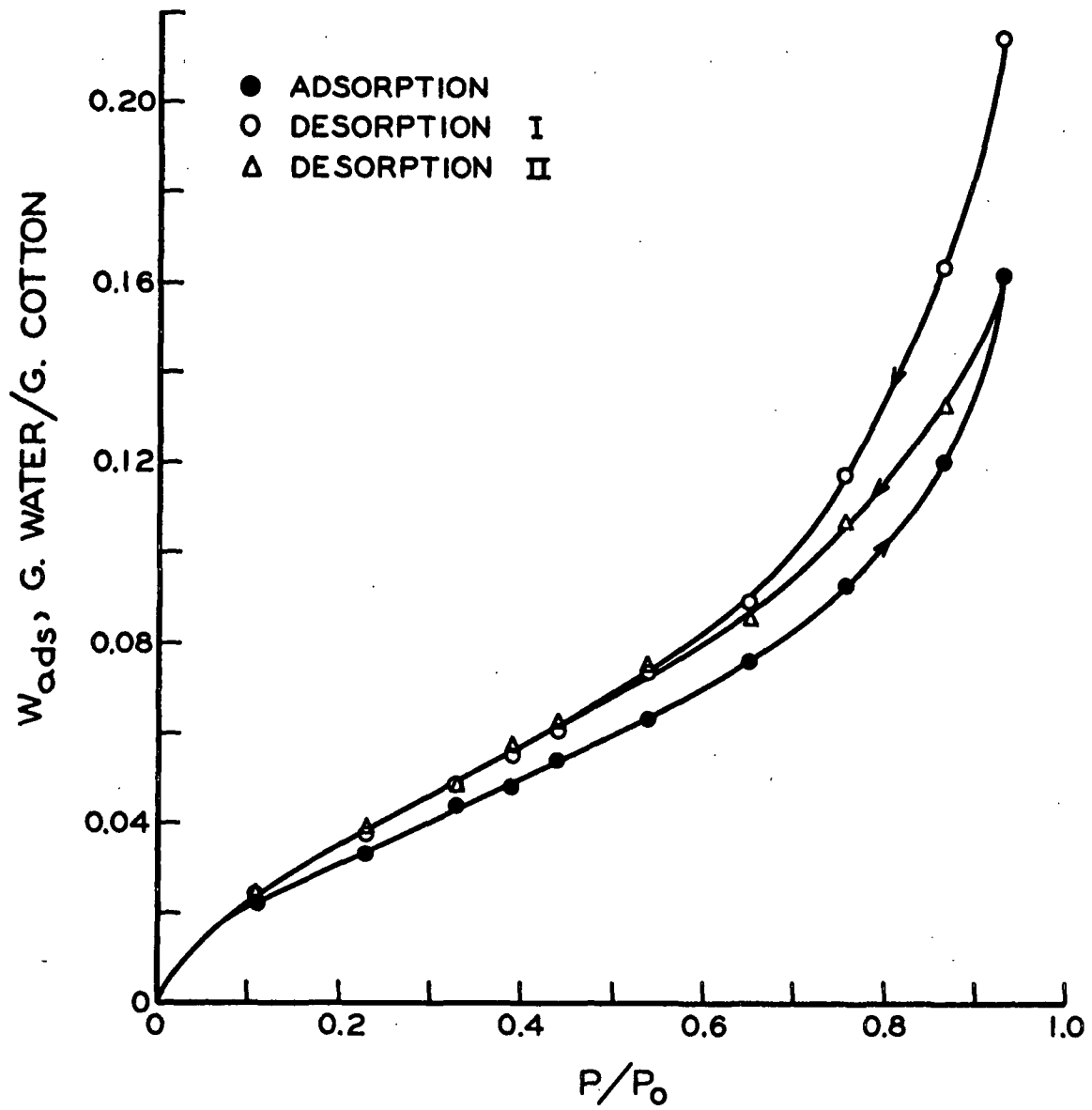


Figure 9. Water-Vapor-Adsorption-Desorption Isotherms

Both the adsorption isotherm of Rowen and Blaine (88) for a cotton yarn and the adsorption and desorption isotherms of Jeffries (89) for a cotton stabilized by several adsorption-desorption cycles at 90°C., generally give lower moisture contents than found in this study. Excluding a few of their points at the low and high relative humidities, their results were from 0 to 9% lower. A brief comparison with the data of Urquhart and Williams (86) also shows generally good agreement.

The main reason for the determination of these isotherms was to obtain the water-vapor adsorption areas. These were calculated from BET plots using the four points for the relative humidities from 0.111 to 0.392, as shown in Fig. 10. The areas were calculated from the data by determining the slope and intercept by the least squares method. The areas were determined using 10.5 sq. A. as the cross-sectional area of the adsorbed water molecule and are given below:

128 sq. m./g. for adsorption,
136 sq. m./g. for the initial desorption, and
140 sq. m./g. for the second desorption.

These values compare with 99 sq. m./g. as reported by Stamm (90) and 113 sq. m./g. as determined by Rowen and Blaine (88). Both of these values were for adsorption on cotton and have been corrected to the cross-sectional area of the water molecule used here.

The selection of a value for the cross-sectional area of the water molecule presented a problem. Generally, values are used which give the same surface area as nitrogen on a nonporous solid. Various values have been used ranging from 10.0 to 14.8 sq. A. (88, 90-93). Since the generally accepted value for the cross-sectional area of the nitrogen molecule is 16.2 sq. A., as calculated from

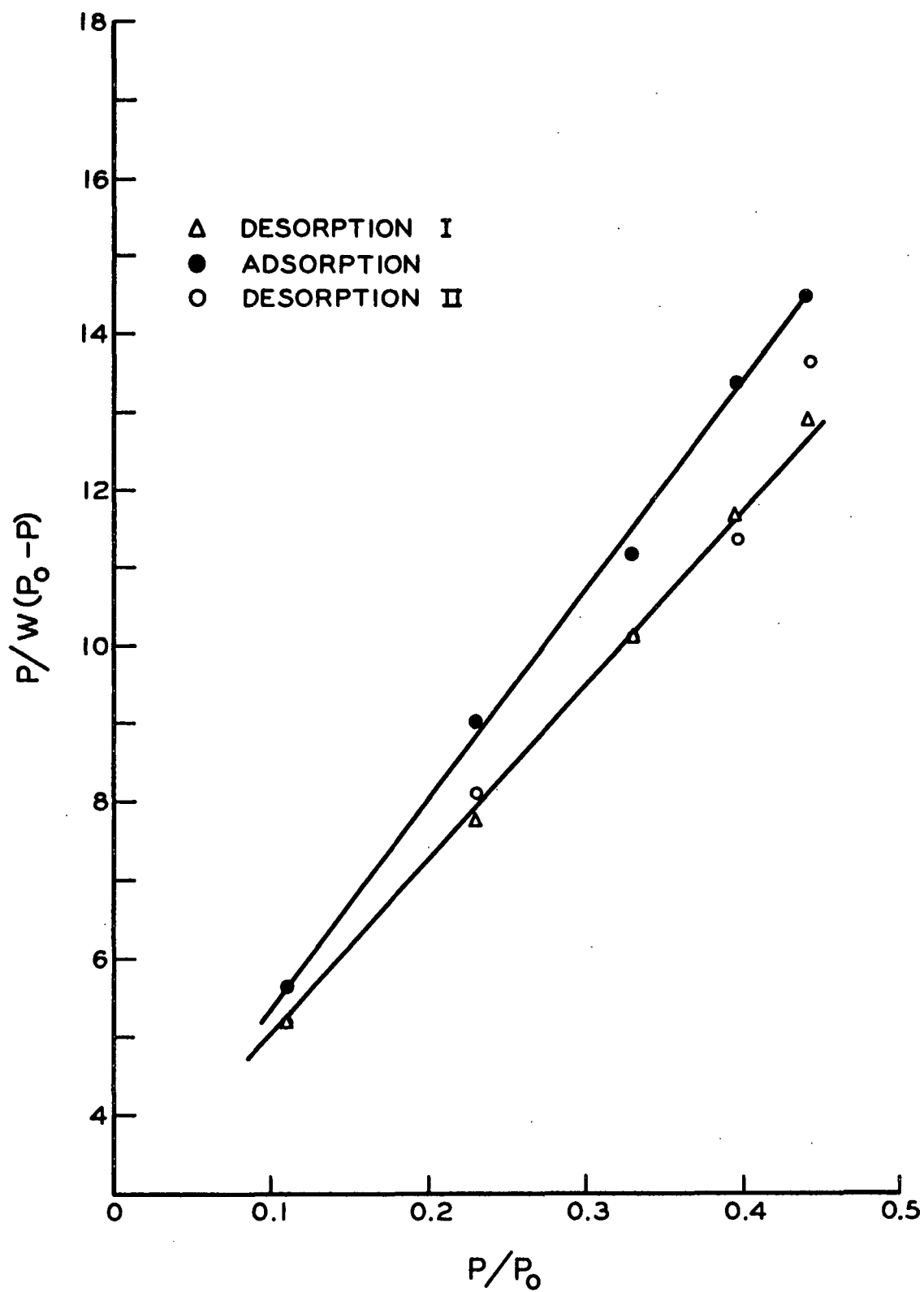


Figure 10.. BET Plots for Water-Vapor Adsorption

an equation of Emmett and Brunauer (94)*, the value of 10.5 sq. A. for the water molecule as calculated from the same equation was accepted. Use of a higher cross-sectional area will give proportionately higher surface-area values.

In comparing the surface areas determined by water-vapor adsorption to those determined by nitrogen adsorption on dried cellulose and other swelling systems, Rowan and Blaine (88) suggested four ways of accounting for the much greater "water" areas:

1. The sites that adsorb water are not restricted to a free surface.
2. If the water-adsorbing sites are restricted to a surface, there may be an additional internal surface specific to certain adsorbates as well as an external surface.
3. The internal surface within the fibrous structure exists only in the presence of a swelling agent such as water.
4. The smaller diameter and the polarity of the water molecule enables it to penetrate into capillaries not accessible to the nitrogen molecule.

Stamm (90) considers the water-vapor adsorption by materials such as cellulose as the result of formation of a solid solution through replacement of molecular contacts between structural units of the cellulose by molecular contacts between solid and condensed vapor. He aptly refers to such areas determined by the BET theory for water-vapor adsorption as "molecular contact areas". In addition to considering the areas between gels and adsorbed vapors in swelling systems, he also determines the molecular-contact areas between solute and solvent in solutions, such as for the adsorption of water vapor by sulfuric acid.

It is therefore not too clear just what relationship this "water" area has to that determined by nitrogen adsorption for the dried sample. The water-vapor

* See Equation (9) on p. 134 of this thesis.

adsorption area is probably a good measure of the area available to water molecules in an aqueous medium. It is doubtful however whether this is the area which is available to a solute molecule in the water-cellulose system unless this solute molecule is quite similar to water in size and attraction to cellulose.

The main question is whether this area which is available to water vapor could in some way be retained in the dry state with respect to nitrogen accessibility. The experimental evidence of this study indicates that elimination of surface tension effects does not yield a dry surface area of the degree found by water-vapor adsorption. Either factors such as the water content of the liquid carbon dioxide as mentioned above are interfering in the preparation of the expanded dry sample or else the area available to water vapor cannot be preserved in the dry state through some such reasons as those given above by Rowen and Blaine (88).

Suppose we consider for a moment water removal by way of solvent exchange as compared to water-vapor desorption. Let us also assume that a very close relationship exists between the cellulose and water, such as the postulated solid solution. When water molecules are removed into the vapor phase, the space occupied by certain of the water molecules is lost through cellulose-cellulose bonding and is manifested by shrinkage and hysteresis. In the solvent-exchange procedure these water molecules are removed to the alcohol phase. It would seem possible that in the solid solution regions some of these water molecules are replaced by cellulose-cellulose bonds rather than by the methanol molecules; and similarly when the methanol is replaced by a nonpolar solvent some of the regions occupied by methanol molecules may form cellulose-cellulose bonds. It is therefore suggested that some of the water-vapor area is possibly lost during solvent exchange. It is difficult however to assess the extent of this loss.

Let us look briefly at some literature results relative to this problem. Merchant (6, 7) found a surface area of 142 sq. m./g. for a fully bleached Mitscherlich spruce sulfite pulp which had been dried from n-pentane at 36°C. For a bleached sulfite pulp, Stamm (90) has reported a water-vapor adsorption area of 202 sq. m./g., or when corrected to a cross-sectional area of 10.5 sq. A. for the water molecule, an area of 144 sq. m./g. Based on the 202 sq. m./g., Stamm (90) points out that the failure of Merchant (6, 7) to obtain this value by drying from pentane is probably due to shrinkage when an unreplaced monolayer of alcohol is removed. More will be said about this monolayer later, but the important thing to point out here is that it appears possible, on the basis of this comparison, to approach the water-vapor area very closely by drying from pentane. However, it is the basis for the above comparison that is questioned; i.e., can the results for two different pulps studied in two different laboratories be logically compared? It is believed that such a comparison must be made with careful reservation.

Campbell (22) has shown that beating of a pulp, even to the point of producing a highly parchmentized sheet, has a relatively insignificant effect with respect to the water-vapor-adsorption curves. Thus, the water-vapor area is also not significantly changed by beating. On the other hand, the surface area as determined in an aqueous medium by the silvering technique (12) or by nitrogen adsorption on pentane-dried samples (9) shows a marked increase with the degree of beating. This latter work of Thode, Swanson, and Becher (9) shows an increase in surface area from 100 sq. m./g. to 202 sq. m./g. for a papermaking grade of bleached sulfite pulp when beaten in a ball mill for 250 minutes.

The effect of relatively mild mechanical action was noted by Merchant (6). Starting with dried pulp he soaked two samples in water for 48 hours, and

WAN-dried them from n-pentane. One sample was stirred during the 48-hour interval and it had an area of 91.9 sq. m./g. compared to 66.7 sq. m./g. for the unstirred sample--an increase of 38%. In comparing the results of a second batch of pulp which had been secured at the same time but which was given a separate but similar washing treatment, he found consistently higher areas. For two samples dried from n-hexane under nearly identical conditions, the sample from the second batch gave an area of 96.3 sq. m./g. compared to 74.6 sq. m./g. for the sample from the first batch--an increase of 29%. Merchant attributed the difference to a variation in the mechanical treatment when slurried with a Lightnin' stirrer. It thus becomes quite evident that mechanical action can readily affect the area retained in a dry state by solvent drying but that the water-vapor area is relatively independent of such treatment.

The above discussion should make it clear that a comparison of WAN-dried areas of one worker with water-vapor areas of another is certainly not valid since besides the variation in the nature of the pulp there is an additional factor regarding the mechanical treatment of the WAN-dried sample. Furthermore, it would appear that water removal by either a vapor or liquid phase will cause a loss of area, the extent of which is, however, not known.

The water-vapor-adsorption areas reported above, therefore, cannot be taken as a measure of the effectiveness of a solvent-exchange procedure without also considering the nature of the areas and the extent of mechanical treatment that the solvent-dried sample has received. In this work the cotton has had a minimum of any such treatment, and therefore according to the above-cited evidence cannot be expected to give the same surface area by both water-vapor adsorption and by drying from a solvent with little or no surface tension. In addition to this the water content of the liquid carbon dioxide appears to be most important in determining the area which is retained.

SOLVENT-DRIED AREAS

Two samples were dried from n-pentane according to procedures discussed on p. 11-13 and 24-6 and were found to have average surface areas of:

46.8 sq. m./g. for Sample c-2bw, and

51.8 sq. m./g. for Sample c-2cw.

Complete details of these and all solvent-dried samples are given in Tables IX to XII in the Appendix on p. 141-4.. The lower area for Sample c-2bw is likely due to a lower drying temperature since although it was dried at room temperature it was found to cool considerably during the initial stages. Sample c-2cw was dried by immersing the bulb in a water bath at 25°C. and hence the effective drying temperature was higher.

It is rather surprising that drying from n-pentane gives essentially the same surface area as the CP-method. Since, in one case, we have surface tension effects and in the other case we should not, and yet the same surface area is obtained, it would appear that something is affecting the area preservation other than the final liquid. This fact along with the strong evidence presented earlier on p. 46-9 regarding the dependence of the final CP-area on the water content of the liquid carbon dioxide, certainly makes it clear that factors other than the surface tension of the final liquid are extremely important. The evidence also suggests that the unreplaced water and also probably any unreplaced methanol can become the determining factors in the surface area once the surface tension of the final liquid has been reduced close to that of n-pentane (15.5 dynes/cm. at 25°C.). It is interesting to note in this respect that before selecting methanol to replace the water, Merchant (6) also tried ethanol and

propanol. Using the same solvent-exchange procedure and drying from n-pentane at room temperature he obtained the surface areas shown in Table IV.

Merchant (6) attributed the lower areas either to the inability to dry the higher alcohols as effectively or to molecular association of the alcohols thus resulting in less water replacement by the larger molecular species. It is interesting to note that the total residual solvents (95), as defined on p. 30 also increased with molecular size even though the final solvent and drying conditions were identical. More will be said about this later.

TABLE IV

RESIDUAL AND SURFACE AREA DATA OF MERCHANT (6, 95)

Intermediate Alcohol	Sample Designation	Surface Area, sq.m./g.	Residual Solvents, % w/w
Methanol	E-44	129	1.3
Ethanol	E-20	108	1.66
Propanol	E-22	103	1.82

These results of Merchant (6, 95) along with the evidence already noted in this study lead to the conclusion that the degree to which the water and/or alcohol is replaced is a significant variable in determining the final surface area.

Merchant (6, 7) found that drying from benzene gave a lower area than drying from n-pentane; presumably due to the higher surface tension of the benzene. For comparison, his areas for drying under similar conditions were 43 sq. m./g. for benzene and 129 sq. m./g. for n-pentane. Since there appeared to be the possibility that part of this difference might be attributed to the

degree to which the methanol is replaced by the final solvent two samples were WAN-exchanged by the writer and dried from benzene under the same conditions. In one sample, however, immediately following the exchanges to methanol, ten exchanges of n-pentane were included before the final benzene exchanges. In both cases the total number of nonpolar solvent exchanges were the same. It was suspected that n-pentane may be more effective in methanol replacement and if this were true the area for the sample with the n-pentane exchanges should give a higher area even though both are dried from benzene at the same surface tension. The average surface areas for these two runs were:

24.8 sq. m./g. for Sample c-2hw, and

18.4 sq. m./g. for Sample c-2gw,

the former being the sample with the n-pentane exchanges. There can be little doubt therefore that unreplaced liquids play an important role in determining the surface area of a dried sample.

LITERATURE AREAS FOR SOLVENT-DRIED COTTON

Assaf, Haas, and Purves (34) found that cotton linters which had been swollen in 10% sodium hydroxide and then solvent-exchanged through methanol and dried from benzene gave BET surface areas of 53.0 and 64.7 sq. m./g. Their solvents were dried either with sodium or by refluxing over magnesium and then distillation prior to use. To minimize the contact with atmospheric moisture their procedure involved "quick manipulation during the transfers" from solvent to solvent.

Hunt, Blaine, and Rowen (35) studied a chemical cotton which had been digested with dilute alkali and bleached. With no further treatment they found BET areas

of 0.5 and 0.6 sq. m./g. When drying a water-swollen sample from benzene according to the procedure of Assaf, Haas, and Purves (17) they found areas of 46.5 to 47.3 sq. m./g. Similarly, for a sample swollen in 10% sodium hydroxide the areas were 67.7 to 71.3 sq. m./g. Forziati, Brownell, and Hunt (36) studied the effects of swelling for a variety of cottons. They solvent exchanged with an apparatus similar to Merchant's (6, 7), dried from benzene or n-pentane, and determined BET areas. The results for drying from n-pentane at 0°C. gave surface areas of:

21 to 34 sq. m./g. for water-swollen cotton,

45 to 48 sq. m./g. for 1% sodium hydroxide
swollen cotton, and

100 to 148 sq. m./g. for cotton mercerized
without tension.

Water-dried raw cotton gave areas of 0.3 to 0.7 sq. m./g.

The values for 1% sodium hydroxide-swollen cotton are in agreement with the values obtained in this study.

ISOTHERMS AND PORE-VOLUME DISTRIBUTIONS

Complete nitrogen-adsorption and desorption isotherms were determined for three samples, namely:

c-2bw (46.9 sq. m./g., dried from n-pentane).

c-2f (23.8 sq. m./g., CP-sample using cotton-dried
carbon dioxide), and

c-2j (39.4 sq. m./g., CP-sample using undried carbon
dioxide).

All three gave Type II isotherms (96)* and the hysteresis characteristic of porous materials. These are shown in Fig. 11 with the data being given in

* p. 150.

