


AN ABSTRACT OF THE THESIS OF

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Title Some Aspects of the Swelling of Cellulose Pulp in Sodium
Hydroxide Solutions and the Influence of Wetting Agents Thereon

Abstract Approved  -----
(Major Professor)

During the bleaching of many pulps, both for paper and for chemical purposes, the pulp is subjected to a caustic extraction employing sodium hydroxide. The pulp swells to a certain extent when exposed to solutions of alkali, the amount of swelling being controllable in part by alteration of conditions of temperature and concentration. Probably the greatest single loss of pulp yield in the entire pulping process occurs during the extraction. There is a definite need for a rapid and convenient method for measuring swelling in order that a greater volume of research might be accomplished in this field.

The following method was developed for the measurement of the swelling of cellulose pulp sheets. A number of disks cut from pulp sheets are placed in a cylinder of suitable cross section and weighted with a weight so constructed that it will not tip appreciably in the cylinder. The cylinder is then immersed in a constant temperature bath along with a bottle containing the solution in which swelling is to be measured and the system is permitted to reach temperature equilibrium. The swelling solution is then introduced into the cylinder and readings of the height of the swelling column taken until no further increase is noted. The height of the swollen column multiplied by 100 and divided by the original height is reported as per cent swelling.

Swelling was studied in sodium hydroxide solutions containing 1, 5, 10, 15, 25 and 35 per cent caustic by weight and at temperatures of 0, 15, 45, 65 and 85° C. The data obtained in these experiments indicated that the rate of swelling was slow in the higher concentrations of alkali and at the lower temperatures. Swelling was observed to be maximum at the lowest temperatures and to pass through a maximum in 15 per cent sodium hydroxide. These results are discussed.

Swelling was also studied under similar conditions but with various wetting agents added. Wetting agents were found to have no appreciable effect on swelling in sodium hydroxide as measured by this method.

SOME ASPECTS OF THE SWELLING OF CELLULOSE
PULP IN SODIUM HYDROXIDE SOLUTIONS
AND THE INFLUENCE OF WETTING AGENTS THEREON

by

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Recommended

COLD SPRINGS BOND

RAC CONTENT

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COLD SPRINGS BOND

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SOME ASPECTS OF THE SWELLING OF CELLULOSE PULP
IN SODIUM HYDROXIDE SOLUTIONS AND THE
INFLUENCE OF WETTING AGENTS THEREON

I. INTRODUCTION

THE IMPORTANCE OF SWELLING OF CELLULOSE. Many solids will absorb appropriate liquids, with the result that they increase in volume. This phenomenon is known as swelling. Few factors are as important to the paper maker or manufacturer of rayon and allied products as is swelling. It is generally recognized that the amount of swelling a pulp has undergone has a direct bearing on the quality of regenerated cellulose or paper that can be made from it. While this relationship is not clearly understood, the fact that an improperly swollen pulp makes a poor product is generally accepted. During bleaching certain pulps are subjected to a caustic extraction employing sodium hydroxide. It is in this step that the major portion of swelling takes place. It is well known that swelling is accompanied by a greater or lesser amount of degradation of the cellulose, actual cleavage of the chain-like molecules. This breakdown is accompanied by a corresponding loss of strength of the pulp and an actual dispersing of a certain fraction of the cellulose in the swelling medium. This dispersion accounts for the greatest single loss of pulp yield in the entire process. It has been found that the amount of swelling can be controlled in part by altering conditions of temperature and concentration (5).

METHODS OF MEASURING SWELLING. A measure of the swelling of many solids of rigid structure such as wood may be obtained by measuring the dimensions of a sample before and after immersion in the desired liquid (13). Another approach is weighing the sample before and after immersion; the gain in weight being a measure of the liquid imbibed.

A procedure successfully used to measure the swelling of gels (6) is the introduction of the sample into a bell shaped container fitted at the top with a capillary connected to a long inclined manometer and closed at the bottom with a porous plug, usually plaster of paris. The sample is surmounted by an inert liquid such as mercury which also fills the capillary. The gel sample forms a seal between the mercury and the porous plug. The bell is then immersed in the desired liquid which diffuses through the plug and causes swelling of the gel which forces the mercury out into the manometer. The length of the thread of mercury in the manometer is a measure of the extent of swelling. If in place of the manometer, the bell is fitted with a cylinder of gas equipped with an accurate pressure guage, the apparatus may be used to measure swelling pressure which is defined as the external pressure that must be applied to just prevent swelling.