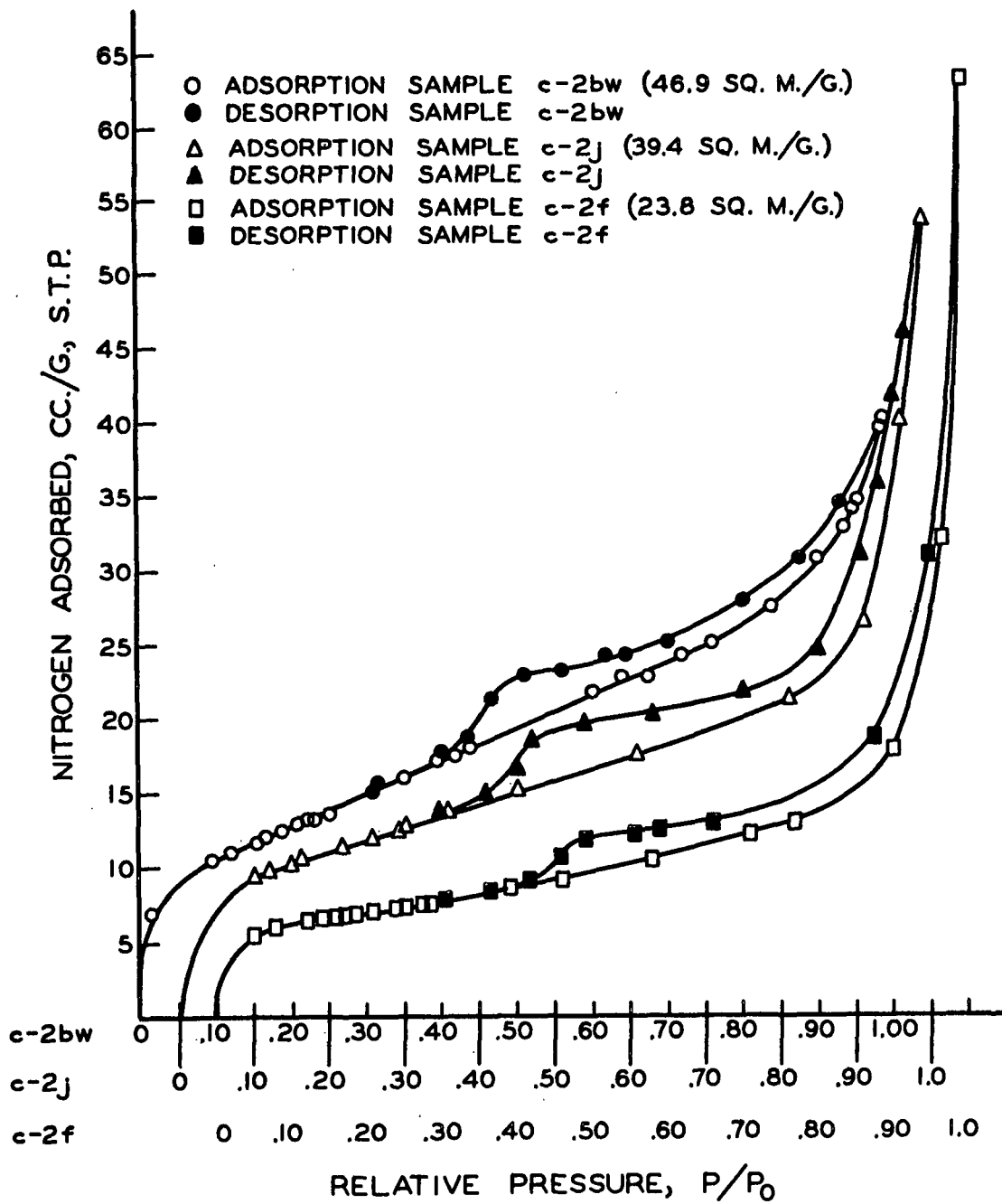


Figure 11. Nitrogen Adsorption Isotherms

Table XXI in the Appendix on p.154 . It should be noted that since the CP-isotherms cross the solvent-dried isotherm the x-axis has been shifted in the figure for greater clarity. These isotherms are very significant. Over most of the relative pressure range they are in the same order as the surface areas; however, above a relative pressure of about 0.9 the low-area CP-samples adsorb more strongly. This indicates that the CP-samples have retained more volume in the large-pore region than the pentane-dried sample. This is unlike the results of Merchant (6, 7) where isotherms for samples dried from n-pentane, cyclohexane, and benzene were in the same order as the respective surface areas over the whole relative pressure range. The main effect of CP-drying therefore seems to be in the large-pore range.

The total pore volumes for the samples, determined at a relative pressure of 0.971 are:

0.0616 cc./g.* for Sample c-2bw (46.9 sq. m./g.),
0.0745 cc./g. for Sample c-2f (23.8 sq. m./g.), and
0.0752 cc./g. for Sample c-2j (39.4 sq. m./g.).

The selection of the relative pressure of 0.971 for the determination of the total pore volume was based on considerations and evidence of Merchant (6) which indicated that this is probably close to the point where most of the internal pores are filled and condensation starts to take place between fibrous elements.

Hunt, Blaine, and Rowen (35) and Haselton (4, 5) determined nitrogen isotherms for both water-dried and benzene-dried samples. Water-swollen

* Note that these volumes are in liquid cc., whereas all other volumes as reported for isotherms or pore-volume distributions are given in cc. of gas at S.T.P. The latter can be converted to liquid cc. by the multiplication factor, 0.001558.

and 10%-alkali-swollen cotton linters (35) and chlorite holocellulose and 5% potassium hydroxide-extracted chlorite holocellulose (4, 5), when dried from benzene gave what appeared to be Type IV isotherms. When dried from water they gave Type II isotherms without hysteresis. When Hunt, Rowen, and Blaine (35) conditioned the alkali-swollen cotton linters at 20 to 25% relative humidity there was still a Type IV isotherm, but when conditioned to 70 to 75% relative humidity a Type II isotherm resulted. No explanation was offered for this but it is probably associated with the relative effects in the different pore-size regions. Merchant (6, 7) determined isotherms for two pentane-dried samples, one of which had been dried previously from water and then resoaked. The latter isotherm, because of the lower surface area, fell below the other over the complete relative pressure range. Because the previously water-dried sample showed a much less rapid increase in adsorption at higher relative pressures, Merchant (6, 7) logically suggested that the fiber structure was different primarily by virtue of fewer large pores. This would indicate that the irreversible loss of structure occurred to a great extent in larger pores. This seems reasonable since water drying is known to destroy the pore structure. Reswelling in water may redevelop the small pores but difficulty probably arises in the larger pores because of the larger dimensions which are involved. On the basis of the above discussion it is evident that different drying conditions including the previous history of a sample, as well as exposure to different relative humidities, has an effect on the pore structure to different degrees in the different pore sizes. As pointed out in an earlier section, however, it is difficult to compare results from different workers.

A common procedure to obtain further information from nitrogen isotherms for porous materials is to calculate the pore-volume distributions. Various methods

have been advanced for this procedure, all of them being based on the idea of capillary condensation. The procedures have certain limitations and objections but in general useful relative information is obtained. The calculations were made according to the method of Pierce (97) using his more recent multilayer values (98) and 3.53 Å. as the thickness of a single layer. The desorption isotherm was used in all of these calculations. Further discussion of this and other methods along with reasons for certain selections are given in the Appendix on p. 128-35.

The cumulative pore volumes and cumulative surface areas as a function of pore radius, and the pore volume distribution, are given in Fig. 12 to 14. The numerical values are given in Tables XXII to XXIV in the Appendix on p. 155-7.

The cumulative pore volume in Fig. 12 shows even more clearly the effect already evident in the isotherms; i.e., that the CP-samples have retained more volume in the large pore region than the pentane-dried sample. The same effect can be seen in the cumulative surface area relationship as shown in Fig. 13. It should be pointed out that the cumulation in Fig. 12 starts at the small-pore region whereas in Fig. 13 it starts at the large-pore region. The choice of a starting point is rather arbitrary; however, in the case of Fig. 13 the effect is not as readily apparent when plotted from the other direction. It can be concluded that the CP-method gives samples in which the large-pore structure is better retained than when dried from n-pentane. In the small-pore region the converse is true.

In addition to the difference between the CP-samples and the pentane-dried sample, there is also a difference between the two CP-samples themselves. It will be noted that the lower-area CP-sample involved passage of the liquid carbon

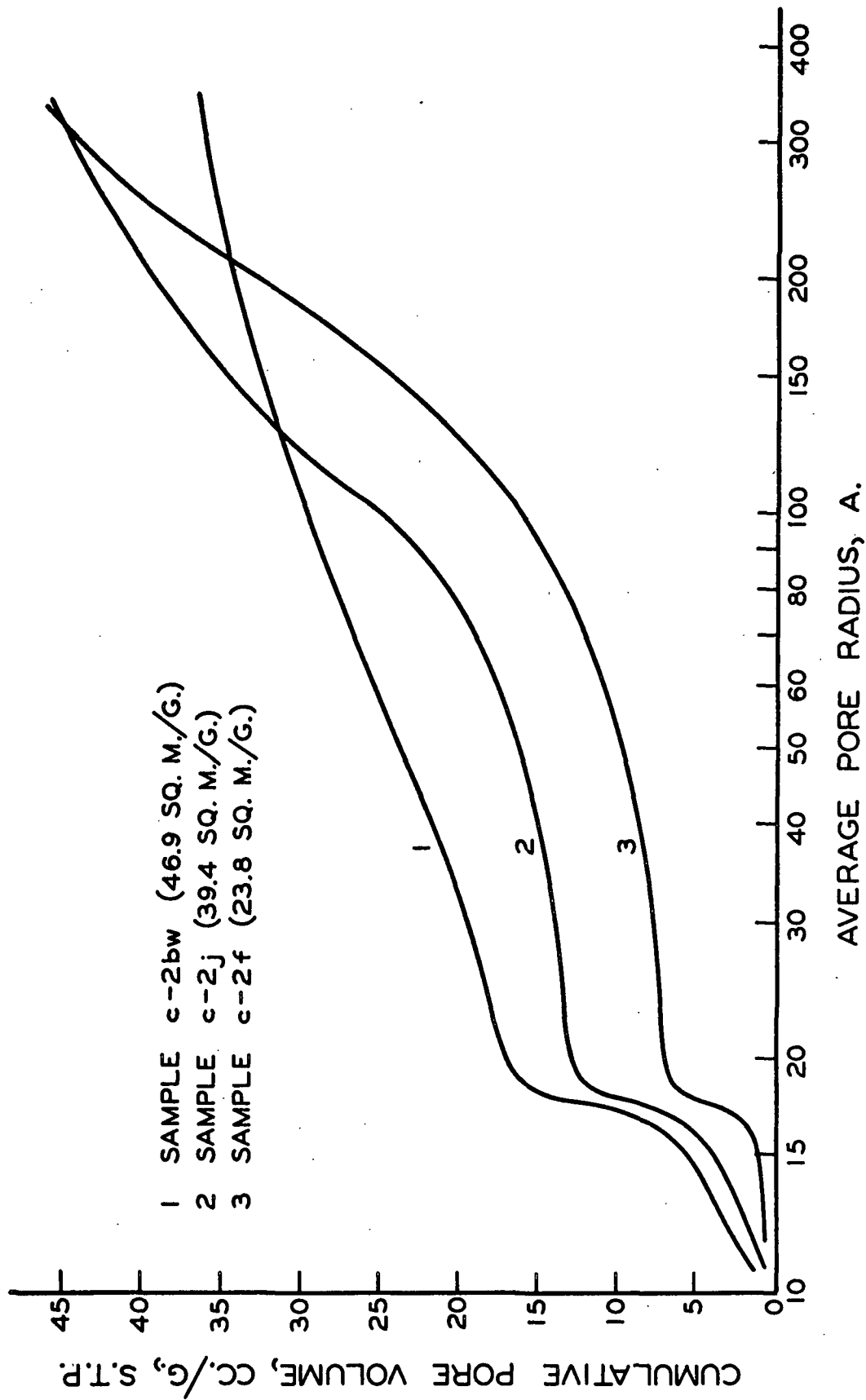


Figure 12. Cumulative Pore Volume

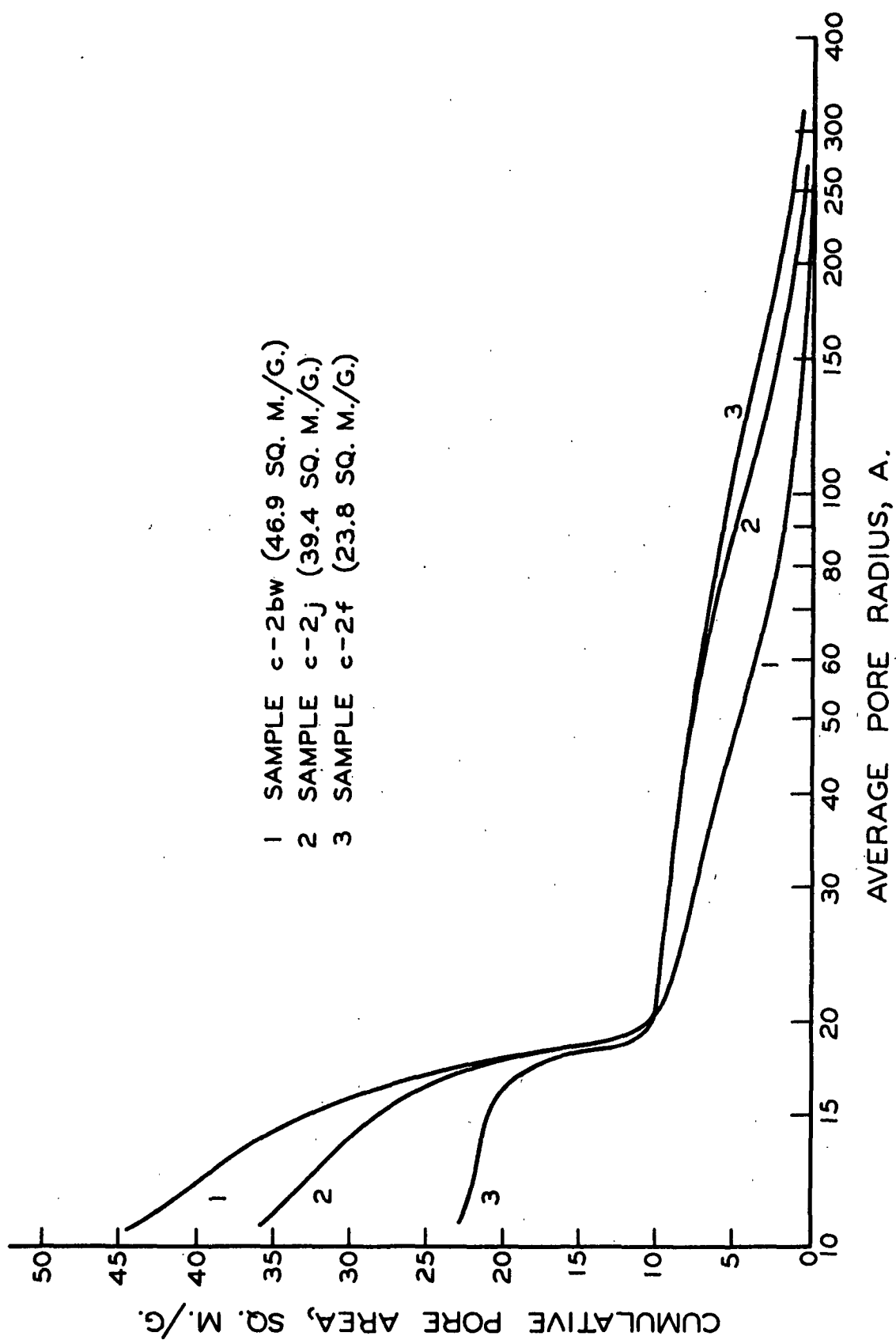


Figure 13. Cumulative Pore Area

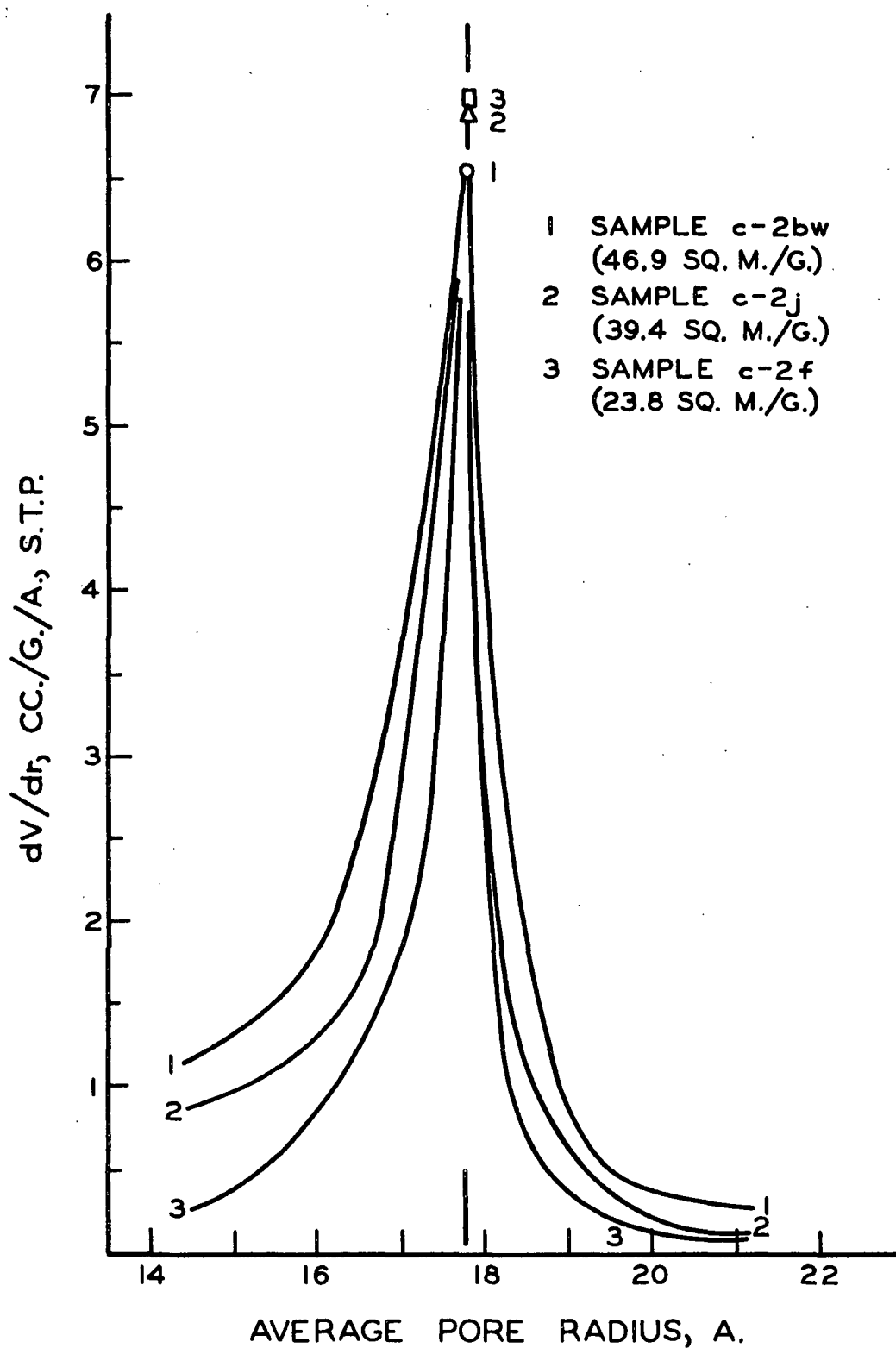


Figure 14. Pore Volume Distribution

dioxide through oven-dried cotton and also a removal temperature of 45°C. compared to 36°C. for the other sample. The main difference lies in the small-pore region and this difference has been attributed to the water content of the sample. Above about 100 A. radius the lower area sample has considerably greater volume. The corresponding area is only slightly larger because for these larger pores the area-to-volume ratio is quite small and the difference is not as apparent. That most of the area is present in the small-pore region is evident from Fig. 13. It would seem that the extra water present caused a lower volume in the small-pore regions but that the higher removal temperature caused a greater volume in the larger pores. The total pore volumes in both cases were quite similar.

The pore-volume-distribution curve in Fig. 14 was determined by taking the slopes, $\frac{dV}{dr}$, of a large-scale plot similar to Fig. 12. The area under this curve is a measure of the pore volume and for a unit width the height gives a measure of the volume.

It is interesting to note that the most common pore size is identical in all three cases; namely a little less than 18 A. in radius. It is also interesting that the pore volume in a small range about this pore size is essentially the same for the three samples.

Other workers also examined the pore-volume distributions for various cellulosic materials. Hunt, Blaine, and Rowen (35) applied the method of Wheeler (99) and Shull (100) to the desorption isotherms for three cotton linter samples which were dried from benzene. The sample swollen in 10% alkali and a similar sample reconditioned to 20 to 25% relative humidity both showed a maximum in the distribution function, $\frac{dV}{dr}$, at a pore radius of 20 A. The curve of the reconditioned sample was slightly narrower and had a maximum in the distribution function of

of 8.8 cc./g./A.* compared to 16.2 cc./g./A. for the sample not exposed to moisture. For the water-swollen sample the maximum was slightly broader at 5.5 cc./g./A. and 16 A. pore radius.

Haselton (4, 5) also used the Wheeler (99) and Shull (100) method but he used the adsorption isotherm. The most common pore radius for his chlorite holocellulose was 19 A. whereas after extraction with 5% potassium hydroxide it was 22 A. with the total volume being slightly greater. In both cases the samples were dried from benzene. Haselton (4, 5) attributed the increase in the most common radius to either the dissolving of "material containing pores of smaller than average size" or to removal of "hemicellulosic materials from the cellulose structure thus enlarging the existing pores to some extent." Considering the results of Hunt, Blaine, and Rowen (35), this increase might have been due to swelling in the 5% alkali.

Merchant (6) and Thode, Swanson, and Becher (9) applied the original method and constants of Pierce (97) to the desorption branch of solvent-dried wood pulps. Merchant (6) determined pore-volume distributions for his bleached spruce sulfite pulp which had been dried from n-pentane, cyclohexane, and benzene. All three distribution curves showed maxima at 19 A. radius, with distribution functions being respectively 76, 33, and 12 cc./g./A. Thode, Swanson, and Becher (9) also found the most common pore radius for their bleached sulfite pulp to be 19 A. This value did not change significantly with their ball mill beating of up to 250 minutes. The total pore volumes in the pore radius range of 16 to 22 A. increased very little with beating whereas that in the 40 to 100 A. range more than doubled.

* All values for $\frac{dV}{dr}$ involve the volume of adsorbed gas in cc. at S.T.P.

It may be concluded from the above experimental results and literature discussion that the pore volume as located in either small pores or large pores is affected differently by mechanical action and by varying conditions of drying.

MOST COMMON PORE SIZE

Thode, Swanson, and Becher (9) have suggested that the most common pore size may be characteristic of the fine structure of cellulose fibers. They further suggested that the elementary building blocks of "solid" cellulose are "laid down in some sort of array (e.g., hexagonal) permitting the regular occurrence of 'holes' approximately the size of an elementary polymer unit."

One such arrangement of hexagonal close packing might consist of cellulosic elements of 36 A. in diameter. An occasional vacancy of an element would leave a pore of 18 A. in radius. Another hexagonal arrangement might consist of close-packed elements of 230 A. in diameter which would leave between every three such elements an inscribed cylinder of 18 A. in radius. A square arrangement of 87 A.-diameter elements would also enclose an inscribed cylinder of 18 A. in radius.

In order to see if these dimensions are consistent with experimental evidence the literature must be consulted. By the use of the electron microscope Frey-Wyssling (101) has been able to observe fibrils of 150 to 250 A. diameter in native celluloses. These can however be further reduced in size by means of hydrolysis, oxidation, or ultrasonics to flat filaments of 70 to 90 A. in width by as low as 30 A. in thickness. Microfibrils in this lower range have been reported by Kinsinger and Hock (102) who used a Waring Blendor for disintegration and by Rånby (103) who utilized ultrasonics. Recently two Russian workers (104) using an abrasion technique in polar liquids have reported microfibrillar bundles

of sixty to several hundred A. in thickness. Frey-Wyssling (101) has postulated a "paracrystalline cellulose" as being responsible for an aggregation of the small elementary fibrils to the larger fibrils or fibrillar bundles. All workers do not however agree with this concept (105, 106).

The most recent discussion of microscopic and fine structure has been given by Rollins and Tripp (1) and gives a good picture of the complex porous structure of cellulose.

It has been pointed out by Ward (107) that the persistence of the most common pore size with extensive beating (9) is consistent with the above discussion since beating apparently does not supply enough energy to break down the fibrillar bundles to the smaller elementary fibrils.

Considering the three suggested values of cellulosic elements, 36, 87, and 230 A. in diameter, it would seem that the latter value is the most compatible with literature observations. Although the hexagonal close packing of cellulose fibrils of 230 A. in diameter could account for the most common pore size, the evidence presented here should not be construed as a suggested proof of such an arrangement, particularly in view of the oversimplified model involved in the pore-size calculations; namely that of cylindrical pores.

RESIDUAL SOLVENTS

Residual solvents have already been defined as those which remain after outgassing and surface area determinations. This residual may consist of the final solvent or intermediate solvents. In the latter case such residual can only arise from incomplete replacement.

The results of the residual determinations are given in Table V.

TABLE V
RESIDUAL DATA

Sample	H ₂ O, ^a cc.	Methanol ^b from Extract, %	Methanol from Condensate, %	Methanol, total %	Residual, total %
c-2bw	80	0.00	--	0.00	0.64
c-2cw	75	0.11	--	0.11	0.67
cc-2gw	35	0.088	0.00	0.088	2.67 (1.81) ^c
c-2hw	35	0.064	0.00	0.064	1.44
c-1a	350	1.6 ^d	--	1.6	0.01
c-1b	50	0.24 ^e	--	0.24	0.54
c-1c ^f	00	--	--	--	0.57
c-2a	50	0.12	0.07	0.19	0.26
c-2e	35	0.033	0.023	0.055	--
c-2f	35	0.13	0.06	0.19	0.053
c-2j	35	--	0.045	0.045	0.066

^aAmount of water that the cotton was soaked in.

^bAll percentages are on the basis of the outgassed weight of the cotton.

^cA check of the outgassed weight was always made. In this case the two values did not agree and therefore both possibilities are given.

^dRedetermination at a later date showed only a trace.

^eRedetermination at a later date could not detect any alcohol.

^fSee p. 122 for a discussion of this sample.

There are several possible reasons for the considerable variation in the total residuals. (1) The sample size was generally about 2 grams and hence the actual weight of the total residual was only in the range of milligrams, thus limiting the precision of the determination. Static electricity effects were

also troublesome during some of the weighings. (2) Although care was taken in removing the CP-samples for the determination of the outgassed weight, some moisture could have been picked up. (3) The variation in the time of outgassing may also directly affect the total residual as well as the methanol residual.

Despite these limitations several conclusions appear possible. The pentane-dried samples appear to have a greater total residual than the CP-dried samples, and the highest total residuals of all occurred with the benzene-dried samples.

Again, the methanol residuals show no obvious pattern. In some cases they even exceed the total, most likely due to experimental error in determining these small quantities. The important fact, however, is that methanol has been found to be present as a residual solvent, thus indicating incomplete replacement.

The determination for residual carbon dioxide for Sample c-1a showed that within the experimental error of the method none was present.

The odor of benzene was quite evident when benzene-dried samples were soaked in water. In the case of pentane-dried samples, however, the odor could not be identified. It is believed that this peculiar odor may have been the result of both methanol and pentane.

It is interesting to note that resoaking and oven drying Sample c-2cw after determination of the total residual lead to an additional loss in weight of 0.11%. It appears that a single wash is not sufficient to remove all the residual.

Numerous workers (6, 7, 108-114) have found that when fibrous or cellulosic materials are dried from organic liquids a small percentage of the liquid cannot be removed even by high vacuum or oven drying. It can be removed by washing in water, however. In most cases the amounts of these residuals were determined

gravimetrically but, in two cases at least, chemical methods were also used (110, 114). The results are not always in agreement. For example, contrary to results of others (6, 7, 112-114), Wiertelak and Garbaczowna (110) found that benzene was not retained.

Evidence has also been presented regarding the failure to completely desorb water and alcohol. Russell, Maass, and Campbell (115) found that the amount of water retained by cellulose after vacuum drying over phosphorus pentoxide reversibly decreased with increased temperature. In studies of methanol adsorption and desorption they found residual alcohol even after prolonged evacuation. This methanol residual was found to have an inverse linear relationship to the temperature of the adsorption and desorption. Daruwalla and Shet (116) found that the method of coming to water adsorption or desorption equilibrium affects the amount adsorbed. It would seem that this might also be the case with regard to residual solvents when drying from organic liquids.

Apparently contrary to the above results Fugassi and Ostapchenko (117) found in their extensive study of the methanol-cellulose system that evacuation caused a return to a weight "practically identical" with that at the start.

The most extensive studies of residual solvents have been made by Staudinger and Döhle (114) and by Merchant (6, 7) and therefore their work will be discussed in some detail.

Staudinger and Döhle (114) studied the acetylation of mercerized and native cotton celluloses by using acetic anhydride in pyridine. They found that the degree of acetylation could be increased by a solvent-exchange procedure even when the cellulose was dried under vacuum at 100°C. for 2 days. The solvent-exchange procedure generally involved the series, water-methanol-ethyl

ether-organic solvent. They found that samples dried from organic solvents in all cases "included" a certain amount of solvent which could be removed by soaking in water and redrying. They attributed the increased reactivity particularly in the mercerized cotton to the ability of the included solvent to prevent hydrogen bonding and thus keep the structure more accessible. This is believed to occur by the entrapment of the solvent molecules between cellulose chains where they are thus prevented from moving by steric reasons. They suggest, since water "can be completely removed in high vacuum even in the cold," that the water molecules, being bound by auxiliary valence forces to the cellulose hydroxyls, can travel from one residue to the next until they are removed at the surface. This agrees with similar ideas of solvent retention suggested by Hermans. (118).

In several cases Staudinger and Döhle analyzed the "inclusion cellulose" by an elemental analysis. For a cyclohexane cellulose their carbon and hydrogen analysis leaves little doubt that the residual is cyclohexane. Pyridine celluloses were found to contain nitrogen and bromobenzene celluloses, bromine, in both cases corresponding approximately to the total gravimetric percentages actually found.

Because of the importance of their work, part of their results are given in Table VI. It will be noted that the effect was not nearly as great in the case of the native cotton cellulose. The solvent-retention values were determined gravimetrically after drying for 2 days at 100°C. in vacuo. Since the amount of methanol retained is relatively quite small, any such residual in an elemental analysis for another organic liquid could easily go unnoticed.

Merchant (6, 7) found that his surface areas gave just as good inverse linear relationships when plotted against residual as when plotted against surface tension.

Here again two different relationships were found, one for n-pentane, n-hexane, and cyclohexane and one for benzene and toluene, the latter group showing less dependence of the residual on surface area.

TABLE VI

DEGREE OF ACETYLATION AND AMOUNT OF INCLUDED SOLVENT (114)

Solvent Included	Merc. Cotton, DP-1570		Native Cotton, DP-1700	
	% CH ₃ CO	% Solvent	% CH ₃ CO	% Solvent
Nonactivating Solvents				
Water	0.32	0.0	2.36	0.0
Glycol	1.2	3.4	10.3	1.9
Methanol	1.3	0.3	10.7	0.8
Activating Solvents; water soluble, volatile				
Ethanol	21.2	2.4	9.1	1.6
Propanol	22.9	3.6	10.2	3.1
Butanol	21.4	4.0	--	--
Tetrahydrofuran	20.5	7.8	8.8	6.7
Acetone	21.3	2.5	10.6	2.0
Pyridine	23.6	6.4	11.0	2.7
Activating Solvents; water insoluble, volatile				
Hexane	19.9	4.0	11.5	4.9
Cyclohexane	20.1	8.1	10.0	3.6
Benzene	19.1	3.4	10.0	2.7
Toluene	20.3	4.6	9.1	2.8
Chlorobenzene	17.9	5.8	8.6	3.3
Bromobenzene	17.4	10.0	9.1	5.3
Carbon disulfide	23.6	3.2	9.4	3.0

Because larger surface areas were associated with small residuals, Merchant (6, 7) concluded that the residual is not held by physical adsorption because if such were the case a large area would be associated with a large residual. In this conclusion he assumes that any solvent retained by physical adsorption would

be uniformly distributed over the surface. This is doubtful. It would seem that in pores of molecular dimensions where adsorbed molecules are subjected on all sides to forces from the pore walls, physical adsorption could be the mechanism of retention. Mair (119), in his discussion of molecular sieves, points out that such molecules are so strongly adsorbed that desorption is effected only with difficulty. Brunauer (96)* presents the amounts of carbon tetrachloride which are still absorbed on activated carbon and silica gel at 100°C. after having been saturated with pure vapor at 25°C. He suggests that the difference between the 29 g./100 g. of carbon and the 2 g./100 g. of silica gel is due to differences in the heats of adsorption caused by adsorption in pores of between one and two molecular diameters. In such small pores, therefore, the forces of physical adsorption and mere steric entrapment as suggested by Staudinger and Döhle (114) and also advanced by Merchant (6, 7) are probably both involved, one complementing the other. The shrinkage caused by the surface-tension forces of the final solvent or by a deswelling during replacement could cause these pores to decrease in size around the molecules which are eventually retained. It might be mentioned in support of entrapment that such phenomena are definitely observed in "inclusion compounds" (120, 121) where crystals enclose molecules of other substances within their crystalline framework. Such compounds are used for certain analytical separations.

Merchant (6, 7) explained the lower areas with higher residuals by the larger surface-tension forces acting to bring the structure closer together. This seems reasonable when there is the same structure at the start. He also found however that water-dried pulp when redispersed and dried from n-pentane gave a lower area and higher residual than for pulp which was only pentane-dried. From the isotherms

* Page 345.

he concluded that the structure of the water-dried sample was different by virtue of having fewer large pores and hence if two samples have equal areas the one with the larger pores will retain less residual. Note that there were fewer small pores too. Merchant's (6) only suggestion as to why the water-dried sample should retain more residual was that there must be a change in the size or shape of the pores since the number would certainly not increase. It may be, however, that the number of a particular size range did increase through shrinkage of larger ones and that this size is more effective in retaining solvents.

Table IV, on page 58, shows another interesting point regarding some previously unpublished residual data of Merchant (95). It would seem that the intermediate alcohol may both cause a smaller area and a larger residual. It is possible that the increase in total residual is actually due to a greater alcohol residual. It is interesting to compare this with the alcohol residuals of Staudinger and Döhle (114) in Table VI, where it will be seen that the residuals, when dried from the respective alcohol, increase in the same order as when they are used as intermediates. This certainly suggests retention of the alcohol itself and since methanol has been found in this study this seems quite reasonable.

Another interesting point regarding retention is that in the CP-method the residual cannot be the result of entrapment due to the surface tension of the final liquid since the latter has been eliminated. It may be due to a shrinkage during the solvent exchange, to surface tension of unreplaced methanol, or to physical adsorption of any of the liquids. More will be said about this in the next section.

In closing this section it can be concluded that despite elimination of the surface tension of the final liquid, residual solvents are still present. Furthermore, contrary to previous evidence and assumptions, the intermediate methanol

makes up part of this residual. This may explain some previously unpublished data of Merchant (95). This is not however inconsistent with Staudinger and Döhle's (114) results since small amounts of alcohol could have been overshadowed in their analyses. Pentane and benzene are also part of the residual where applicable but carbon dioxide apparently is not.

UNREPLACED SOLVENTS

Unreplaced solvents are distinguished from residual solvents in that they include all solvents, other than the final liquid, which are present before drying is started. Some of these unreplaced solvents are removed during drying and some are retained as residuals. The effect of unreplaced solvents shows up in the final dry area and structure.

DEGREE OF WATER REPLACEMENT

A measure of the degree and rate at which the water was replaced by the methanol was obtained by determining the water content of the dried and the displaced methanol. The procedure involved the Karl-Fischer titration and has already been described elsewhere. The results are given in Table VII with those for Sample c-2a also plotted as a function of time in Fig. 15.

The limits of the analysis were again approached and it is quite likely that the actual concentrations in some cases were less than those given in Table VII. The evidence for this is that for some of the lower concentrations only one drop of Karl-Fischer reagent was required to reach the end point. In such a case the calculated concentration would depend upon the sample size. The values given are the averages for triplicate determinations with the sample size being 15.0 ml. for the dried alcohol or CP-displacements, and 7.0 ml. for displacements of Sample c-2bw.

TABLE VII
WATER CONTENTS OF METHANOL

Sample	Displacement	Contact Time, hr. min.	Water Content of Dried Methanol, ^a mg./ml.	Water Content of Displaced Methanol, mg./ml.
c-2a	D33	25	--	0.017
	D34	25	0.017	0.011
	D35	94	0.006	0.026
	D36	25	0.015	0.015
	D37	167 30	0.015	0.039
	D38	20	0.019	0.024
	D39	337	0.019	0.0625
	D41	506	0.037	0.059
	D44	15	0.011	0.0092
c-1b	D53	3323	--	0.040
	D56	10	0.0074	0.0074
c-2bw	D15	1	0.0084	0.034
	D16	1	0.0062	0.036
	D17	4	0.0048	0.020
	D18	12	0.0070	0.0097
	D20	25	--	0.0145

^a Methanol which was added during the previous displacement.

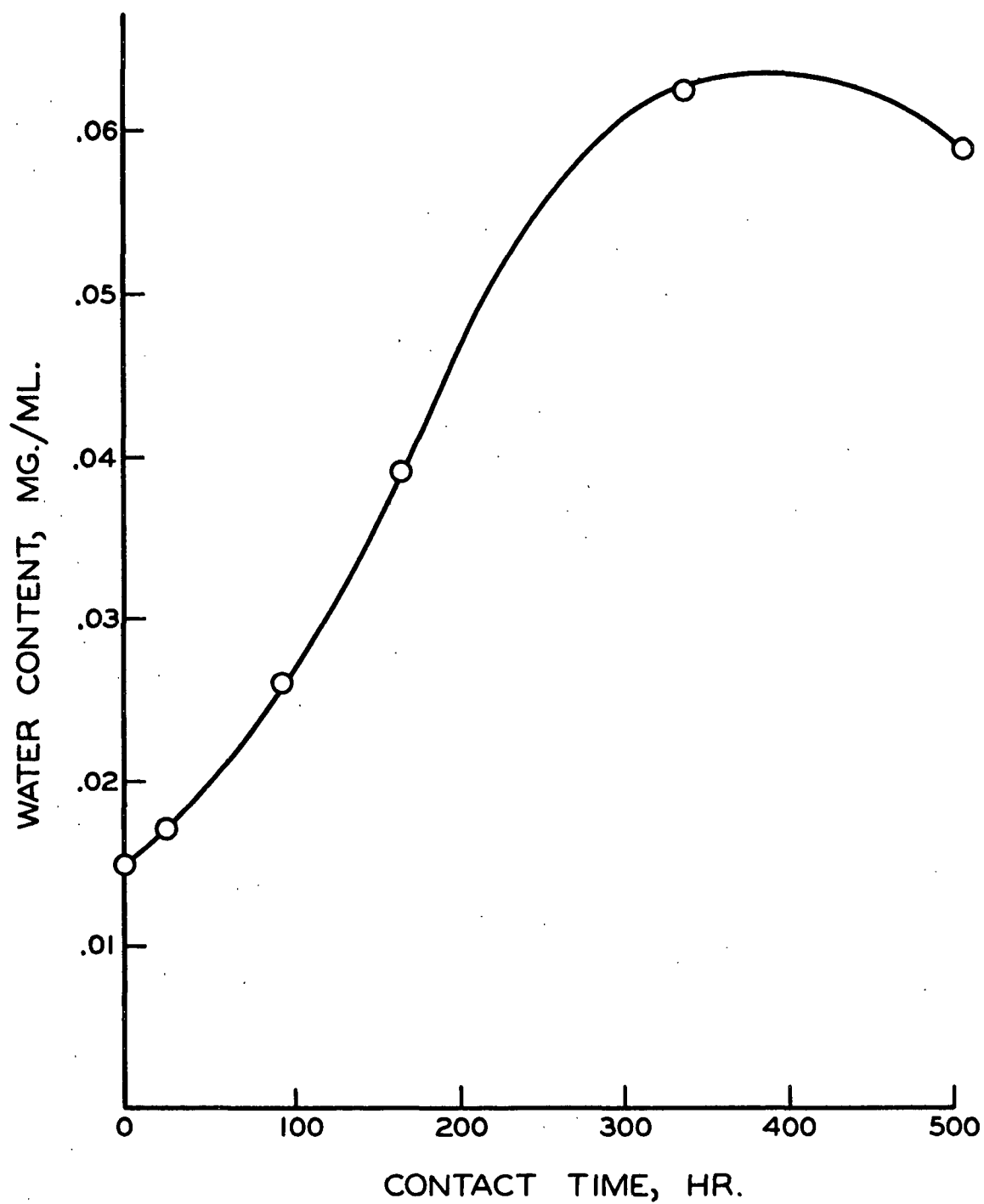


Figure 15. Water Content of Displaced Methanol

The buret was graduated in 0.05-ml. increments but was estimated to the nearest 0.01 ml. Estimating the precision of a determination as ± 1 drop of reagent would give ± 0.003 mg. water/ml. for 15.0-ml. samples and ± 0.007 mg. water/ml. for 7.0-ml. samples.

Generally, the methanol was dried to about 0.01 mg. water/ml., as compared to 0.063 mg. water/ml. as found by Merchant (6) for dried methanol after standing several hours.

The results shown in Fig. 15 are most significant since prior to this it has been generally assumed that the water replacement is essentially complete even under conditions much less conducive for complete replacement. Sample c-2a had already been given 32 methanol displacements prior to these results. It appears from this that about 2 weeks are required at this point to reach equilibrium in the water-cellulose-methanol system. This long time to reach equilibrium in the removal of water by alcohol might be compared to the long times required in the water vapor desorption experiment. The point at 506 hours appears to show a decrease in the water content. Considering the fact that the water content of the dried alcohol which was used in this displacement was quite high, 0.037 mg. water/ml., this point would probably be lower if a drier alcohol had been used. This drop in the curve supports the contention that equilibrium has been reached and that now each subsequent equilibrium displacement will show less and less water until the value for the dried alcohol is finally reached.

The data in Table VII for Sample c-1b further supports this, since after 52 displacements an extended contact time of over 4 months only gave a water concentration of 0.040 mg. water/ml. The next displacement after 10 hours gave the same water content as the dried alcohol, 0.0074 mg. water/ml.

The results for Sample c-2bw require an explanation, since it appears that up to Displacement 18 an increase in contact time gives a lower water content in the displaced methanol. It is suggested that up to this point water is being removed from the bulk liquid whereas after this point it is being removed from the pore structure where removal is more difficult due to internal diffusion along the pores and difficulty in replacement of the more strongly held water. Therefore, in the first few displacements with dried alcohol the water content is so high that time effects are less important. These results are therefore quite reasonable when one considers that Displacement 15 is only the fourth exchange with dried methanol. It would appear then that about six exchanges of dried methanol are necessary in order to remove the water in the bulk liquid.

Even if all possible water were removed by the methanol the limitation in the final water content in the CP-method as used here is the water in the liquid carbon dioxide. This has already been discussed.

It becomes quite evident that water removal by methanol is not as complete as previously assumed. Some water therefore is quite likely left due to non-replacement as well as some due to a readsorption from the liquid carbon dioxide. Probably just as important, however, is the fact that if the polar hydroxyl containing methanol, which swells cellulose about $2/3$ that of water (122), can replace the water only with difficulty, then the replacement of the alcohol by a nonpolar and nonswelling liquid will certainly be more difficult and quite likely incomplete.

DEGREE OF METHANOL REPLACEMENT BY LIQUID CARBON DIOXIDE

For six of the CP-runs a measurable amount of methanol was collected from the initial carbon dioxide displacements during the release and leveling steps.

These varied from 57 to 80 cc. for Displacement 1, 5 to 9 cc. for Displacement 2, and 0 to 7 cc. for Displacement 3. The liquid methanol removed in displacements after the first is likely that retained in the reservoir and the connecting tubing.

For Sample c-1a, gas samples were collected from Displacements 10 and 11 and also from the carbon dioxide being removed above its critical point at 36°C . These three samples were analyzed with the gas chromatograph but showed no indication of methanol. Since the limit of detection of this method is someplace below 7 mg. methanol/g. carbon dioxide, it was concluded that since no detectable methanol was present that 36°C . was probably an acceptable removal temperature.

Later, during the routine removal of the carbon dioxide from Sample c-2e at 45°C . part of it was passed through a phosphorus pentoxide tube in order to provide an additional precaution against moisture entering the sample when atmospheric pressure was attained. A warming of the drying tube was noted and since the tare weight was known from an earlier experiment the total gain in weight was found to be 0.3270 g. After calculating the total weight of carbon dioxide passed from the pressure-volume data, it was found that the gain in weight corresponded to 28 mg./g. carbon dioxide. On the basis of the cotton this is 76 mg./g. A similar analysis was made for Displacement 12 from Sample c-2j by passing the displaced gas through a phosphorus pentoxide tube over a period of about an hour. In this case 0.1574 g. was found for an estimated 2 mg./g. carbon dioxide, or on the basis of the cotton 80 mg./g. Since the water content of the carbon dioxide could only account for a few per cent of these amounts, it is assumed that the gain in weight is methanol.

The methanol, however, may or may not be coming from the cellulose since there is a good possibility that it could have been retained in the mercury reservoir

and/or connecting system. Retention of only 0.3 g. methanol in this part of the apparatus would not seem unreasonable.*

There is evidence, therefore, although not conclusive, that the carbon dioxide does not remove the methanol as completely as possible and that methanol is still being removed after 12 displacements.

DEGREE OF METHANOL REPLACEMENT BY BENZENE

After most of the liquid benzene had been removed from Sample c-2gw with phosphorus pentoxide-dried nitrogen, a tared phosphorus pentoxide drying tube was placed in the exit nitrogen stream as described on p. 29. A total gain in weight of 0.1327 g. was found. Again it was assumed to be unreplaced methanol and on the basis of the outgassed cotton was 55 mg./g.