Pulp by its very nature does not lend itself to any of the above methods. There is a large void volume between the fibers which precludes using weight of liquid taken up as a true measure of swelling (5) (16). Because of the liquid taken up between the

individual fibers, pulp tends to become a slurry in the swelling medium and, therefore, linear dimension increase of a block of the substance is difficult to measure. For both of the above mentioned reasons the swelling of pulp could not be measured in the bell with porous plug apparatus.

A solution to the problem has been found in microscopic examination of individual fibers before and after swelling (3), but this is a tedious procedure at best. It has been learned that a cellulose fiber actually shrinks in length during swelling which takes place laterally (2) (7). Since in a pulp sheet the fibers are, for the most part, laid flat, a measure of swelling may be obtained by noting the increase in thickness of the sheet (12). In order to magnify this increase, it is best to measure the swelling of several sheets laid one on top of the other. The method of August Noll (8) embodies this principle.

STATEMENT OF PROBLEM. There is a definite need for a rapid and comparatively accurate method for the measurement of swelling of pulps and similar cellulosic materials in order that a greater volume of research in this field may be accomplished.

If a better method of controlling swelling in the caustic extraction step in bleaching could be found a great saving could be afforded those engaged in pulp manufacture.

It was therefore decided to aim this study at the development of a rapid, convenient method of measuring swelling and to study by that method the swelling of pulp in sodium hydroxide at

various concentrations and temperatures. It was thought that wetting agents might possibly have an effect on swelling of pulps. It was decided, therefore, to study swelling in sodium hydroxide solutions to which wetting agents had been added.

II. EXPERIMENTAL PROCEDURE

APPARATUS. The apparatus used in this study to measure swelling consisted of six pyrex cylinders 5.4 cm. in diameter by 30.5 cm. long closed at the bottom with suitable rubber stoppers. For each cylinder there was provided a weight constructed of a cylindrical section of corrosion resistant steel 2.20 cm. in diameter by 2.54 cm. long fitted at either end with a perforated disk of plexiglass 5.3 cm. in diameter and 3 mm. thick. The plexiglass was secured to the steel with flat headed machine screws. Also provided was a bath that could be maintained at any temperature from 0 to 100 plus or minus 0.5° C.

MATERIALS. Swelling measurements were run on semi-bleached kraft pulp in the form of disks cut from sheets formed and dried on a Kamy machine.

Sodium hydroxide stock solution was prepared and stored in a 20-liter carboy fitted with a soda lime tube to exclude carbon dioxide. No attempt was made to rid the solution of silicates. The concentration of the stock solution was determined by means of a hydrometer.

Wetting agents used in this study were Triton N-100, Triton K-60 and Triton 770 obtained from Rohm and Haas Company, Philadelphia, Pennsylvania, and Kreelox 4-D obtained from Wyandotte Chemicals Corporation, Wyandotte, Michigan. Stock solutions containing 25 grams of wetting agent per liter were prepared and stored in 1 liter stoppered bottles. The solutions to be used in swelling measurements were made up in the required concentrations by dilution of the above mentioned stock solutions.

METHODS. Five disks of pulp 5.3 cm. in diameter by 2.2 mm. thick were placed in each cylinder and a weight placed on top of each pulp pile. The cylinders were then immersed in the bath. 250 ml. portions of swelling solutions of the desired concentrations contained in 8-ounce wide mouth bottles were also immersed in the bath and the system allowed to reach temperature equilibrium. The swelling solutions were then poured into the cylinders and readings taken from time to time of the heights of the swelling columns.

This procedure was rigidly adhered to in every respect in order to eliminate errors due to variations in method.

III. EXPERIMENTAL RESULTS AND DISCUSSION

THE EFFECT OF VARYING VOLUME OF SWELLING SOLUTIONS. In order to determine what ratio of sodium hydroxide solution to pulp should be used, experiments were performed in which the swelling of 11.0 gram samples was studied in 125, 250, and 375 ml. of 15 per cent caustic. This concentration was chosen because it had been

found to produce maximum or near maximum swelling over the temperature range. As will be indicated in later data, time of swelling in these experiments was long enough to establish swelling equilibrium. The results are given in Table I. Values in the table are given as per cent swelling defined by the relationship:

$$\% \text{ Swelling} = \frac{(\text{Height of swollen column in in.} - 0.45) 100}{0.45}$$

0.45 in. was taken as the height of the unswollen column after it was found that the average of 25 original heights before the addition of swelling solution was 0.45 in. and that none deviated more than 0.10 in. The deviations noted were due to warping of the pulp disks rather than irregularities in thickness. The swollen pulp, because of the softening action of the swelling medium, showed no warping.