It is therefore quite evident that some methanol has not been replaced by benzene but has been removed during drying.

DISCUSSION

Since the evidence strongly suggests both unreplaced methanol and water in the sample the questions naturally arise as to where this material is, why it has not been replaced, and what effect its removal during drying has on the resulting structure and surface area. It is doubtful that these questions can be adequately answered on the basis of existing data but some speculations may be valid. In this respect it is again appropriate to examine the literature.

Merchant's (6, 7) standard solvent-exchange procedure involved the passage of 40-ml. quantities of liquid every 10 minutes. He used 10 displacements with

* Upon dismantling the apparatus some methanol was found in the mercury reservoir, thus supporting this possibility.

reagent-grade methanol, 5 with dried alcohol, and 10 with a nonpolar solvent. Merchant varied some of the conditions of his standard exchange procedure in order to see if there was any change in the final surface area. For two samples dried from benzene he increased the contact time to 20 minutes. He also varied the total amounts of dried methanol and the final hydrocarbon. In the latter case, however, he used methanol-hydrocarbon solutions of increasing hydrocarbon concentration finally arriving at the pure hydrocarbon. The standard quantity of the pure hydrocarbon was then used. Because of no significant difference in the surface areas he concluded that "the standard exchange method gave complete removal of water and methanol, or that these liquids had been displaced to a constant amount which could not be decreased by further exchanges". The experimental evidence obtained in this study indicates, however, the opposite conclusion; namely, that the effect of increasing the contact time does remove more water but this is only evident after extended periods of time. Since there is also unreplaced methanol, at least in the case of the benzene-dried sample, it is expected that, similarly, increased contact time will remove more alcohol per exchange. The fact that alcohol replacement is not complete is probably closely related to the different areas and residuals that Merchant (6, 7, 95) found using different alcohols as intermediates.

Work of Stamm and Hansen (123) has been the basis of the suggestion that all but a monolayer of the intermediate polar solvent can be replaced by a nonpolar solvent without shrinkage (2, 123, 124). Because of the obvious importance to this study considerable space will be devoted to the basis and exact nature of their suggestion in order to avoid misinterpretation and to provide a sound basis for comparison with the results of this study. First, it should be made clear that they used blocks of pine heartwood 2 by 2 by 9 cm., with the short dimension

in the fiber direction. These apparently had been given no chemical treatment. Water was replaced by Cellosolve (ethylene glycol monoethyl ether) which is completely miscible with water and has a boiling point of 130 to 136°C. The water-saturated blocks were soaked in Cellosolve and daily for one week the water was removed by distillation at 40 to 45°C. under a vacuum of 60 cm. of mercury. Determination of the remaining water after this treatment by distilling several samples to dryness and analysis of the distillate showed about 0.2% water on the dry weight of the wood or less than 0.1% water for a cotton linters alpha-cellulose. Since no shrinkage occurred it was concluded that "virtually all of the free and adsorbed water in wood can thus be replaced by Cellosolve" (123) without any shrinkage. This was thereafter generalized to replacement of the water by a water-soluble-intermediate. The next step was to replace the Cellosolve by a non-polar liquid such as benzene, toluene, petroleum ether, or waxes, by continuous extraction for a week or longer with the wood blocks being continually submerged. At this point they found about 20% of the shrinkage which would normally occur when drying from water. Only a few tenths of a per cent of Cellosolve remained. On the basis of water adsorption at the fiber saturation point of about 30% and from earlier work which indicated "in the case of both cotton and wood that shrinkage of the fiber substance on drying is practically equal to the volume of the water lost" (124) they estimated that the 6% actual shrinkage accompanied the solvent removal of an equivalent volume of Cellosolve. Then, since about 6% water vapor adsorption is in the order of a monomolecular layer of water it was concluded that "a nonpolar liquid such as the n-pentane can replace all but the first molecular layer of alcohol without shrinkage" (90) and that further replacement is possible but only with the loss of 20% of the water-swollen structure. Stamm (2) further comments: "When swollen sections containing these various non-polar liquids are dried, a large part of the normal shrinkage occurs even though

these liquids have so little affinity for wood as to cause no swelling of dry wood. The nonpolar liquids must thus be held almost entirely by capillary condensation and the shrinkage must result entirely from capillary forces."

One question immediately arises as to the effect of the extraction of non-cellulosic materials on the shrinkage. Since this is not known some reservation is required in the interpretation of such shrinkage.

The fact that Stamm and Hansen (123) found about 6% shrinkage cannot be disputed. Whether this shrinkage is due to removal of a monolayer of methanol must be given further consideration however.

Probably the best evidence for further analysis is the work of Giles and Hassan (125) and Giles, MacEwan, Nakhwa, and Smith (126). In their extensive study of adsorption from solution they included the adsorption of methanol on a viscose rayon at three different temperatures. Both a "normally dried" (125) and an "intensively dried" (126) sample were used. The isotherms for the "intensively dried" cellulose were of the Langmuir type with the curve leveling off to give a plateau at about 1.4% adsorption by weight. The isotherm for the "normally dried" sample gave an isotherm having a similar plateau but it departs slightly from a Langmuir type at low concentrations to a very slight "S" shape, presumably due to competition between methanol molecules and water molecules for the adsorption sites. Taking the plateau as the point of a monolayer coverage and 20 sq. A. as the cross-sectional area of the methanol molecule the surface area comes out to be about 55 sq. m./g., a reasonable value.

Assuming that there is no hysteresis in this system the desorption will follow the same general type of isotherm. It would therefore seem that replacement of the methanol by a nonpolar solvent would follow a path similar to these isotherms.

Some shrinkage likely takes place during removal of the monolayer but whether any prior shrinkage might take place is not known. It is interesting to note here that when Kistler (40) tried to replace the swelling solvent in a rubber with a nonswelling one, shrinkage occurred giving the original volume. Since this occurs for at least one high polymer it would seem that for cellulose some shrinkage may be expected in at least certain parts of the structure.

Looking once again at the 5.5% methanol which was found in this study to be unreplaced by benzene but removable on drying, one can calculate a surface area of about 200 sq. m./g.* This value is fairly close to the water-vapor-adsorption area, especially if one of the higher values for the cross-sectional area of the water molecule is used. However, since there is no evidence that the point of a monolayer existed this must be dismissed as merely an interesting point.

Some shrinkage may likely also occur during the replacement of the water by alcohol. Stamm (123) did not find any but he was using blocks of wood. Lauer, Ayer and Seoud (128) in their recent study of the cellulose-methanol system expressed belief that for never-dried cotton, methanol can replace part of the bound water but only with breakdown of the original structure. It has already been pointed out earlier that some loss of structure would be expected during this exchange.

Merchant (6) pointed out that such a monolayer as suggested by Stamm and Hansen (123) could not exist because if it did it would control the surface area on drying and he found different areas when dried from different nonpolar solvents. The shrinkage accompanying removal of the methanol however would not control the

*Using 18 sq. A. as the cross-sectional area of the methanol molecule as calculated from Equation (9), p. 134, the surface area is calculated as 220 sq.m./g.

surface area since additional shrinkage results when drying from the nonpolar solvent. It may contribute to the loss of structure, however, with its relative contribution increasing as the surface tension of the final solvent and the accompanying shrinkage decreases. Thus, in the CP-method this may actually become the controlling factor in the retention of the structure.

In the experiment described above where it was found that methanol in an amount of 5.5% based on the cotton was not replaced by benzene but was removed on drying, it is possible that if this methanol had been replaced by a more efficient exchange a roughly equivalent loss of pore volume may have resulted. Removing the same amount by drying would possibly result in the same loss but here it is intimately associated with the effects due to the surface tension forces of the benzene and as we shall see later also on the flexibility of the structure in its response to these forces. It is not known therefore whether the same shrinkage will result when the last 5 or 6% of methanol is removed through replacement by benzene or by removal into the gas phase on drying.

In going from water to methanol we go from a liquid which swells cellulose 90% to one which swells cellulose 62% (122). The next step to the nonpolar solvent involves a decrease in swelling to essentially zero. Therefore if more intermediate solvents of decreasing swelling ability were used in going to the non-swelling liquid more of the swollen structure might be retained. This is suggested by the observations of Daruwalla and Shet (116) that the amount of water vapor adsorbed by cellulose at equilibrium during desorption was found to be greater for smaller relative humidity changes. Thus, in water-vapor desorption more of the structure is retained by using a more gradual removal.

Where is this unreplaced solvent? Since it most likely is in a hard-to-replace spot it seems that the smaller pore structure with higher energy adsorption sites is the probable location. The diffusion into and out of these small pores would be the slowest of any location and also in such places the unreplaced solvent would be held by strong adsorption forces due to its proximity to relatively greater solid surface and, hence, the corresponding greater number of active sites per molecule of liquid.

Why is this material not replaced? Part of this reason is likely due to the time required for the diffusion process and also that required for the desorption equilibrium to occur. A most recent study by Giles and Nakhwa (129) found that up to 6 hours were required for adsorption equilibrium with porous solids such as charcoals. Another reason which has not been mentioned is the mutual miscibility of the two liquids involved. Merchant (6, 7) used some nonpolar solvents with less than complete miscibility with methanol but this apparently did not affect his surface area-surface tension relationships. His conclusion was that miscibility does not control the surface area. One would have to agree. This does not say however, that it doesn't have any effect or that in some cases it cannot become quite important. Examination of the ternary diagrams for methanol and water with either n-pentane or liquid carbon dioxide, as shown in Fig. 16 and 17, shows that small amounts of water can easily lead to a two liquid phase system. This may further hinder the removal of the methanol in the small pore region where there is likely to be a higher water concentration. The ternary diagrams for benzene, n-hexane, and cyclohexane are also similar (130). There is a possibility here that increased water in the liquid carbon dioxide might also cause a loss in small pore area through the decreased miscibility with the methanol, which itself always contains some water. If such a liquid-liquid interface did exist a compressive force due to the interfacial tension also could become important.

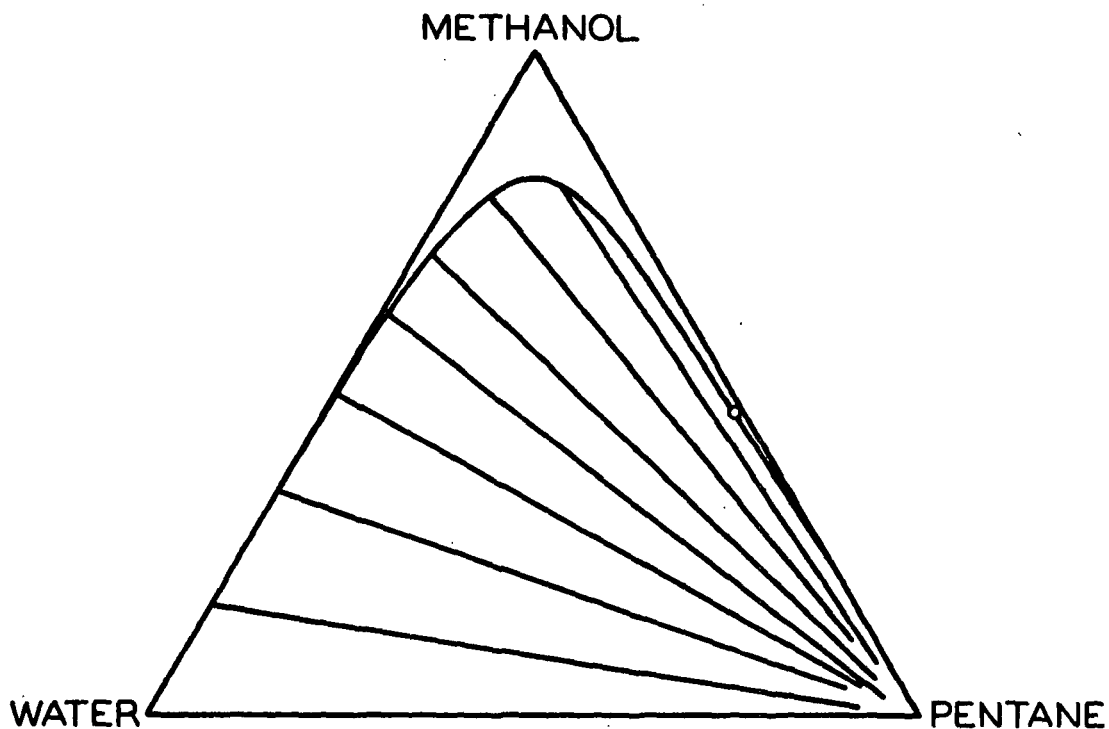


Figure 16. Water-Methanol-Pentane Miscibility at 25°C. (44)

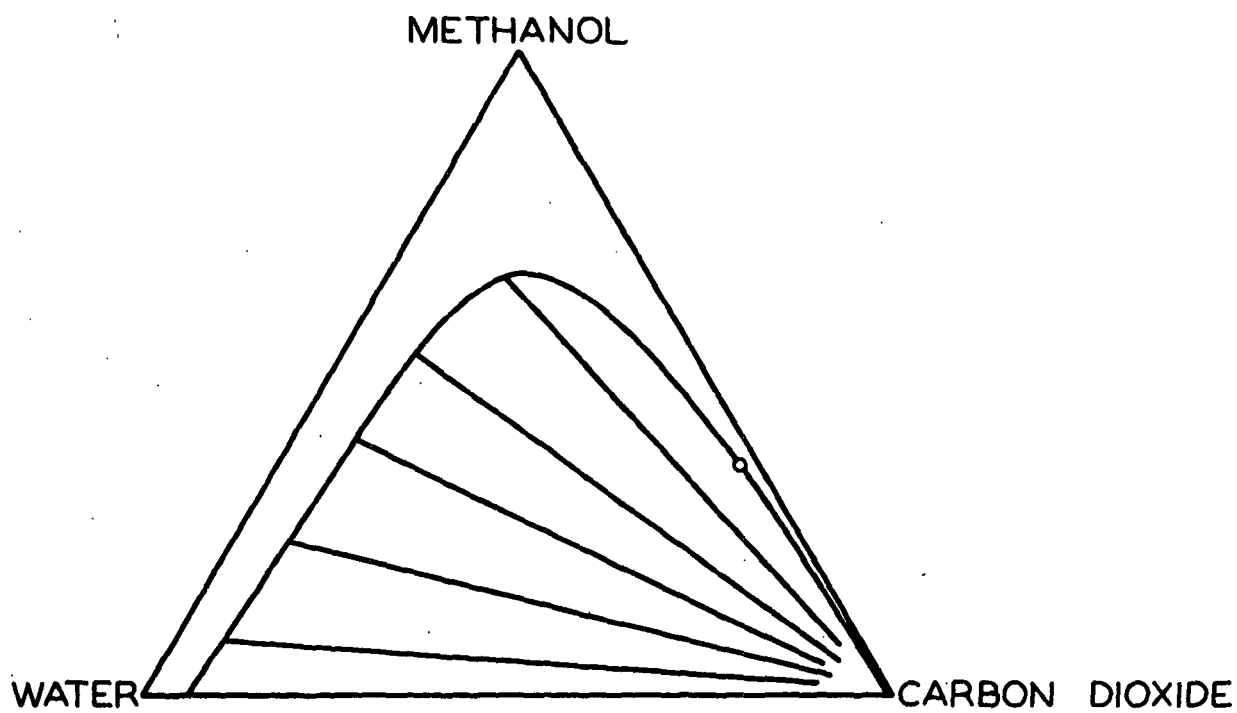


Figure 17. Water-Methanol-Carbon
Dioxide Miscibility at 21-26°C. (130)

What is the effect of unreplaced solvents? It is believed that they will reduce the final surface area and pore structure but how this might occur is probably just as important. The effect of the surface tension of the final liquids has been well shown by Merchant (6, 7). Unreplaced solvents would also exhibit surface tension forces and since they would be polar liquids the effect is likely to be relatively greater. It should be pointed out however that surface tension is merely a manifestation of the molecular forces of a liquid and a physical property which can be measured. It does not take into account the molecular forces involved between the liquid and the solid except by way of the contact angle which is generally taken as zero for nonpolar liquids on cellulose. This solid-liquid interaction which is not measured by surface tension is probably the reason for a failure of the surface tension-surface area relationship for nonpolar hydrocarbons to hold for polar solvents (6).

Staudinger, Döhle, and Heick (18) found a decrease in chemical reactivity when a solvent-dried cellulose was exposed to atmospheric moisture. Haselton (4, 5) and Hunt, Blaine, and Rowen (35) found the surface area of solvent-dried cellulose to decrease when conditioned to atmospheres of various relative humidities. When Haselton (4, 5) humidified some of his benzene-dried pulp at a relative humidity of 0.229 he found the surface area decreased from 67 to 24 sq. m./g. Although no capillary condensation is expected at this low relative humidity it would seem that this area loss could be attributed to the strong molecular attractive forces between the water and cellulose when the adsorbed moisture is removed during the subsequent outgassing and to the release through an increase in the flexibility of the structure of both dried-in stresses and those arising from the above attractive forces. Also, if cellulosic hydroxyls have been oriented inward when dried from benzene (37) the adsorbed moisture may enhance their reorientation and some subsequent bonding. A similar effect of increased

flexibility and outward orientation of hydroxyl groups would be expected from small amounts of unreplaced water and methanol.

The importance of swelling and the accompanying fiber flexibility in the development of fiber-to-fiber bonding is well known (32, 131-135). Thode and Guide (131) pointed out that the surface area of cellulose dried from a nonpolar solvent can be related to the degree of plasticization or swelling by the non-polar liquid. Making certain assumptions their thermodynamic reasoning led to an inverse relationship between the surface area and the solubility parameter (136) of the final nonpolar liquid. Plotting some of Merchant's (6) data they found good agreement. It should be pointed out however that the solubility parameter, like surface tension, is but a manifestation of the molecular attractive forces. As a matter of fact there exists an empirical relationship between these two quantities (136). It would seem that the molecular interactions during drying can be visualized as a combination of the forces tending to bring the structural units together and the resistance to these forces due to the rigidity of the structure. If these two effects could be varied independently it is expected that increasing either the flexibility or the compressive forces would lead to more bonding and a lower surface area. Unreplaced polar liquids will greatly increase the flexibility and may also contribute to the surface tension forces when they are partially removed.

LOSS OF AREA OF A DRY SAMPLE

Because it is quite likely that water in the liquid carbon dioxide causes a decrease in the surface area, an attempt was made to gain some information regarding this effect by passing carbon dioxide gas through a pentane-dried sample. Sample c-2cw was used for this experiment after the determination of several surface areas and a complete nitrogen isotherm. The carbon dioxide was dried by

passage through a small tared phosphorus pentoxide drying tube and then through a larger column of activated coconut charcoal and phosphorus pentoxide. The dried carbon dioxide was passed through the sample, a flowmeter, another drying tube, and finally to the atmosphere. The gas flow rate was approximately 240 cc./min. for 41 hours giving a total of about 590,000 cc. During this time the first drying tube absorbed 0.0281 g. of water. This passage of dried carbon dioxide resulted in a decrease of surface area from 51.7 to 46.3 sq. m./g., a decrease of 10.4%.

A similar treatment was then given to the same sample except that the carbon dioxide was not dried. The flow rate was approximately 240 cc./min. for 38 hours for a total of about 530,000 cc. A tared phosphorus pentoxide drying tube located after the flowmeter absorbed 0.0291 g. of water. This caused the surface area to decrease from 46.3 to 44.6 sq. m./g. for a 3.7% decrease.

It was expected that the undried carbon dioxide would result in a greater area loss. It now appears that the low water content of the dried gas was still sufficient to cause a loss in the less stable part of the structure; namely, those parts with the largest dried-in stresses. The lower effect from the undried gas may be due to the fact that a large portion of the low moisture-sensitive structure had already been lost.

A similar experiment was performed with the passage of dried prepurified nitrogen through CP-Sample c-2e. The nitrogen was passed for 19.5 hours at an average rate of 90 cc./min. for a total of about 105,000 cc. The water removed from the nitrogen was 0.0188 g. The surface area in this case decreased from 49.3 to 46.3 sq. m./g. for a decrease of 6.1%.

Merchant (6) found that an increase in the flow rate during one experiment from 50 to 125 ml./min. caused a 7% decrease in surface area from 129 to 121 sq. m./g. He attributed this to evaporative cooling but it may have been due to the increased volume of nitrogen which had been passed.

An apparent instability of the solvent-dried structure has also been noted by others. Hunt, Blaine and Rowen (35) found that, in general, repeat surface area determinations for the same sample led to lower areas. Merchant (6) also found a loss in area with continued outgassing or even by just aging in the evacuated bulb. For example, the area for a n-pentane-dried sample aged 43 days decreased 9.3% while a benzene-dried sample aged 49 days decreased 19.8%. Outgassing at higher temperatures reduced the areas considerably more. The humidification study of Haselton (4, 5) has already been mentioned where the largest area decrease was found at the lower relative humidity.

Merchant (6) also found an apparent effect of temperature on the solvent-dried structure. Drying from n-hexane at 69°C., an increase in the passage of nitrogen from 28 minutes to 8 hours, gave an 11.2% lower area. Also drying at 60°C. consistently gave lower areas than when dried at lower temperatures.

It is interesting to note that in this study no definite trend toward decreasing areas with repeat determinations was noted. Only with Sample c-2bw did additional outgassing appear to cause a decrease in area but when compared with the prior three determinations it appears to have been just experimental error. A similar increase in outgassing time for Sample c-1b showed no effect. Since Sample c-1a showed no apparent effect of exposure to a dry carbon dioxide atmosphere for about 5 months before determination of the surface area it would seem that either moisture or continued removal of residual solvents might be the cause of a decrease in area.

From the above discussion it would certainly seem that part of the structure which is formed by drying from a nonpolar solvent or from carbon dioxide by the CP-method can be readily lost in certain circumstances. The mechanism may involve an increase in flexibility of the structure due to adsorbed water vapor, further removal of residual solvents, and/or bonding of adjacent elements when they come into proximity through thermal movement. Capillary condensation of water vapor during exposure to the very low concentrations involved here can be discounted since it is doubtful if such condensation in the normal sense takes place below 40% relative humidity (137). As a result of this tendency for the surface area to decrease any area experimentally determined will be a minimum value, the actual area of the sample as originally prepared being either equal or greater.

ANALYSIS OF THE SOLVENT EXCHANGE MECHANISM

On the basis of previous discussions of the experimental evidence obtained in this study and the results of previous workers a qualitative mechanism for the solvent-exchange procedure can be suggested.

Involved in this process are the physical and chemical properties of the liquids as well as the cellulose, the interactions of these properties, and also the effect of the structure of the cellulose by way of its porosity and the way in which the cellulosic polymer units make up the molecular and fibrillar arrangement. The main interactions arise from secondary valence forces and hydrogen bonding.

We start with cellulose in a water medium where it is swollen and flexible by virtue of the strong relationship between the water and the cellulosic hydroxyl groups mainly as the result of hydrogen bonding. Methanol is then added to this system in an effort to replace the water. Removal of some of this water quite likely leads to a decrease in the expanded structure through bonding of cellulosic hydroxyls before the sites can be occupied by methanol molecules. The degree of this loss is not known but it is expected that it is minor with respect to losses which occur later. All of the water cannot be replaced because it is not possible to obtain a completely water-free alcohol. In addition, experimental evidence shows that some water still remains which could have been removed by inconveniently long time intervals or some means of mechanical agitation. This water is believed to remain in the smallest pore structure where the forces of attraction are the strongest and the limitations of diffusion are most pronounced. The over-all effect of the water removal will likely cause a small decrease in the expanded

structure and a small increase in its rigidity through replacement of part of the water by the lower swelling methanol and also by some cellulose-to-cellulose hydrogen bonds.

Similar problems occur in the attempt to replace the methanol by a nonpolar liquid. It is expected that the degree of replacement will be lower and the loss of the swollen structure higher than in the exchange of water by alcohol. This arises from the attempt to replace a swelling polar liquid with a nonswelling nonpolar one. A lower effectiveness in the exchange is also suggested by the fact that small amounts of moisture can prevent complete miscibility in the polar-nonpolar system and that considerable unreplaced methanol was found after attempts to replace it with benzene.

Effects due to removal of the final solvent are complicated by the small amounts of unreplaced alcohol and water. Drying from the nonpolar solvent therefore involves the contributions of the molecular interactions between the cellulose and three different liquids. In macroscopic terms, each liquid may be looked upon as contributing to the collapse of the structure through its forces of surface tension and its effect on the flexibility of the structure.

Removal of the final liquid as a gas above its critical point eliminates the surface-tension forces of the final liquid but only in those parts of the structure where it has been effective in replacement of the alcohol. These areas of complete replacement are most likely in the larger pore regions and therefore it is here that the CP-method becomes effective in preservation of the structure. The unreplaced liquids conversely show their effect mainly in the smaller pore regions where because of incomplete replacement the surface tension of the final liquid is of little consequence.

Since the ratio of surface area to pore volume is greater in the small-pore regions, the over-all surface area of a CP-dried cellulose may not differ greatly from that of a solvent-dried cellulose, and where replacement is less effective it may even be lower. The pore volume retained for the CP-sample in the large-pore region will however exceed that of a solvent-dried sample since that is where the surface tension forces were successfully eliminated.

There are also possible contributions to the final structure through steric retention by the nonpolar liquid or to loss by means of the high pressures of the CP-method. If these effects do exist they are believed to be relatively small however.

Even though this is likely an oversimplified picture it should bring out the fact that we can no longer consider a solvent-exchange procedure as used in this study to be complete. Furthermore, we cannot attribute the dried structure solely to the properties of the final solvent, except as a first approximation in some cases.

GENERAL SUMMARY

A surface area study has been conducted using a 1% alkali-swollen cotton cellulose. It was solvent exchanged from water to dried methanol and then to one of several nonpolar liquids, final removal of which included release as a gas above the critical point.

1. By means of a high-pressure apparatus a number of samples were prepared by the critical point (CP) - method which used liquid carbon dioxide with its removal above the critical point of 30°C. BET surface areas of 39.4 to 52.8 sq. m./g. were found when undried liquid carbon dioxide was used. These values compare with 46.8 and 51.7 sq. m./g. for samples dried from n-pentane and 122 to 133 sq. m./g. as determined by water-vapor adsorption. Contrary to expectations, there was little difference between the surface areas for CP-dried and n-pentane-dried samples and both gave areas lower than that for water-vapor adsorption.

2. Attempts to dry the liquid carbon dioxide by passage through phosphorus pentoxide or oven-dried cotton yielded CP-areas of 49.5 and 23.8 sq. m./g., respectively, thus indicating the strong effect of small amounts of water.

3. Analysis of the water content of methanol before and after being in contact with the cotton indicated that as much as 2 weeks may be necessary to reach equilibrium in the water-cellulose-methanol system. Evidence was also obtained gravimetrically and by means of the gas chromatograph showing both that methanol is not completely replaced by the nonpolar liquid and that some methanol remains even after extended outgassing.

4. Drying two samples from benzene, one of which included n-pentane as an intermediate, showed areas of 24.8 and 18.4 sq. m./g., the higher area involving the pentane. This supported contentions that the amounts and nature of unreplaced intermediates have an effect on the dry area.

5. Complete adsorption-desorption isotherms were determined for one pentane-dried sample and two CP-samples, and these isotherms were used to determine pore-size distributions. These showed a considerable difference between the two methods. CP-samples, despite lower areas, possessed greater total pore volumes, most of which was retained in the large-pore range. The most common pore radius for all three samples was about 18 Å.

6. Passage of either dried or undried gas through a highly outgassed sample, followed by further outgassing, resulted in a lower surface area.

7. A new mechanism has been suggested for the solvent-exchange procedure which attributes at least part of the structure change in the small-pore region to the unreplaced solvents.

CONCLUSIONS

1. Contrary to previous assumptions, the method of solvent exchanging used here does not provide complete replacement of previous liquids. Furthermore, the evidence suggests that inconveniently long contact times are required for equilibrium. Mechanical agitation is probably necessary to improve the efficiency of the replacements.

2. The structure and surface area of a solvent-dried cellulose depends not only on the properties of the final liquid but also on the amounts, location, and nature of previous unreplaced solvents. As suggested by the results of using n-pentane as an intermediate, the differences between the surface areas when dried from different solvents may in part be due to the effectiveness of the replacements.

3. The pore-volume distributions and other considerations lead to the conclusion that unreplaced solvents show their effect primarily in the small pore regions whereas the final liquid shows its effect primarily in the larger pore regions where it has been successful in the replacement.

4. In the critical-point method, where the surface-tension forces of the final liquid have been eliminated, the unreplaced liquids most likely become the controlling factor as far as the final surface area is concerned and this effect is most pronounced in the small-pore regions where the area-to-volume ratio is high. Therefore, in order to preserve a larger area in the final sample more efficient replacements are required and not necessarily lower surface tensions of the final liquid.

5. Conversely, in order to obtain a dry sample with a larger total pore volume, particularly with more volume in the larger pores, the efficiency of the exchange is of less importance than the surface tension of the final liquid.

6. It must also be concluded that the total surface area is not a sufficient measure of the dry structure as is well shown in a comparison of the areas for the CP- and pentane-dried samples. A better measure would include in addition to the surface area the pore-size distribution, or at least the total pore volume.

7. Although it is difficult to evaluate the effect of fiber flexibility, especially since it is probably influenced by both the nature and amount of liquid, it must be concluded that both flexibility of the structure and surface tension forces are involved.

8. Correlation of surface area with the surface tension of the final liquid would seem valid only when other contributions are negligible or carefully controlled to some constant or at least reproducible level.

9. No evidence has been found to contradict the contention of Stamm and Hansen (123) that when the final monolayer of methanol is replaced an equivalent shrinkage occurs. Actually, it is concluded that some shrinkage is likely to occur during this replacement and also during the water replacement; the amount of such shrinkage, however, is left open to speculation.

10. The most common pore radius of 18 A. is consistent with the results of previous workers and similarly to Thode, Swanson and Becher (9) it is suggested as a characteristic dimension of the structure of cellulose. Although this would be the radius of an inscribed cylinder between three close-packed fibrils of 230 A. in diameter, caution must be exercised in drawing conclusions regarding the

cellulosic structure particularly because a cylindrical pore model was used in the calculations.

11. Finally, it would seem that the full potentialities of the CP-method can only be realized when the unreplaced solvents are reduced to the possible minimum.

SUGGESTIONS FOR FUTURE WORK

1. The results of this study indicate that the surface area and pore structure of a dry cellulose depend not only on the final liquid but also on small amounts of previous solvents. Future work in this area should examine the effects of unreplaced solvents more closely. Steps to increase the efficiency of the exchange process might include some type of mechanical mixing and/or the use of more and varied intermediate solvents. Use of a model system with different porosities and surface characteristics may be easier to analyze in this respect. Such a study might include surface areas, pore-size distributions, and quantitative data on each particular residual solvent. Use of formamide as an intermediate or final solvent is also suggested since it swells cellulose more than water (122) and yet has a lower surface tension.

2. It would be useful to learn whether the pore structure of different celluloses respond to mechanical action and drying conditions in the same way. Use of pore-volume distributions or at least surface areas and the total pore volumes would be required since surface area alone may be misleading. This study might also include the determination of the most common pore radius in order to further elucidate its significance.

3. It would be of considerable interest to be able to determine pore-size distributions from the adsorption and desorption isotherms of swelling vapors such as water and methanol. The change in structure during adsorption complicates matters but an approach might be based on some such theory as that of Cassie (138) where the effects of swelling are isolated. Such a technique would be most useful especially since molecules of different size, shape, and swelling ability could be used.

4. The studies of Giles and co-workers (125, 126) have indicated a possibility of using adsorption of methanol from benzene as a means of determining the surface area of a dry cellulose. Since the replacement of methanol by benzene is eventually a desorption it would seem that a study of such desorption isotherms may prove fruitful for determining the water-swollen surface areas. Use of celluloses dried to different degrees and from different solvents along with the use of different alcohol-nonpolar systems might be able to provide basic information concerning the changes in the cellulose structure. Quite recently, Giles and Nakhwa (129) have pointed out that adsorption of p-nitrophenol from nonswelling solvents by fibers after only short times may be useful for determining the superficial area. More details were promised in a forthcoming article.

The rates for adsorption or desorption equilibrium for different systems should also give information concerning the interactions and the structure.

Such adsorption studies should also give important information concerning the relative affinity of cellulose for various liquids. Iler (139) has carried out a qualitative study of similar nature for silica gel where he determined the adsorption of various liquids when in equilibrium with a 0.2% solution in isooctane.

5. More information is also desirable regarding the shrinkage which takes place during the various solvent-exchange steps. Of particular interest is the degree of such shrinkage, the relation to the nature of the liquids, and when during the replacement that it occurs. A technique, such as that used by Morehead (127) in microscopically studying the cross-sectional swelling of fibers as a function of relative humidity, may be useful.

It may be possible to correlate the total swelling in polar liquids with solubility parameter (136) and Lieberman's (140) empirical hydrogen bonding number.

6. Kistler (40) in one of his earlier experiments attempted to remove water from silica gel by removal above the critical point, which is 374°C . and 3200 p.s.i.a. He found that the silica was apparently peptized because on reduction of the solvent density he obtained a voluminous powder. It is interesting to speculate on the results of such an experiment when cellulose is used. It would certainly be of interest to make some preliminary studies in this respect.

7. The discussion of critical phenomena in small pores, which is given in the Appendix on p. 125-8, suggests a study of physical adsorption on various materials above the critical point to try to determine the nature of the adsorption and whether or not capillary condensation and/or hysteresis can exist.

ACKNOWLEDGMENT

The author wishes to acknowledge the help and encouragement given by the late Dean of Students, Edwin W. Schoenberger, without which this research would never have been started.

LITERATURE CITED

1. Rollins, Mary L., and Tripp, Verne W., Forest Prods. J. 11, no. 11:493-504 (Nov., 1961).
2. Stamm, Alfred J. Surface properties of cellulosic materials. In Wise and Jahn's Wood chemistry. 2d ed. Vol. 2. p. 691. New York, Reinhold, 1952. 1343 p.
3. Brunauer, Stephen, Emmett, P. H., and Teller, Edward, J. Am. Chem. Soc. 60: 309-19(1938).
4. Haselton, William R. An investigation of the adsorption of gases by wood and its components and of gas adsorption techniques as a means of studying the area and structure of pulp and paper. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1953. 172 p.
5. Haselton, William R., Tappi 37, no. 9:404-12(Sept., 1954); 38, no. 12:716-23 (Dec., 1955).
6. Merchant, Morris V. A study of certain phenomena of the liquid exchange of water-swollen cellulose fibers and their subsequent drying from hydrocarbons. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1957. 124 p.
7. Merchant, Morris V.; Tappi 40, no. 9:771-81(Sept., 1957).
8. Swanson, John W., and Steber, Anthony J., Tappi 42, no. 12:986-94(Dec., 1959).
9. Thode, Edward F., Swanson, John W., and Becher, Joseph J., J. Phys. Chem. 62, no. 9:1036-9(Sept., 1958).
10. Urquhart, Alexander R., J. Textile Inst. 20:T125-32(1929).
11. Anderson, Olle, and Fahlin, Bo, Svensk Papperstidn. 59, no. 14:503-8(July 31, 1956).
12. Clark, James d'A. Properties and treatment of pulp for paper. In Ott and Spurlin's High polymers. 2d ed. Vol. 5. Part 2. pp. 621-72. New York, Interscience, 1954.
13. Jayme, Georg, and Hunger, Günther, Monatsh. Chem. 87, no. 1:8-23(Feb. 15, 1956).
14. Jayme, Georg, and Hunger, Günther, Das Papier 11, no. 7/8:140-5(April, 1957).
15. Jayme, G., and Hunger, G., Mikroskopie 13, no. 1/2:24-38(1958); Das Papier 12, no. 21/22:L109(Nov., 1958).
16. Thode, Edward F., Chase, Andrew J., and Hu, Yel, Tappi 38, no. 2:88-9(Feb., 1955).
17. Assaf, A. G., Haas, R. H., and Purves, C. B., J. Am. Chem. Soc. 66:59-65(1944).

18. Staudinger, H., Döhle, W., and Heick, O., J. Prakt. Chem. 161, no. 8-10: 191-218(Jan. 12, 1943).
19. Hasebe, Ryo, Matsumoto, Kenji, and Maeda, Hirokuni, J. Soc. Textile and Cellulose Inds., Japan. no. 1:203-7(March, 1956).
20. Goldfinger, G., Mark, H., and Siggia, S., Ind. Eng. Chem. 35:1083-6(1943).
21. Conrad, C. G., and Scroggie, A. G., Ind. Eng. Chem. 37:592-8(1945).
22. Campbell, W. Boyd. The cellulose-water relationship in papermaking. Forest Service Bulletin 84, Dept. of Interior, Ottawa, Canada, 1933. 52 p.
23. Campbell, W. Boyd, Paper Trade J. 95, no. 8:29-32(Aug. 25, 1932).
24. Campbell, W. Boyd, Ind. Eng. Chem. 26:218-19(1934).
25. Adam, Neil K. The physics and chemistry of surfaces. 3d ed. London, Oxford University Press, 1941. 436 p.
26. Bikerman, J. J. Surface chemistry, theory and applications. 2d ed. New York, Academic Press, 1958. 501 p.
27. Swanson, John W., Tappi 43, no. 3:176A-80A(March, 1960).
28. Swanson, John W., Tappi 44, no. 1:142A-81A(Jan., 1961).
29. Swanson, John W., and Jones, Edward J., Pulp Paper Mag. Can. 63, no. 5:T251-8 (May, 1962).
30. Lyne, L. M., and Gallay W., Tappi 37, no. 12:698-704(Dec., 1954).
31. Robertson, A. A., Tappi 42, no. 12:969-78(Dec., 1959).
32. Van den Akker, J. A., Tappi 35, no. 1:13-15(Jan., 1952).
33. Marchessault, R. H., Lodge, W. C., and Mason, S. G., Svensk Papperstidn. 59, no. 24:859-69(Dec. 31, 1956).
34. Assaf, A. G., Haas, R. H., and Purves, C. B., J. Am. Chem. Soc. 66:66-73(1944); also (17).
35. Hunt, Charles M., Blaine, Raymond L., and Rowen, John W., J. Research Natl. Bur. Standards 43:547-54(Dec., 1949); Textile Research J. 20, no. 1:43-50(Jan., 1950).
36. Forziati, Florence H., Brownell, Robert M., and Hunt, Charles M., J. Research Natl. Bur. Standards. 50:139-45(March, 1953).
37. Broughton, Geoffrey, and Wang, James P., Tappi 38, no. 7:412-15(July, 1955).
38. Emerton, H. W. Fundamentals of the beating process. Kenley, The British Paper and Board Industry Research Association, 1957. 198 p.

39. Casey, James P. Pulp and paper. Chemistry and chemical technology. 2d ed. Vol. 2. New York, Interscience, 1960.
40. Kistler, S. S. Coherent expanded aerogels. J. Phys. Chem. 36:52-64(1932).
41. Anderson, Thomas F. Preparation and preservation of biological specimens. Preservation of structure in dried specimens. In The proceedings of the third international conference on electron microscopy, London, 1954. p. 122-9. London, Royal Microscopical Society, 1956. 705 p.
42. Anderson, Thomas F., Trans. N.Y. Academy of Sciences 13:130-4(1950-51).
43. Emerton, H. W., Brit. Paper and Board Makers' Assoc., Proc. Tech. Sect. 36, no. 3:595-614; discussion:615(Dec., 1955).
44. Francis, Alfred W., J. Phys. Chem. 58:1099-1114(1954).
45. Lowry, H. H., and Erickson, W. R., J. Am. Chem. Soc. 49:2729-34(1927).
46. Stone, Hosmer W., Ind. Eng. Chem. 35:1284-6(1943).
47. Lund, Hakon, and Bjerrum, Jannik, Ber. 64B:210-13(1931); C.A. 25:3310.
48. Snell, Chester A., Anal. Chem. 20, no. 2:186(1948).
49. Harkins, William D., and Jura, George, J. Am. Chem. Soc. 66:1366-73(Aug., 1944).
50. Wise, Louis E., and Jahn, Edwin C. Wood chemistry. 2d ed. 2 vols. New York, Reinhold, 1952. 1343 p.
51. Conrad, Carl M. Chemical properties of cotton cellulose. In Ward's Chemistry and chemical technology of cotton. New York, Interscience, 1955. 782 p.
52. Kettering, James H., and Conrad, Carl M., Ind. Eng. Chem., Anal. Ed., 14, no. 5:432-4(May 15, 1942).
53. Operating and Maintenance Instructions. 308B. Model KF-2 and KF-3 Aquameters. Beckman Division, Beckman Instruments, Inc., Fullerton, Calif., Oct. 1955. 35 p.
54. Mitchell, John, Jr., and Smith, Donald M. Aquametry. Application of the Karl Fischer Reagent to quantitative analyses involving water. p. 65. New York, Interscience, 1948.
55. Fales, Harold A., and Kenny, Frederic. Inorganic quantitative analysis. New York, D. Appleton-Century, 1939. 713 p.
56. Ewing, Galen W. Instrumental methods of chemical analysis. New York, McGraw-Hill, 1954. 434 p.
57. Reid, V. W., and Truelove, R. K., Analyst 77:325-8(June, 1952).

58. Reid, V. W., and Salmon, D. G., *Analyst* 80:704-5(Sept., 1955).
59. Wink, Willmer A., *Ind. Eng. Chem.* 18, no. 4:251-2(April 15, 1946).
60. Wink, W. A., and Sears, George R., *Tappi* 33, no. 9:96A-9A(Sept., 1950).
61. Wink, W. A., *Tappi* 44, no. 6:171A-80A(June, 1961).
62. Browning, B. L., Sell, L. O., and Abel, W., *Tappi* 37, no. 7:273-83(July, 1954).
63. Browning, B. L., and Sell, L. O., *Tappi* 39, no. 7:489-98(July, 1956).
64. Sell, L. O., and Browning, B. L. Unpublished work, 1958. (A method for determining the intrinsic viscosity of cellulose at zero rate of shear. Progress report four to the Technical Association of the Pulp and Paper Industry, Chemical Methods Committee, Joint TAPPI-ACS-ASTM Disperse Viscosity Subcommittee, March 10, 1958).
65. Pfeiffer, G. H., and Osborn, R. H. Practical applications of viscosity. In *Ott's Cellulose and cellulose derivatives*, p. 966-8. New York, Interscience, 1943.
66. The Swedish Association of Pulp and Paper Engineers Technical Communication, Series CCA, *Svensk Papperstidn.* 60, no. 14:513-21(July 31, 1957).
67. Lindsley, Charles H. Tentative method of test for intrinsic viscosity of cellulose, as sent to all members of the Joint ASTM-ACS-TAPPI- Subcommittee, Disperse Viscosity of Cellulose, Dec. 4, 1958.
68. The refrigerating data book. Basic volume. 6th ed. p. 128-33. New York, Am. Soc. of Refrigerating Engineers, 1949.
69. International Critical Tables. 1st ed. Vol. 3. p. 12-13, 38. New York, McGraw-Hill, 1928. [data is that of Amagat, *Ann. chim. phys.* 29:68(1893) and 28:5(1913)].
70. International Critical Tables. 1st ed. Vol. 3. p. 12-13. New York, McGraw-Hill, 1928. [data is that of Keesom, *Verslag koninklijke Akademie van Velenschappen te Amsterdam* 12:391, 544, 616, 621(1903)].
71. Sweigert, R. L., Weber, Paul, and Allen, R. L., *Ind. Eng. Chem.* 38, no. 2: 185-200(Feb., 1946).
72. Kobe, Kenneth A., and Lynn, R. Emerson, Jr., *Chem. Rev.* 52:117-236(1953).
73. Schmidt, Ernst, and Thomas, W., *Forsch. Gebeite Ingenieurw.* 20B:161-70 (1954); *C.A.* 50:9078.
74. Glasstone, Samuel. Text-book of physical chemistry. p. 467-8. New York, D. Van Nostrand, 1940.
75. Ipatieff, V. N., and Monroe, G. S., *Ind. Eng. Chem., Anal. Ed.* 14, no. 2: 171-4(1942).

76. Kay, W. B., Ind. Eng. Chem. 30:459-65(1938).
77. Thiele, E. W., and Kay, W. B. The significance of the critical temperature of mixtures. In American Institute of Physics' Temperature, its measurement and control in science and industry. p. 1079-89. New York, Reinhold, 1941.
78. Hirschfelder, Joseph O., Curtiss, Charles F., and Bird, R. Byron. Molecular theory of gases and liquids. p. 336-91. New York, Wiley, 1954.
79. Hougen, Olaf A., and Watson, Kenneth M. Chemical process principles, Part 2, thermodynamics. New York, Wiley, 1947.
80. Boyd, Charles A., J. Phys. Coll. Chem. 54:1347-57(1950).
81. Comings, Edward W. High pressure technology. p. 294-309. New York, McGraw-Hill, 1956. 572 p.
82. Sage, B. H., Budenholzer, R. A., and Lacey, W. N., Ind. Eng. Chem. 32, no. 9: 1262-77(Sept., 1940).
83. Booth, Harold S., and Bidwell, Richard M., Chem. Revs. 44:477-513(1949).
84. Sterrett, Robert S. The Matheson Co., Inc., Joliet, Ill. Private communication, May 31, 1961.
85. Scornavacca, Frank. The Matheson Co., Inc., East Rutherford, N. J. Private communication, Feb. 6, 1962.
86. Urquhart, Alexander R., and Williams, Alexander M., J. Textile Inst. 15: T138-43(1924).
87. Mellon, Edward F., Korn, Alfred H., and Hoover, Sam R., J. Am. Chem. Soc. 69:827-31(April, 1947); 70:1144-6(March, 1948).
88. Rowen, John W., and Blaine, R. L., J. Research Natl. Bur. Standards 39: 479-86(Dec., 1947); Ind. Eng. Chem. 39, no. 12:1659-63(Dec., 1947).
89. Jeffries, R., J. Textile Inst. 51, no. 9:T339-74(Sept., 1960).
90. Stamm, Alfred J., Tappi 40, no. 9:761-5(Sept., 1957).
91. Emmett, Paul H. Measurement of the surface area of solid catalysts. In Emmett's Catalysis. Vol. 1. p. 31-74. New York, Reinhold, 1954.
92. Harkins, William D., and Jura, George, J. Am. Chem. Soc. 66:1362-6(Aug., 1944).
93. Livingston, H. K., J. Colloid Sci. 4:447-58(1949).
94. Emmett, P. H., and Brunauer, S., J. Am. Chem. Soc. 59:1553-64(Aug., 1937).
95. See Reference (6).

96. Brunauer, Stephen. The adsorption of gases and vapors. Princeton, Princeton University Press, 1945. 511 p.
97. Pierce, Conway, J. Phys. Chem. 57, no. 2:149-52(Feb., 1953).
98. Pierce, Conway, J. Phys. Chem. 63:1076-9(July, 1959).
99. Wheeler, A. Report S-9829 circulated to the PAW "Recommendation 41 group" of the Petroleum Industry, June 1945; presented at AAAS Gordon Conference on Catalysis, Gibson Island, 1945 and 1946.
100. Shull, C. G., J. Am. Chem. Soc. 70:1405-10(April, 1948).
101. Frey-Wyssling, A., Science 119:80-2(Jan. 15, 1954).
102. Kinsinger, William G., and Hock, Charles W., Ind. Eng. Chem. 40, no. 9: 1711-19(Sept., 1948).
103. Rånby, Bengt G., Tappi 35, no. 2:53-8(Feb., 1952).
104. Usmanov, Kh. U., and Nikonovich, G. V., Uzbek. Khim. Zhur. no. 6:11-15(1960); A.B.I.P.C. 32:7158.
105. Howsmon, John A., and Sisson, Wayne A. Structure and properties of cellulose fibers. B. Submicroscopic structure. In Ott and Spurlin's High polymers. 2d ed. Vol. 5. Part 1. p. 231-347. New York, Interscience, 1954.
106. Hock, Charles W. Structure and properties of cellulose fibers. C. Microscopic structure. In Ott and Spurlin's High polymers. 2d ed. Vol. 5. Part 1. p. 347-92. New York, Interscience, 1954.
107. Ward, Kyle, Jr. Personal communication, 1962.
108. Shutt, Richard S., and Mack, Edward, Jr., Ind. Eng. Chem. 25:687-91(1933).
109. Mease, R. T., Ind. Eng. Chem., Anal. Ed. 5:317(1933).
110. Wiertelak, J., and Garbaczowna, I., Ind. Eng. Chem., Anal. Ed. 7:110-11 (1935).
111. Hermans, P. H., and de Leeuw, A. J., Kolloid Z. 82:58-67(1938); C.A. 32: 2735.
112. Richter, George A., Herdle, Lloyd E., and Wahtera, Waino E., Ind. Eng. Chem. 49, no. 5:907-12(May, 1957).
113. McKnight, T. S., Marchessault, R. H., and Mason, S. G., Pulp Paper Mag. Can. 59, no. 2:81-8(Feb., 1958).
114. Staudinger, Herman, and Döhle, Wolfgang, J. Prakt. Chem. 161, no. 8+10: 219-40(1943).

115. Russell, J. K., Maass, O., and Campbell, W. B., Can. J. Research 15B:13-37 (1937).
116. Daruwalla, E. H., and Shet, R. T., Textile Research J. 32, no. 2:165-7 (Feb., 1962).
117. Fugassi, P., and Ostapchenko, G., Fuel 38:259-70; 271-6(1959).
118. Hermans, P. H. Contributions to the physics of cellulose fibres. New York, Elsevier, 1946. 221 p.
119. Mair, Beveridge J. Chromatography: columnar liquid-solid adsorption processes. III. Fractionation with molecular sieve adsorbents. In Kolthoff, Elving, and Sandell's Treatise on analytical chemistry. Part 1. Vol. 3. Chap. 34. New York, Interscience, 1961.
120. Hermann, John A., and Suttle, John F. Precipitation and crystallization. Inclusion compounds. In Kolthoff, Elving, and Sandell's Treatise on analytical chemistry. Part 1. Vol. 3. Chap. 32. New York, Interscience, 1961.
121. Brown, John F., Jr. Inclusion compounds. Sci. American 207, no. 1:82-92 (July, 1962).
122. Kress, Otto, and Bialkowsky, Harold, Paper Trade J. 93, no. 20:35-44 (Nov. 12, 1931).
123. Stamm, Alfred J., and Hansen, L. A., Ind. Eng. Chem. 27:1480-4(1935).
124. Stamm, Alfred J., and Tarkow, Harold, J. Phys. Colloid Chem. 54:745-53(1950).
125. Giles, C. H., and Hassan, A. S. A., J. Soc. Dyers Colourists 74:846-57(1958).
126. Giles, C. H., MacEwan, T. H., Nakhwa, S. N., and Smith, D., J. Chem. Soc. 786:3973-93(Oct., 1960).
127. Morehead, Frederick F., Textile Research J. 22, no. 8:535-9(Aug., 1952).
128. Lauer, K., Ayer, J. E., and Seoud, Abdel L. A., J. Polymer Sci. 24, no. 105:67-74(March, 1957).
129. Giles, C. H., and Nakhwa, S. N., J. Appl. Chem. 12, no. 6:266-73(June, 1962).
130. Francis, Alfred W. In Seidell and Linke's Solubilities of inorganic and organic compounds. Supplement of the 3d ed. New York, D. Van Nostrand, 1952. 1254 p.
131. Thode, Edward F., and Guide, Robert G., Tappi 42, no. 1:35-9(Jan., 1959).
132. Thode, Edward F., and Ingmanson, William L., Tappi 42, no. 1:74-83(Jan., 1959).

133. Van den Akker, J. A., Tappi 42, no. 12:940-7(Dec., 1959).
134. Van den Akker, J. A., Wink, W. A., and Bobb, F. C., Tappi 42, no. 4:340-4 (April, 1959).
135. Rance, H. F. The porous structure of paper. In Everett and Stone's The structure and properties of porous materials. London, Butterworths, 1958. 389 p.
136. Hildebrand, Joel H., and Scott, Robert L. The solubility of nonelectrolytes. 3d ed. New York, Reinhold, 1950. 488 p.
137. Howsmon, John A. Structure and properties of cellulose fibers. D. Structure-sorption relationships. In Ott and Spurlin's High polymers. 2d ed. Vol. 5. Part 1. p. 404. New York. Interscience, 1954.
138. Cassie, A. B. D., Trans. Faraday Soc. 41:458-64(1945).
139. Iler, Ralph K. The colloid chemistry of silica and silicates. p. 150-1. Ithaca, N.Y., Cornell U. Press, 1955. 324 p.
140. Lieberman, E. P., Official Digest 34, no. 444:30-50(Jan., 1962).
141. Adamson, Arthur W. Physical chemistry of surfaces. New York, Interscience, 1960. 629 p.
142. Lange, Norbert A. Handbook of chemistry. 6th ed. Sandusky, Ohio, Handbook Publishers, 1946. 1767 p.
143. Jayme, Georg, and Rothamel, Ludwig, Das Papier 2, no. 1/2:7-18(Jan., 1948).
144. Morris, H. E., and Maass, O., Can. J. Research 9:240-51(1933).
145. Edwards, J., and Maass, O., Can. J. Research 13B:133-9(1935).
146. Edwards, J., and Maass, O., Can. J. Research 12:357-71(1935).
147. de Boer, J. H. Structure and texture of catalysts. In Advances in catalysis. Vol. 9. p. 138-40. New York, Academic Press, 1957.
148. Wheeler, Ahlborn. Reaction rates and selectivity in catalyst pores. In Emmett's Catalysis. Vol. 2. p. 105-65. New York, Reinhold, 1955.
149. Barrett, Elliott P., Joyner, Leslie, G., and Halenda, Paul P., J. Am. Chem. Soc. 73:373-80(1951).
150. Cranston, R. W., and Inkley, F. A. The determination of pore structures from nitrogen adsorption isotherms. In Advances in catalysis. Vol. 9. p. 143-54. New York, Academic Press, 1957.
151. Halsey, George, J. Chem. Phys. 16, no. 10:931-7(Oct., 1948).

152. Frenckel, J. Kinetic theory of liquids. London, Oxford U. Press, 1946
[as cited by (103)].
153. Hill, T. L. Address in catalysis. Vol. 4. New York, Academic Press, 1932.
[as cited by (103)].
154. Bowers, R., Phil. Mag. 44, no. 7:4676(1953). [as cited by (103)].
155. Merchant, Morris V. Unpublished work, 1956.

APPENDIX

HIGH-PRESSURE AND HIGH-VACUUM LEAK PROBLEMS

It has already been pointed out that considerable difficulty was encountered with leaks in the stainless steel apparatus. Several months were lost as a direct result of such difficulties.

Most of the leak problems occurred at the gasket in the stainless steel vessels as shown in Fig. 18. Repeated attempts to obtain a seal with the stainless-steel gaskets as supplied with the vessels met with failure. Various attempts included removal of the gaskets and cleaning, intense tightening, use of a thin coat of high-vacuum grease around the gasket, and even annealing of the gaskets in an inert atmosphere and hand polishing to a perfect fit. Copper gaskets were finally obtained from the manufacturer and were found to generally give a tight seal. Since these could not be used in the mercury reservoir, gaskets were finally made for those vessels out of 2-mm. thick teflon gasket material. These were found most satisfactory.

Two other leaks were found and were finally corrected by the substitution of a stainless-steel gasket at the gage by one machined from copper, and the insertion of a brass gasket at the rupture disk to eliminate a steel-to-steel contact.

Once these steps were taken only one sample was lost by a pressure leak. Two were lost through high vacuum leaks, one leaking only when immersed in liquid nitrogen.

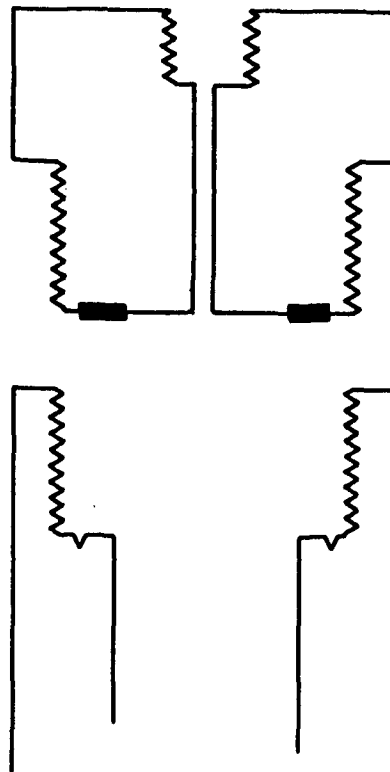


Figure 18. Gasket in Vessel Head

MISCELLANEOUS NOTES ON EXPERIMENTAL RESULTS

WATER CONTENT OF THE TWO CARBON DIOXIDE SOURCES

Several determinations were made of the moisture in the carbon dioxide in the two cylinders used, their order of use being designated by 1 and 2.

The procedure, in general, consisted in passing the carbon dioxide through a flowmeter, a series of drying tubes and a wet test meter graduated to the nearest 0.001 cu. ft. for determining the total wet volume of gas. The flow rate was kept close to 200 cc./min. for a period of about 6 days. For calculations the wet volume was converted first to a dry basis at S.T.P., and then to a weight basis, the average ambient temperature and barometric pressure being used.

The first series involved a Drierite-Anhydrone tube, two phosphorus pentoxide tubes of about 9 by 20 mm., followed by two more phosphorus pentoxide tubes. All but the last tube was used in the determination of the weight increase. This set-up was used for both cylinders and water contents were found to be:

0.0544 mg./g. for Cylinder 1, and

0.583 mg./g. for Cylinder 2.

It was felt that the large variation in the temperature in the above series would hinder a direct comparison of the two cylinders because the water concentration of the vapor phase will depend upon the temperature. In one case the temperature had been generally about 70°F. and in the other it exceeded the critical several times. A second series was therefore run in a controlled temperature room at 71°F. Also, in this series one Anhydrone tube and four phosphorus pentoxide tubes were used, the weights of all but the last tube being determined. The water contents were found to be:

0.0622 mg./g. for Cylinder 1, and

0.0647 mg./g. for Cylinder 2.

The reason for the slightly higher values in the second series is believed due to better water removal through greater drying capacity.

In both cases Cylinder 2 contained more water, being 4% higher in the second series.

PHOSPHORUS PENTOXIDE FOR DRYING LIQUID CARBON DIOXIDE

Two samples were exchanged with liquid carbon dioxide passed through phosphorus pentoxide. Sample c-2e has already been mentioned with reference to charring

when dried from water. It was also noted when removing the sample that about the top inch and a half of cotton had a dirty-gray color and was also more compacted than the rest of the sample which was white and quite fluffy. This change most likely occurred during the carbon dioxide exchange since the methanol exchange was in the reverse direction. From its physical appearance it probably had a lower surface area. Considering that it contributed nothing to the surface area, the area for the rest of the material would be about 63 sq. m./g. It would seem that if the phosphoric acid had not been carried into the cotton the area may therefore have been greater than the 49.5 sq. m./g.

The other sample was c-1c which was exchanged directly from water to carbon dioxide. As will be seen later considerable water remained after the exchange and was removed by passage of dried nitrogen. The point of interest here, however, is the physical appearance of the sample after outgassing and removal. The cotton was quite fluffy but some of it tended to stick to the walls of the glass liner contrary to previous samples. This may have been due to the partial water drying. The inside of the liner also contained tiny droplets of an apparently nonvolatile material since the sample had been outgassed. It appeared quite greasy of about the consistency of vacuum grease and was no doubt the result of material carried over from the phosphorus pentoxide drying tube.

Oven drying of this sample without wetting resulted in severe charring in several small places. A weight loss of 0.57% was noted presumably due to the charring.

VACUUM LEAK IN SAMPLE C-2hw

During the outgassing of Sample c-2hw (the benzene-dried sample with the pentane intermediate) the ground-glass joint connecting the sample to the gas

adsorption apparatus loosened, because the male part was too long, and air was pulled into the apparatus for an unknown period of up to 4 hours. The leak was quite small, however, as noted by the sound of the pump. Some of the surface area for this sample therefore may have been lost. Since the area was higher than for Sample c-2gw (the benzene-dried sample) despite the possible loss, the effect of the pentane intermediate can hardly be doubted.

FLOW STOPPAGE DURING PASSAGE OF DRIED CARBON DIOXIDE

In the early part of the passage of dried carbon dioxide through Sample c-2cw it is possible that the flow had stopped for a period of up to 50 minutes due to a defective needle valve. Since the phosphorus pentoxide drying tube after the flowmeter was not added until after this incident it is possible that some moisture may have diffused back into the sample.

Several facts seem to indicate that most likely this did not happen. Besides the ball of the flowmeter acting as a sort of check valve there was approximately 57 cm. of 2-mm. bore capillary tubing between the sample and the flowmeter which would tend to minimize moisture diffusion. Also, the fact that the passage of dried nitrogen through Sample c-2e caused a significant loss of area supports the effect found by the dried carbon dioxide.

POSSIBLE EFFECTS OF UNREPLACED METHANOL ON THE CRITICAL POINT AND SURFACE TENSION

It has been pointed out that in one case up to 28 mg. of unreplaced methanol may have remained in each gram of carbon dioxide which was removed above the critical point. It is interesting to note what effect this might have on the critical point and surface tension of the carbon dioxide if it existed as a uniform methanol-carbon dioxide solution. If we accept as an approximation the 8.8°C.

rise in critical point per mole per cent of solute (83) the 28 mg./g. would give a critical point of about 63°C. If this is true, removal at say 36°C. involves a liquid-vapor interface with surface tension forces. Again, as an approximation, taking the surface tension of the solution as the sum of the mole fraction contributions of the two components (26, 141) and for surface tensions at 30°C. of 22 dynes/cm. for methanol and 0.06 dyne/cm. for liquid carbon dioxide (142), the 28 mg./g. solution would have a surface tension of about 0.9 dyne/cm. Even though likely an overestimation it compares with a surface tension of n-pentane at 30°C. of about 15 dynes/cm. (6) and a decrease in Merchant's (6, 7) extrapolated surface area of 2 to 3% per increase in surface tension of 1 dyne/cm. It would therefore seem that even if such a concentration of methanol in liquid carbon dioxide did exist, its effect on the final surface area would not be greatly significant. It would seem most likely, however, that the unreplaced methanol remains essentially in the small pore regions.

The fact that the total pore volume of the CP-sample with a removal temperature of 45°C. is slightly higher than for 36°C. may be explained as a combination of the lowered surface tension and decreased plasticizing effect (143) of the unreplaced liquids and/or any dilute methanol-carbon dioxide solution which may exist.

WATER-TO-CARBON DIOXIDE EXPERIMENT

Sample c-1c was solvent exchanged directly from water to liquid carbon dioxide in hope that most of the water surrounding the external surface of the fibers would be displaced but that water within the pore structure would still remain. This then should give a sample for which the external surface area could be determined.

Contrary to alcohol to carbon dioxide exchanges only 37 cc. of liquid water was recovered. Since considerable difficulty was encountered with freezing of valves, part of the water may have remained in the reservoir as ice.

Removal was conducted at 40°C. with some water being expelled during each emptying of the reservoir. The final drying was done by the passage of dried nitrogen at about 100 cc./min. with a tared phosphorus pentoxide tube at the exit for following the water removal.

Approximately 8 days were required before the removal rate finally decreased appreciably. In all, 16.37 g. of water were removed with final rate being about 0.0037 g./hr. Since the unreplaced water was about 12 g./g. of cotton, considerably more water than that associated with the internal structure had remained. No surface area was determined because of a high vacuum leak when immersed in liquid nitrogen.

This method of determining the external surface area may still have some merit if conditions could be used for replacement of most of the external water by alcohol and then drying from n-pentane or carbon dioxide. Study of the pore distribution would substantiate the success.

EFFECT OF PORE SIZE ON CRITICAL PHENOMENA

One question which has been asked and which is likely to arise in the mind of the reader is whether or not the critical point of a liquid in fine pores is the same as in the bulk liquid, or in other words can the pore walls exert enough influence on the adsorbate to cause capillary condensation above the critical temperature of the bulk liquid? There does not appear to be an answer to this question either by this work or by that reported in the literature. Some discussion however can be given.

First, even if the liquid could persist it would likely be of little significance since even below the critical temperature, at 20°C., the surface tension of liquid carbon dioxide is only 1.16 dynes/cm. (142).

Generally, the basis of this question is the fact that the boiling point of a pure wetting liquid in a fine capillary is higher than that for the same liquid with a plane surface. This increase in boiling point is due to the lowering of the vapor pressure over a meniscus concave to the vapor phase. This reduction is given by the Kelvin equation:

$$\mu - \mu_o = \ln (P/P_o) = (2\gamma V)/(RT_r) \quad (1)$$

where

μ = chemical potential of a liquid with a curved surface.

μ_o = chemical potential of a liquid with a plane surface or the equilibrium vapor phase.

\underline{P} = vapor pressure over a curved surface of radius \underline{r}

\underline{P}_o = vapor pressure over a plane surface

γ = surface tension of the liquid

\underline{V} = molar volume

\underline{R} = gas constant

\underline{r} = radius of the meniscus

\underline{T} = temperature, °K.

Equilibrium occurs over a plane surface when

$$\mu = \mu_o \quad (2)$$

whereas over a curved surface when

$$\mu - (2\gamma V)/(RT_r) = \mu_o. \quad (3)$$

As the critical temperature is approached as a limit the surface tension approaches zero as a limit and therefore it would appear that above the critical temperature the equilibrium conditions are

$$\mu = \mu_0 \quad (2)$$

and there will be no capillary condensation. Physical adsorption, at least as a monolayer, still may exist.

It would also seem that since no external pressure no matter how large can bring gas molecules above the critical temperature close enough for their attractive forces to cause condensation, the attractive forces of a capillary wall will not do so either.

Maass and co-workers (144, 145) found that up to 15°C. above the critical point there was no apparent discontinuity in their adsorption data thus indicating that multilayer adsorption still exists. Edwards and Maass (145) interpreted these results as a negative indication of a change in the critical temperature of the capillary liquid. They reasoned that if the critical temperature of the liquids were raised, sorption above the critical temperature would be dependent on the distribution of pore sizes and when the critical temperature in the smallest capillary was finally reached, sorption would become zero. Since sorption above the critical point showed only the normal temperature coefficient, they believe that the conception of capillary condensation above the critical temperature cannot be true. They offered no explanation however for the similarity in the isotherms above and below the critical temperature.

They (144, 145) also observed a discontinuity in adsorption in going from a liquid to a gas at the critical temperature. There was no indication of adsorption

from the liquid but as the critical temperature was exceeded a strong adsorption from the gas occurred. This would indicate a difference between the liquid and gaseous molecules. Above the critical temperature the increase in molecular energy apparently causes the liquid-to-solid attraction to exceed that of the liquid-to-liquid attraction.

In the CP-method it would seem that the removal of carbon dioxide gas may in effect be desorbing from multilayers. Some of the very small pores may have been filled by means of multilayer adsorption but it is not known if the attractive forces are such as to cause collapse on removal or not. These very small pores are in a realm where little is known regarding such phenomena and where even the concept of surface tension becomes debatable.

Although not proven, indications are that there is no capillary condensation above the critical temperature.

Brunauer (96) has also given this topic a brief discussion.

DETERMINATION OF PORE-VOLUME DISTRIBUTION

CHOICE OF METHOD

The determination of pore-volume distributions from nitrogen-adsorption isotherms has been reviewed by de Boer (147) and Wheeler (148), the former being very brief and the latter quite extensive.

Wheeler (99) presented his theory in 1945 which pointed out that the pore radius is equal to the sum of the radius predicted by the Kelvin radius, and the thickness of an adsorbed multilayer on the unfilled capillary. His theory can be summarized by one of his equations,

$$V_s - V = \pi \int_{R_{P_n}}^{\infty} (R - t)^2 L(R) dR \quad (4)$$

where

\underline{V}_s = volume adsorbed at saturation

\underline{V} = volume adsorbed at pressure \underline{P}

$\underline{L}(\underline{R})\underline{dR}$ = total length of pores between radii \underline{R} and $\underline{R} + \underline{dR}$

\underline{R}_{P_n} = radius of largest pore still filled at pressure \underline{P} .

\underline{t} = thickness of multilayer at \underline{P} .

$\pi = 3.1416$

Wheeler's original method (99) assumed a pore size distribution function $\underline{L}(\underline{R})$ and compared the isotherm determined from it with the experimental curve. This was improved and extended by Shull (100) to give what is commonly known as the Wheeler-Shull method. Here the assumption is made that the pore distributions are of a simple Gaussian or Maxwellian form.

Barrett, Joyner, and Halenda (149) (BJH) further improved the method by devising a procedure which does not assume any particular pore size distribution. Their method, tabular in nature, does involve, however, a more or less arbitrary and sometimes not too well-defined constant, \underline{c} .

Pierce (97) was able to eliminate this arbitrary constant in his tabular procedure, which is still based on the BJH method. Unlike Barrett, Joyner, and Halenda (149) however, Pierce (97) calculates the pore volume over a given decrement of relative pressure as the difference between the amount of gas desorbed, and that removed from unfilled capillaries by taking the product of the change in multilayer thickness and the summed area of the unfilled or true pores. To be accurate, the area of the capillaries formed by the adsorbed multilayer, the Kelvin pores, should be used. This would complicate the calculation since the area of the Kelvin pores varies with the thickness of the adsorbed multilayer while the area of the true pores is constant.

More recently Wheeler (148) and Cranston and Inkley (150) have presented improvements of the BJH method which are more accurate than Pierce's (97) method by virtue of using the area of the Kelvin pores, as mentioned above. Both procedures were developed independently and are based on essentially the same mathematical relationship. Using the same symbols, Wheeler's (148) relationship is:

$$V_{12} = R^2 \Delta V / (R - t)^2 - \left[R^2 / (R - t)^2 \right] 2\pi \Delta t \Sigma (R - t) L(R) \Delta R \quad (5)$$

and Cranston and Inkley's (150) relationship is:

$$V_{12} = R_{12} \left(\Delta V - k_{12} \Sigma (R - t_{12}) / (2R^2) V(R) \Delta R \right) \quad (6)$$

where

$$R_{12} = (R_2 - R_1) / \int_{R_1}^{R_2} \left[(R - t_1)^2 / R^2 \right] dR$$

$$\approx R^2 / (R - t_1)^2$$

$$\underline{t}_{12} = (\underline{t}_1 + \underline{t}_2)/2$$

$$\underline{k}_{12} = 4(\underline{t}_2 - \underline{t}_1)$$

$$\underline{V}_{12} = \text{volume of pores between } \underline{R}_1 \text{ and } \underline{R}_2$$

$$\underline{R} = \text{pore radii}$$

$$\underline{\Delta V} = \text{total volume desorbed}$$

$$\underline{\Delta t} = \underline{t}_2 - \underline{t}_1 = \text{change in multilayer thickness}$$

$$\underline{L}(\underline{R})\underline{\Delta R} = \text{length of pores in } \underline{\Delta R} \text{ range.}$$

$$\underline{V}(\underline{R})\underline{\Delta R} = \text{volume of pores in } \underline{\Delta R} \text{ range}$$

Wheeler (148) uses the distribution function in terms of length $\underline{L}(\underline{R})$ and arrives at his equation mathematically.* Cranston and Inkley (150) use the distribution function in terms of volume $\underline{V}(\underline{R})$ and arrive at their equation by a more intuitive approach.

Wheeler (148) gives a procedure for using the exact equation as well as an analytical solution to a differential equation from a simplified version. The simplified version apparently uses the true pore area in place of the Kelvin pore area. Wheeler (148) points out that this simplified version is similar to that used by Barrett, Joyner, and Halenda (149) and its use may give somewhat too high values for the pore-size-distribution function, especially at the small pore range.

It is believed by this writer that Barrett, Joyner, and Halenda's (149) equation is exact and uses the Kelvin pore area by virtue of their arbitrary constant. This is true at least in their basic relationship before numerical evaluation.

* One step utilizes the Leibnetz rule of advanced calculus.

Cranston and Inkley (150) present a tabular method for using their equation and illustrate the operation with a detailed example. This greatly improves the utility of their method and is therefore preferable to that of Wheeler (148).

The choice thus comes to either the procedure of Pierce (97) or the procedure of Cranston and Inkley (150). The main question here is whether the use of the true pore area instead of the Kelvin pore area will have a significant effect on the results.

Using essentially the same multilayer thickness, t , values as Cranston and Inkley (150), the Pierce method (97) was applied to data of the former. Down to and including the relative pressure of 0.350 or a pore radius of 15 A., the two methods agreed very well. After a relative pressure of 0.130 or pore radius of 9 A., the procedure broke down. Cranston and Inkley (150) carried their procedure to even lower relative pressure values before their method failed. This is certainly a questionable practice, as is just going down much below the radius of 15 A. At the relative pressure of 0.130 the summation of the pore volumes was 4% lower by Pierce's method (97), whereas the summation of pore area was about 10% lower. The maximum in the distribution curve was the same in the two cases.

It thus appears that little error is involved by using Pierce's method (97) and therefore because of its simplicity it was used in the pore volume calculations in this work.

NUMBER OF ADSORBED LAYERS AS A FUNCTION OF RELATIVE PRESSURE

The statistical number of adsorbed layers, n , or the thickness of the adsorbed multilayer, t , varies with the relative pressure, P/P_0 .

In general, \underline{t} or \underline{n} values have been determined from nitrogen-adsorption isotherms of nonporous solids such as powdered metal oxides. There is always the possibility that there is some capillary condensation between particles in the higher relative-pressure range. Agreement between different sources in the lower relative-pressure range is generally quite good.

After closely examining the basis for selection of \underline{t} and \underline{n} values for the various pore-volume distribution methods discussed in the previous section, two more recent methods were considered.

One was the equation of Halsey (151) for nitrogen as given by Wheeler (148) as:

$$t = 4.3 \left[5 / \ln(P_0/P) \right]^{1/3} \quad (7)$$

This equation apparently comes from Frenckel (152) and Hill (153) as cited by Pierce (98).

The other was that of Pierce (98) who noted in his study of heats of adsorption that one cannot assume that there is no interparticle condensation in adsorption isotherms on nonporous powder samples. He points out that the \underline{n} values he used in earlier work (97) are in error because there was interparticle condensation.

Pierce (98) gives composite values of \underline{n} by combining data for many powder samples at lower relative pressures with data of Bowers (154) for a single sheet of metal foil at high relative pressures. These values are in good agreement with those of Shull (100) below a relative pressure of 0.95 and Pierce (98) found them to fall on a straight line from a relative pressure of 0.2 to 0.99 when tested by a Frenckel-Halsey-Hill plot. The straight line gave the equation:

$$n = \left[1.30 / \log(P_0/P) \right]^{1.275} = \left[2.99 / \ln(P_0/P) \right]^{1.275} \quad (8)$$

This differs slightly from that given by Wheeler (148), but since it fits numerous experimental data, Pierce's (98) n values were used in this work.

THICKNESS OF AN ADSORBED LAYER

Having selected the method and the n values the selection of the thickness of one adsorbed layer still remained. There appears to be two values in use, 4.3 A. (99, 100, 149) and 3.6 A. (97), the latter being determined by dividing the molecular volume by the cross-sectional area of the nitrogen molecule, 16.2 sq. A.

The equation for determining the cross-sectional area of an adsorbed molecule suggested by Emmett and Brunauer (94) and later given in the books by Emmett (91) and Brunauer (96) has already been mentioned and is:

$$\text{area} = 2 \sqrt{3} \left[M / (4 \sqrt{2} A d) \right]^{2/3} \quad (9)$$

where

\underline{M} = molecular weight

\underline{A} = 6.023×10^{23}

\underline{d} = density

Since the area for the nitrogen molecule determined by this equation is 16.2 sq. A. and has generally been accepted it was decided to examine the origin of this equation.

The geometric assumptions underlying this equation are that the nitrogen molecules are hard spheres in a close packed hexagonal arrangement. The radius of such a molecule comes out to be:

$$\text{radius} = \left[M / (4 \sqrt{2} A_d) \right]^{1/3} \quad (10)$$

which in the case of nitrogen is 2.16 A. This is apparently the basis for 4.3 A. as the thickness of a single layer since this is the diameter and therefore the thickness of the first layer. The distance between planes passing through the molecular centers of succeeding layers is:

$$\text{distance} = (2/3)(\sqrt{6} r) \quad (11)$$

which gives 3.53 A. for nitrogen. This then is the value which was used for the thickness of one adsorbed layer.

ESTIMATE OF NONPORE OR EXTERNAL SURFACE AREA

The calculation of the pore-volume distribution starts at a given high relative pressure and proceeds in increments to the low relative-pressure region. At some lower limit where the pore sizes become of molecular dimensions the calculations are stopped because the surface tension is no longer that defined by a bulk liquid. At this point there is generally a certain volume of adsorbed gas which has not been accounted for. It would seem that if the analysis has been reasonably correct some account should be made for this material. Realizing the danger of such an attempt when even the method of analysis and its basic assumptions are open to question, several calculations were performed with somewhat interesting results.

The only additional assumption made is that this unaccounted gas volume consists of three parts, (1) that which is multimolecularly adsorbed on the surface area cumulated so far, (2) that which remains in still smaller pores which as yet has not been determined, and (3) that which has been multimolecularly adsorbed on

the nonporous or external surface area and which is not considered in the method. Along with this one can attribute the difference between the BET area and that cumulated to this point to the sum of the area in the very small pores and that of the nonporous surface. These statements are given in the following equations which can be solved for the respective quantities.

Let

A_N = nonporous area, sq. m.

A_S = undetermined small pore area, sq. m.

V_N = total volume adsorbed on A_N at $P/P_0 = 0.971$, cc. gas at S.T.P.

V_S = volume adsorbed in the very small pores below a radius of 10 A. at $P/P_0 = 0.186$, cc. gas at S.T.P.

$V_{.971}$ = total volume of gas adsorbed at $P/P_0 = 0.971$, cc. gas at S.T.P.

$V_{.186}$ = total volume of gas adsorbed at $P/P_0 = 0.186$, cc. gas at S.T.P.

$t_{.186}$ = thickness of the multilayer at $P/P_0 = 0.186$, A.

$t_{.971}$ = thickness of the multilayer at $P/P_0 = 0.971$, A.

\int_a^b = cumulation of the given quantity from $P/P_0 = a$ to $P/P_0 = b$

r_p = average pore radius over a given increment, A.

0.0639 = constant which converts cc. to cc. of gas at S.T.P. and also compensates for the units.

31 = constant which converts cc. of gas at S.T.P. to cc. and also incorporates the factor 2 and compensates for units.

Then

$$V_{.186} = \left(\sum_{.186}^{.971} A \right) (t_{.186}) (.0639) + V_N + V_S \quad (12)$$

and

$$A_{\text{BET}} - \left(\sum_{.186}^{.971} A \right) = A_N + A_S \quad (13)$$

Since

$$t_{.186} = 4.33 \text{ A.},$$

$$t_{.971} = 18.93 \text{ A.},$$

and assuming

$$\bar{r}_p = 5 \text{ A.},$$

then

$$V_N = (A_N)(18.93)(0.0639) \quad (14)$$

and

$$V_S = (5 A_S)/31 \quad (15)$$

Substituting into Equation (12) gives:

$$V_{.186} = \left(\sum_{.186}^{.971} A \right) (4.33)(.0639) + (A_N)(18.93)(.0639) + (5A_S)/31 \quad (16)$$

which can be solved simultaneously with Equation (13).

The values used and those calculated are given in Table VIII for the three samples for which pore volume distributions were determined.

It will be noticed that this procedure, which makes the cumulative areas equal the BET areas, also makes the total pore volumes and the cumulative volumes agree better.

The negative values are of course ridiculous. The two positive values of 0.39 and 0.52 sq. m./g. for the external surface are quite reasonable.

TABLE VIII

CALCULATED SMALL PORE AND EXTERNAL SURFACE AREAS

	Sample c-2f	Sample c-2j	Sample c-2bw
A_{BET} , sq.m./g.	23.83	39.36	47.27
$\sum_{.186}^{.971} A$, sq.m./g.	22.93	35.92	44.46
$V_{.186}$, cc. S.T.P.	7.0	11.0	12.6
$V_{.971}$, cc. S.T.P.	47.0	47.4	38.8
$\sum_{.186}^{.971} V$, cc. S.T.P.	45.98	45.21	36.70
A_{S} , sq.m./g.	0.51	2.92	2.95
A_{N} , sq.m./g.	0.39	0.52	-0.14
V_{S} , cc. S.T.P.	0.08	0.47	0.48
V_{N} , cc. S.T.P.	0.47	0.63	-0.17
$\sum_0^{.971} A$, sq.m./g.	23.83	39.36	47.27
$\sum_0^{.971} V$, cc. S.T.P.	46.53	46.31	37.01

It appears possible therefore to account for that nitrogen which is still adsorbed when the pore volume calculations are discontinued. Caution must be exercised in assigning any significant conclusions to the values determined in this way because of the admitted approximation of the whole method.

MERCHANT'S CRITICAL-POINT ATTEMPT

Although not published, Merchant (155) did prepare two samples by a critical-point technique with liquid propane. His technique is particularly of interest since it differed considerably from that used by the author. The sample bulb and bomb assembly is shown in Fig. 19.

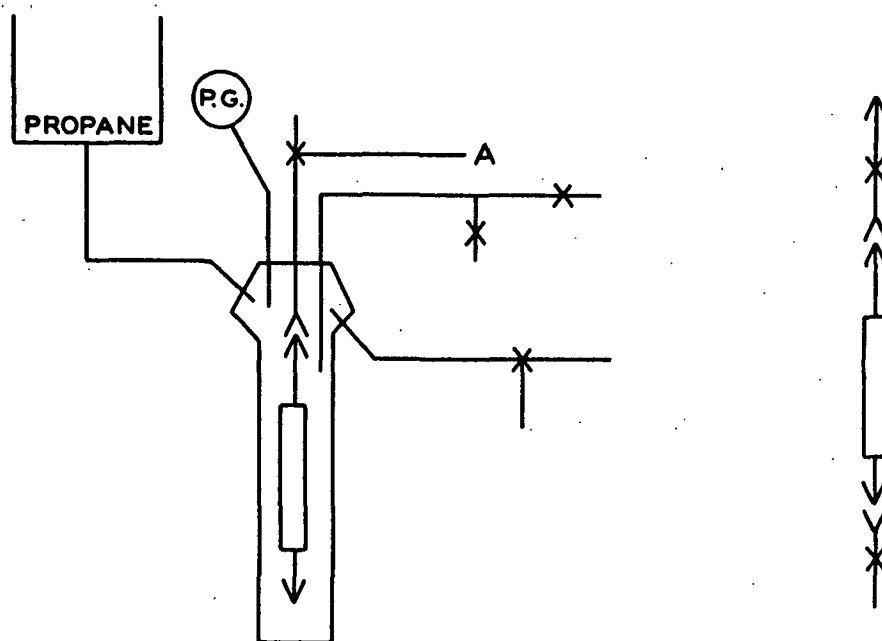


Figure 19. Merchant's (155) Pressure Vessel and Sample Bulb Assembly

Following the normal methanol exchange, the sample, under methanol in the glass bulb, was connected into the bomb as shown in Fig. 19. The bomb was cooled in a dry ice bath and by suitable valve manipulation propane was allowed to condense into the bomb until it was observed to come out of an overflow at the top.

Nitrogen pressure was then used to displace liquid out of A and into a 20-cc. capacity bulb immersed in another dry ice bath until an overflow was noted. This procedure was repeated every 10 minutes for 10 times.

Finally, after the last removal of 20 cc. the valves were closed and the temperature raised to 120°C. in a glycerin bath with the pressure reaching 1900 p.s.i. The propane was removed by opening a valve until the pressure reached 25 p.s.i. and then passing hot dried nitrogen through the sample. One stopcock was then joined to the sample during the nitrogen flow after which the bulb was disconnected and sealed with the other stopcock.

A second sample, E-204, involved exchanges of 30 cc. every 10 minutes. This run resulted in two small leaks at high pressure.

The results were as follows:

73.9 sq. m./g. for Sample E-203, and

102 sq. m./g. for Sample E-204.

The former was also reported to have a 0.53% total residual which is lower than the values he generally obtained. Of particular interest is the fact that he was able to use a glass sample bulb for his surface area determination and also that his exchanges were made at atmospheric pressure, though at a lower temperature.

TABLE IX

SURFACE AREAS AND STATISTICS OF SAMPLE (c-2bw (3.3673 g.)^a)

Run	Area, sq.m./g.	Experimental Points	Outgassing Time, hr. or other treatment ^b
Deadspace			47
I	47.88	5	64
II	46.69	6	99
III	47.23	6	164
IV	45.51	7	415
average	46.8		

Time outgassed, hr.	Pressure Increase, microns Hg/hr. ^c
18	0.05; 0.02
29	0.02; 0
43	0.002; 0

Displacement Size, cc.	Material	Exchanges	Minimum Contact Time, hr. min.
50	Methanol	D1 to D11	30
50	Dried methanol	D12 to D21	1
50	Dried methanol	D22 to D27	30
50	Dried methanol ^d	D28 to D34	30
50	Dried pentane	D1 to D11	20

Dried at 50 cc./min. for 38 hours.

^aOutgassed sample weight.

^bExcludes the time of area determinations.

^cSucceeding values are for additional time intervals.

^dUsing the Physical Chemistry Department exchange apparatus.

TABLE X

SURFACE AREAS AND STATISTICS OF SAMPLE c-2cw (3.9057 g.)

Run	Area, sq.m./g.	Experimental Points	Outgassing Time, hr. or other treatment
Deadspace			45
I	51.43	8	50
II	<u>52.05</u>	7	64
average	51.7		
III	46.33	7	137 + dry CO ₂
IV	44.62	7	+ CO ₂

	Time Outgassed, hr.	Pressure Increase, microns Hg/hr.
	2	1.2
	41	0.03
	43	0.03; 0.04; 0
	before IV	0.01; 0.01

Displacement Size, cc.	Material	Exchanges	Minimum Contact Time, hr. min.
200	Methanol	D1	
50	Methanol	D2 to D11	30
50	Dried methanol	D12 to D33	1
50	Dried pentane	D1 to D11	30

Dried at 50 cc./min. for 39 hours.

TABLE XI

SURFACE AREAS AND STATISTICS OF SAMPLE c-2gw (2.4011 g.)

Run	Area, sq.m./g.	Experimental Points	Outgassing Time, hr. or other treatment	
Deadspace			32	
I	18.34	4	44	
II	18.56	7	50	
average	18.4			

Time Outgassed, hr.		Pressure Increase, microns Hg/hr.	
27		0.02; 0.01	

Displacement Size, cc.	Material	Exchanges	Minimum Contact Time,	
			hr.	min.
100	Methanol	D1		
45	Methanol	D2 to D8		30
45	Methanol	D9	10	
45	Methanol	D10 to D11	1	
45	Dried methanol	D12 to D24	1	
45	Dried methanol	D25	15	
45	Dried benzene	D1 to D5		30
45	Dried benzene	D6	10	
45	Dried benzene	D6 to D22		30

Dried at 50 cc./min. for 66 hours.

TABLE XII

SURFACE AREAS AND STATISTICS OF SAMPLE c-2hw (2.9554 g.)

Run	Area, sq.m./g.	Experimental Points	Outgassing Time, hr. or other treatment
Deadspace			25
I	24.78	6	35
II	24.89	8	41
average	24.8		

Time Outgassed, hr.	Pressure Increase, microns Hg/hr.
22	0.003; 0.003

Displacement Size, cc.	Material	Exchanges	Minimum Contact Time, hr. min.
100	Methanol	D1	
45	Methanol	D2 to D8	30
45	Methanol	D9	10
45	Methanol	D10 to D11	1
45	Dried methanol	D13 to D24	1
45	Dried methanol	D25	15
45	Dried pentane	D1 to D8	30
45	Dried pentane	D9	3
45	Dried pentane	D10	30
45	Dried benzene	D1 to D5	30
45	Dried benzene	D6	10
45	Dried benzene	D7 to D9	30
45	Dried benzene	D10	7
45	Dried benzene	D11 to D12	30

Dried at 50 cc./min. for 61 hours.

TABLE XIII

SURFACE AREAS AND STATISTICS OF SAMPLE c-1a (2.6857 g.)

Run	Area, sq.m./g.	Experimental Points	Outgassing Time, hr. or other treatment	
Deadspace			144	
I	51.68 ^a	6	149	
II	<u>51.83</u>	6	164	
average	51.8			

	Time Outgassed, hr.	Pressure Increase, microns Hg/hr.
	19	0.3
	26	0.2
	43	0.04; 0.02; 0.01; 0.02; 0.01
	120	0.009
	140	0.003

Displacement Size, cc.	Material	Exchanges	Minimum Contact Time, hr. min.	
125	Methanol	D1 to D11	10	
125	Dried methanol	D12 to D16	10	
125	Dried methanol	D17	3	
125	Dried methanol	D18	15	
125	Dried methanol	D19		10
125	Dried methanol	D20	3	30
125	Dried methanol	D21	52	
125	Dried methanol	D22	66	
145	Carbon dioxide	D1 to D12	10	

CO₂ removed at 36°C. and 1340 p.s.i.a.

^aArea run about 5 months after carbon dioxide removal.

TABLE XIV

SURFACE AREAS AND STATISTICS OF SAMPLE c-1b (2.0098 g.)

Run	Area, sq.m./g.	Experimental Points	Outgassing Time, hr. or other treatment
Deadspace			128
I	53.17	6	140
II	52.65	4	162
III	<u>52.61</u>	5	477
average	<u>52.8</u>		

	Time Outgassed, hr.	Pressure Increase, microns Hg/hr.
	3	4.4
	26	0.24
	54	0.10
	77	0.04
	91	0.06; 0.03; 0.03
	115	5.3
	116	9.0; 6.0; 6.8
	worked Hg	0.02
	126	0.005
After I	9	0.03
	15	0.03
	93	0.02
After II	72	0.006
	192	0.006

Displacement Size, cc.	Material	Exchanges	Minimum Contact Time, hr. min.
125	Methanol	D1 to D14	10
125	Dried methanol	D15 to D52	10 (odd)
125	Dried methanol	D53	12 (even)
125	Dried methanol	D54 to D55	3300 10
145	Carbon dioxide	D1 to D10	10

CO₂ removed at 36°C. and 1740 p.s.i.a.

TABLE XV

EXCHANGE STATISTICS OF SAMPLE c-2a (4.5913 g.)

Displacement Size, cc.	Material	Exchanges	Minimum Contact Time,	
			hr.	min.
125	Methanol	D1 to D10		10
125	Dried methanol	D11 to D15		10
125	Dried methanol	D16	1	
125	Dried methanol	D17		10
125	Dried methanol	D18	2	
125	Dried methanol	D19		10
125	Dried methanol	D20	4	
125	Dried methanol	D21		10
125	Dried methanol	D22	8	
125	Dried methanol	D23		10
125	Dried methanol	D24	16	
125	Dried methanol	D25		10
125	Dried methanol	D26	32	
125	Dried methanol	D27		10
125	Dried methanol	D28	6	
125	Dried methanol	D29 to D30		10
125	Dried methanol	D31	48	
125	Dried methanol	D32		10
125	Dried methanol	D33	25	
125	Dried methanol	D34		25
125	Dried methanol	D35	94	
125	Dried methanol	D36		25
125	Dried methanol	D37	167	30
125	Dried methanol	D38		20
125	Dried methanol	D39	337	
125	Dried methanol	D40		10.
125	Dried methanol	D41	506	
125	Dried methanol	D42 to D44		10
145	Carbon dioxide	D1 to D10		10

CO₂ removed at 36°C. and 1570 p.s.i.a.

TABLE XVI

SURFACE AREAS AND STATISTICS OF SAMPLE c-2e (4.3266 g.)

Run	Area, sq.m./g.	Experimental Points	Outgassing Time, hr. or other treatment
Deadspace			194
I	49.69	7	199
II	<u>49.26</u>	5	214
average	49.5		
III	46.30	7	dried N ₂

Time Outgassed, hr.	Pressure Increase, microns Hg/hr.
55	0.06; 0.03; 0.03; 0.03
94	0.02; 0.03
117	0.03; 0.03
142	0.02
152	0.02; 0.03
168	0.01; 0.01
172	0.01; 0.02
189	0.02; 0.01
after N ₂ 4	0.03; 0.5
46	0.04; 0.02; 0.03; 0.03

Displacement Size, cc.	Material	Exchanges	Minimum Contact Time, hr. min.
125	Methanol	D1 to D11	30
115	Dried methanol	D12 to D19	1
115	Dried methanol	D20 to D27	2
145	P ₂ O ₅ dried CO ₂	D1 to D10	30

CO₂ removed at 45°C. and 2300 p.s.i.a.

TABLE XVII

SURFACE AREAS AND STATISTICS OF SAMPLE c-2f (2.0895 g.)

Run	Area, sq.m./g.	Experimental Points	Outgassing Time, hr. or other treatment
Deadspace			136
I	23.68	8	148
II	23.98	6	181
average	23.8		

	Time Outgassed, hr.	Pressure Increase, microns Hg/hr.
	32	0.10
	78	0.01
	112	0.02; 0.03
	125	0.01; 0.08; 0.01
		0.03; 0.03; 0

Displacement Size, cc.	Material	Exchanges	Minimum Contact Time, hr. min.
125	Methanol	D1 to D2	5
125	Methanol	D3 to D12	30
115	Dried methanol	D13 to D21	1
115	Dried methanol	D22	11
115	Dried methanol	D23 to D27	2
175	Dried methanol	D28	12
145	Cotton dried CO ₂	D1 to D10	30

CO₂ removed at 45°C. and 2340 p.s.i.a.

TABLE XVIII

SURFACE AREAS AND STATISTICS OF SAMPLE c-2j (1.9559 g.)

Run	Area, sq.m./g.	Experimental Points	Outgassing Time, hr. or other treatment
Deadspace			126
I	39.07	7	148
II	<u>39.66</u>	7	161
average	<u>39.4</u>		

Time Outgassed, hr.	Pressure Increase, microns Hg/hr.
122	0.01

Displacement Size, cc.	Material	Exchanges	Minimum Contact Time,	
			hr.	min.
125	Methanol	D1 to D2		5
125	Methanol	D3 to D11		15
115	Dried methanol	D12		15
115	Dried methanol	D13 to D20	1	
115	Dried methanol	D21	9	
115	Dried methanol	D22	4	
115	Dried methanol	D23	6	
115	Dried methanol	D24	4	
115	Dried methanol	D25	10	
230	Dried methanol	D26	1	
145	Carbon dioxide	D1 to D15		30

CO₂ removed at 36°C. and 1700 p.s.i.a.

TABLE XIX

SUMMARY OF WATER-VAPOR ADSORPTION DATA

Isotherm	R.H.	Sample	Equil. Wt., g.	Adsorbed Water, g.	Adsorption, g.water/ g.cotton
D ₁	P ₂ O ₅	A	1.7784		
A	0.439	A	1.8751	0.0967	0.0544
A	0.929	A	2.0677	0.2893	0.1627
D ₂	0.755	A	1.9693	0.1909	0.1073
D ₂	0.541	A	1.9120	0.1336	0.0751
D ₂	0.392	A	1.8794	0.1010	0.0568
D ₁	P ₂ O ₅	B	2.1271		
A	0.329	B	2.2192	0.0921	0.0433
A	0.865	B	2.3833	0.2562	0.1204
A	0.929	B	2.4675	0.3404	0.1600
D ₂	0.229	B	2.2103	0.0832	0.0391
D ₁	0.111	C	2.1910	0.0529	0.0247
D ₁	P ₂ O ₅	C	2.1381		
A	0.111	C	2.1908	0.0527	0.0229
A	0.329	C	2.2356	0.0975	0.0439
A	0.439	C	2.2565	0.1184	0.0537
A	0.929	C	2.5042	0.3661	0.1695
D ₂	0.439	C	2.2739	0.1358	0.0618
D ₁	0.229	D	2.3840	0.0881	0.0384
D ₁	P ₂ O ₅	D	2.2959		
A	0.648	D	2.4712	0.1753	0.0764
A	0.929	D	2.6670	0.3711	0.1616
D ₂	0.329	D	2.4065	0.1106	0.0482
D ₁	0.329	E	2.5719	0.1188	0.0484
D ₁	P ₂ O ₅	E	2.4531		
A	0.229	E	2.5346	0.0815	0.0332
A	0.392	E	2.5718	0.1187	0.0484
A	0.541	E	2.6055	0.1524	0.1621
A	0.929	E	2.8463	0.3932	0.1603
D ₂	0.329	E	2.5723	0.1192	0.0486

TABLE XIX (continued)

SUMMARY OF WATER-VAPOR ADSORPTION DATA

Isotherm	R. H.	Sample	Equil. Wt., g.	Adsorbed Water, g.	Adsorption, g. water/ g. cotton
D ₁	0.392	F	2.2736	0.1189	0.0552
D ₁	P ₂ O ₅	F	2.1547		
A	0.929	F	2.4973	0.3426	0.1590
D ₂	0.865	F	2.4408	0.2861	0.1328
D ₂	0.648	F	2.4300	0.1853	0.0860
D ₂	0.111	F	2.2073	0.0526	0.0244
D ₁	0.541	H	2.0608	0.1421	0.0741
D ₁	0.439	H	2.0368	0.1181	0.0616
D ₁	P ₂ O ₅	H	1.9187		
A	0.229	H	1.9812	0.0625	0.0326
A	0.755	H	2.0964	0.1777	0.0926
D ₁	0.648	J	2.2590	0.1858	0.0896
D ₁	0.439	J	2.1969	0.1237	0.0597
D ₁	0.392	J	2.1876	0.1144	0.0552
D ₁	P ₂ O ₅	J	2.0732		
D ₁	0.755	K	2.2737	0.2390	0.1175
D ₁	0.111	K	2.0831	0.0484	0.0238
D ₁	P ₂ O ₅	K	2.0347		
A	0.111	K	2.0779	0.0432	0.0212
A	0.648	K	2.1892	0.1545	0.0759
D ₁	0.865	L	2.2939	0.3225	0.1636
D ₁	0.229	L	2.0461	0.0747	0.0379
D ₁	P ₂ O ₅	L	1.9714		
A	0.111	L	2.0149	0.0435	0.0221
A	0.541	L	2.0966	0.1252	0.0635
D ₁	0.929	M	2.1722	0.3838	0.2146
D ₁	0.329	M	1.8752	0.0868	0.0485
D ₁	P ₂ O ₅	M	1.7884		
D ₁	P ₂ O ₅	N	2.1357		
A	0.392	N	2.2386	0.1029	0.0482
A	0.755	N	2.3358	0.2001	0.0937
A	0.929	N	2.4838	0.3481	0.1630

TABLE XX

REARRANGED WATER-VAPOR ADSORPTION DATA

Isotherm	R. H.	Samples	Adsorption, g. water/g. cotton	Average
A	0.111	C,K,L	0.0229, 0.0212, 0.0221	0.0221
D ₁	0.111	C,K	0.0247, 0.0238	0.0242
D ₂	0.111	F	0.0244	0.0244
A	0.229	E,H	0.0332, 0.0326	0.0329
D ₁	0.229	D,L	0.0384, 0.0379	0.0382
D ₂	0.229	B	0.0391	0.0391
A	0.329	B,C	0.0433, 0.0439	0.0436
D ₁	0.329	E,M	0.0484, 0.0485	0.0484
D ₂	0.329	D,E	0.0482, 0.0486	0.0484
A	0.392	E,N	0.0484, 0.0482	0.0483
D ₁	0.392	F,J	0.0552, 0.0552	0.0552
D ₂	0.392	A	0.0568	0.0568
A	0.439	A,C	0.0544, 0.0537	0.0540
D ₁	0.439	H,J	0.0616, 0.0597	0.0606
D ₂	0.439	C	0.0618	0.0618
A	0.541	E,L	0.0621, 0.0635	0.0628
D ₁	0.541	H	0.0741	0.0741
D ₂	0.541	A	0.0751	0.0751
A	0.648	D,K	0.0764, 0.0759	0.0762
D ₁	0.648	J	0.0896	0.0896
D ₂	0.648	F	0.0860	0.0860
A	0.755	N,H	0.0937, 0.0926	0.0930
D ₁	0.755	K	0.1175	0.1175
D ₂	0.755	A	0.1073	0.1073
A	0.865	B	0.1204	0.1204
D ₁	0.865	L	0.1636	0.1636
D ₂	0.865	F	0.1328	0.1328
A	0.929	A,B,C,D	0.1627, 0.1609, 0.1695, 0.1616	
A	0.929	E,F,N	0.1603, 0.1590, 0.1630	0.1623
D ₁	0.929	M	0.2146	0.2146

TABLE XXI

NITROGEN ISOTHERM DATA

Sample c-2bw			Sample c-2f			Sample c-2j		
$\frac{P}{P_0}$	$V_{ads.}^a$		$\frac{P}{P_0}$	$V_{ads.}$		$\frac{P}{P_0}$	$V_{ads.}$	
0.0140	7.07	Ads.	0.1182	6.49	Ads.	0.1008	9.67	Ads.
0.0163	7.34	Run	0.1410	6.68	Run	0.1203	9.95	Run
0.0954	10.57	I	0.1619	6.83	I	0.1479	10.41	I
0.1214	11.20		0.1738	6.91		0.1631	10.63	
0.1678	12.14		0.1815	6.97		0.2148	11.43	
0.1875	12.64		0.1914	7.03		0.2553	11.99	
0.2230	13.42		0.2412	7.37		0.2923	12.51	
0.3505	16.11		0.2768	7.65				
0.4188	17.68					0.1024	9.42	Ads.
0.4371	18.12		0.0535	5.64	Ads.	0.1213	9.95	Run
0.4397	18.22		0.0842	6.06	Run	0.1496	10.38	II
0.6012	21.77		0.1529	6.72	II	0.1650	10.64	
0.6438	22.77		0.2102	7.12		0.2205	11.49	
0.7204	24.39		0.2492	7.37		0.2624	12.09	
0.7585	25.30		0.2864	7.62		0.3018	12.82	
0.8377	27.60		0.3900	8.72		0.3556	13.70	
0.9033	31.02		0.4604	9.36		0.4506	15.24	
0.9483	34.38		0.5808	10.65		0.6118	17.64	
0.9532	34.84		0.7086	12.28		0.8132	21.44	
0.9840	39.79		0.7733	13.10		0.9106	26.62	
			0.9005	17.99		0.9633	40.17	
0.9293	34.70	Des.	0.9646	32.25		0.9898	53.76	
0.7966	27.97	Run	0.9904	63.34				
0.6233	24.48	I				0.9673	46.21	Des.
0.5076	23.12		0.9449	31.11	Des.	0.9490	41.66	Run
0.4644	21.38		0.8753	18.83	Run	0.9284	36.00	II
0.4003	17.73		0.6599	13.17	II	0.9060	31.31	
0.3149	15.72		0.5964	12.68		0.8470	24.77	
			0.5557	12.46		0.7482	21.78	
0.1206	11.05	Ads.	0.4939	12.02		0.6305	20.39	
0.1547	11.77	Run	0.4566	10.82		0.5401	19.68	
0.1911	12.51	III	0.4166	9.28		0.4727	18.55	
0.2134	13.03		0.3640	8.53		0.4488	16.93	
0.2297	13.36		0.3061	8.00		0.4084	15.09	
0.2522	13.82					0.3445	13.88	
0.6746	22.94							
0.9370	32.94							
0.9862	40.28							
0.8743	30.88	Des.						
0.7019	25.27	Run						
0.6450	24.44	III						
0.5594	23.36							
0.4347	18.76							
0.3956	17.25							
0.3106	15.34							

^aVolume adsorbed in ml./g. at S.T.P.

TABLE XXII

PORE VOLUME DISTRIBUTION DATA FOR SAMPLE c-2bw

P/P_0	t^a	r_p^b	\bar{r}_p	V_p^c	$\sum A_p^d$	$\sum V_p^e$	dy/dr^f
0.9715	18.93	350	(500)	0			
0.966	17.80	300	325	0.798	0.076	36.70	
0.960	16.75	250	275	.799	0.166	35.90	
0.950	15.50	200	225	1.047	0.310	35.10	
0.944	14.90	180	190	0.703	0.425	34.06	
0.938	14.35	160	170	.587	0.532	33.35	
0.928	13.57	140	150	1.074	0.754	32.76	
0.916	12.75	120	130	1.075	1.010	31.69	
0.897	11.65	100	110	1.456	1.420	30.62	
0.885	11.17	90	95	0.859	1.700	29.16	
0.871	10.75	80	85	0.876	2.020	28.30	
0.852	10.27	70	75	1.156	2.498	27.42	
0.829	9.74	60	65	1.299	3.118	26.27	
0.792	8.95	50	55	1.840	4.155	24.97	
0.742	8.15	40	45	1.877	5.448	23.13	
0.704	7.68	35	37.5	1.049	6.316	21.25	
0.654	7.16	30	32.5	0.858	7.134	20.20	
0.636	6.99	28	29	0.397	7.558	19.35	
0.610	6.76	26	27	0.532	8.169	18.95	
0.595	6.65	25	25.5	0.080	8.267	18.42	
0.579	6.53	24	24.5	0.260	8.596	18.34	
0.562	6.40	23	23.5	0.249	8.924	18.08	
0.553	6.34	22.5	22.75	0.129	9.099	17.83	
0.544	6.27	22.0	22.25	0.116	9.261	17.70	
0.534	6.21	21.5	21.75	0.127	9.442	17.58	
0.525	6.15	21.0	21.25	0.129	9.630	17.46	0.27
0.515	6.09	20.5	20.75	0.128	9.821	17.33	0.29
0.506	6.03	20.0	20.25	0.128	10.017	17.20	0.34
0.496	5.98	19.5	19.75	0.141	10.239	17.07	0.32
0.486	5.92	19.0	19.25	0.548	11.122	16.93	0.60
0.474	5.85	18.5	18.75	0.954	12.699	16.38	1.29
0.462	5.78	18.0	18.25	1.812	15.778	15.43	2.66
0.448	5.71	17.5	17.75	2.473	20.096	13.62	6.56
0.435	5.64	17.0	17.25	1.798	23.328	11.14	4.50
0.421	5.56	16.5	16.75	1.532	26.164	9.34	3.05
0.406	5.48	16.0	16.25	1.067	28.200	7.81	2.10
0.391	5.39	15.5	15.75	1.021	30.209	6.75	1.69
0.375	5.30	15.0	15.25	0.300	30.819	5.72	1.36
0.342	5.12	14.0	14.50	1.106	33.184	5.42	1.25
0.306	4.94	13.0	13.50	1.087	35.680	4.32	0.97
0.268	4.74	12.0	12.50	0.943	38.018	3.23	0.89
0.228	4.54	11.0	11.50	1.209	41.277	2.29	0.81
0.186	4.33	10.0	10.50	1.080	44.464	1.08	0.81

^aMultilayer thickness, A.

^bTrue pore radius, A.

^cPore volume, ml./g. S.T.P.

^dCumulative pore area, sq.m./g.

^eCumulative pore volume, ml./g., S.T.P.

^fSlope of $\sum V_p$ vs. \bar{r}_p curve.

TABLE XXIII

PORE VOLUME DISTRIBUTION DATA FOR SAMPLE c-2f

$\frac{P}{P_0}$	$\frac{V}{V_p}$	$\frac{\sum A}{\sum A_p}$	$\frac{\sum V}{\sum V_p}$	$\frac{dV}{dr}$
0.9715				
0.966	4.104	0.391	45.980	
0.960	4.800	0.937	41.876	
0.950	6.521	1.831	37.076	
0.944	3.382	2.383	30.555	
0.938	2.560	2.850	27.173	
0.928	3.269	3.526	24.613	
0.916	2.644	4.156	21.344	
0.897	3.106	5.031	18.700	
0.885	1.370	5.478	15.594	
0.871	1.277	5.944	14.224	
0.852	1.267	6.468	12.947	
0.829	1.109	6.997	11.680	
0.792	0.958	7.537	10.571	
0.742	1.130	8.315	9.613	
0.704	0.412	8.656	8.483	
0.654	0.546	9.177	8.071	
0.636	0.000	9.177	7.525	
0.610	0.120	9.314	7.525	
0.595	0.065	9.394	7.405	
0.579	0.053	9.461	7.340	
0.562	0.041	9.514	7.287	
0.553	0.027	9.551	7.246	
0.544	0.014	9.570	7.219	
0.534	0.086	9.692	7.205	
0.525	0.006	9.701	7.119	0.12
0.515	0.087	9.831	7.113	0.12
0.506	0.128	10.027	7.026	0.15
0.496	0.141	10.249	6.898	0.20
0.486	0.128	10.455	6.757	0.36
0.474	0.324	10.991	6.629	0.30
0.462	0.755	12.273	6.305	0.92
0.448	2.289	16.270	5.550	7.00
0.435	0.948	17.974	3.261	2.25
0.421	0.468	18.840	2.313	1.53
0.406	0.467	19.731	1.845	1.04
0.391	0.436	20.589	1.378	0.75
0.375	0.195	20.986	0.942	0.50
0.342	0.146	21.299	0.747	0.22
0.306	0.143	21.627	0.601	0.13
0.268	0.066	21.790	0.458	0.11
0.228	0.064	21.963	0.392	0.11
0.186	0.328	22.930	0.328	0.09

TABLE XXIV

PORE VOLUME DISTRIBUTION DATA FOR SAMPLE c-2j

$\underline{P/P_o}$	$\underline{V_p}$	$\underline{\sum A_p}$	$\underline{\sum V_p}$	$\underline{dV/dr}$
0.9715				
0.966	1.596	0.152	45.21	
0.960	2.058	0.384	43.61	
0.950	3.149	0.818	41.55	
0.944	1.994	1.143	38.40	
0.938	1.646	1.443	36.41	
0.928	2.863	2.035	34.76	
0.916	3.116	2.778	31.90	
0.897	4.650	4.089	28.78	
0.885	1.932	4.720	24.14	
0.871	1.840	5.391	22.20	
0.852	1.842	6.152	20.36	
0.829	1.267	6.756	18.52	
0.792	1.271	7.473	17.25	
0.742	0.976	8.146	15.98	
0.704	0.587	8.632	15.01	
0.654	0.373	8.987	14.42	
0.636	0.182	9.181	14.05	
0.610	0.304	9.530	13.86	
0.595	0.062	9.605	13.56	
0.579	0.049	9.667	13.50	
0.562	0.039	9.718	13.45	
0.553	0.123	9.886	13.41	
0.544	0.012	9.902	13.29	
0.534	0.024	9.936	13.28	
0.525	0.024	9.971	13.25	0.12
0.515	0.126	10.159	13.23	0.13
0.506	0.023	10.194	13.10	0.13
0.496	0.347	10.739	13.08	0.38
0.486	0.334	11.277	12.73	0.51
0.474	0.530	12.153	12.40	0.77
0.462	1.174	14.147	11.87	1.46
0.448	2.709	18.878	10.69	6.90
0.435	1.811	22.133	7.98	4.10
0.421	0.871	23.745	6.17	2.00
0.406	0.639	24.964	5.30	1.53
0.391	0.596	26.138	4.66	1.12
0.375	0.595	27.348	4.07	0.95
0.342	0.707	28.859	3.47	0.88
0.306	0.957	31.056	2.77	0.76
0.268	0.556	32.435	1.81	0.70
0.228	0.832	34.678	1.25	0.74
0.186	0.421	35.922	0.42	0.64