TABLE I

THE EFFECT OF VARYING VOLUME OF SWELLING SOLUTION

VOL. OF 15% NaOH ml.	PER CENT SWELLING						
	0°	8°	15°	25°	45°	65°	85°
125	502	484	456	393*	273	153	107*
250	511	511	444	427	278	153	100
375	522	489	469	434	278	160	100

It should be noted that with the exception of the two values marked with the asterisks all swelling values fall within the limits of experimental error, the magnitude of which is established in a later section of this paper. For this reason 250 ml. was

selected for all later experimental work. It is quite possible that 125 ml. might have sufficed, but 250 ml. was thought to be safer.

MAGNITUDE OF EXPERIMENTAL ERROR. In order to obtain a measure of the magnitude of experimental error in the measurement of swelling by this method, one group and a number of pairs of duplicate measurements were made. In these experiments enough time was allowed for equilibrium swelling to be attained based on swelling-time data reported in a later section of this paper. The results of these runs are given in Table II.

TABLE II
DUPLICATE SWELLING MEASUREMENTS

TEMPERATURE °C.	PER CENT SWELLING	
	5% NaOH	15% NaOH
0		522
		512
15		428
		444
		433*
		476*
		485*
		455*
		435*
		467*
45	67	302
	62	278
65	62	162
	56	153
85	33	100
	40	100

The values marked with the asterisks were all taken from a single run.

The mean of all values for swelling at fifteen degrees and in fifteen per cent caustic is 453 per cent, the mean deviation from this average being 18 or 3.97 per cent. The maximum deviation is 32 or 7.07 per cent. Swelling values obtained for the other conditions listed in this table all fall within these limits except at 85° C. and in 5 per cent caustic under which conditions, however, the amount of swelling was very small.

TIME TO ESTABLISH EQUILIBRIUM SWELLING. In order to ascertain the length of time necessary to reach swelling equilibrium at the various temperatures and at the various concentrations of caustic soda, several experiments were run according to the method described in a previous section. Swelling was studied in 1, 5, 10, 15, 25, and 35 per cent sodium hydroxide solutions and at temperatures 0, 15, 45, 65, and 85° C. Readings were taken from time to time until 30 minutes additional swelling caused no further increase beyond the limits of experimental error, the magnitude of which is established in an earlier section. This value was taken as equilibrium swelling. The results of these experiments are given in Table III.

TABLE III
TIME TO REACH EQUILIBRIUM SWELLING

% CONC. OF NaOH	TIME IN MINUTES				
	0°	15°	45°	65°	85°
1	40	15	5	5	5
5	50	20	5	5	5
10	110	25	5	5	5
15	75	30	5	5	5
25	150	30	5	5	5
35	140	50	5	5	5

It should be noted that swelling is very rapid at the higher temperatures for all concentrations studied. In all subsequent experiments swelling was allowed to reach equilibrium by permitting swelling to continue at least as long as the time recorded in the above table.

EFFECT OF TEMPERATURE AND CONCENTRATION OF SODIUM HYDROXIDE ON SWELLING. Tables IV through VIII present the results of swelling versus time experiments at 0, 15, 45, 65, and 85° C. respectively. The data from Tables IV and V are plotted in Figures I and II respectively with per cent swelling as ordinate and time in minutes as abscissa. Since swelling was so rapid and equilibrium swelling was reached so quickly at all the higher temperatures, it

was decided to present only these two lower temperature runs graphically.

It should be noted that equilibrium swelling was reached quickly for the lower concentrations of sodium hydroxide, but that this rate drops off rapidly with increasing concentration of caustic. At 0° the samples immersed in 25 per cent and 35 per cent sodium hydroxide were still swelling slowly at the end of 180 minutes. It is probable that this continued slow swelling at low temperatures would eventually lead to dispersion of the pulp in the swelling medium.

Figures III and IV show the data from Tables IV and V with per cent swelling as ordinate and per cent concentration of sodium hydroxide as abscissa. It is noteworthy that although in lower concentration of sodium hydroxide swelling equilibrium is reached rapidly; in all other concentrations this condition is attained more slowly as concentration increases.

TABLE IV

PER CENT SWELLING VERSUS TIME AT 0° CENTIGRADE

TIME IN MINUTES	PER CENT CONCENTRATION OF NaOH					
	1	5	10	15	25	35
5	33	67	127	71	0	0
10	33	96	204	116	18	7
15	31	113	240	193	33	13
20	38	127	284	238	63	15
30	40	129	325	329	80	33
40	51	131	369	438	107	49
50	49	144	402	511	134	67
60	49	144	422	516	167	89
75	49	144	442	522	189	102
90	47	142	442	524	215	122
110	47	142	467	526	245	151
120	49	140	463	522	256	175
140	49	142	465	526	248	196
155	--	---	---	---	300	196
170	--	---	---	---	311	198
180	49	140	482	522	313	198

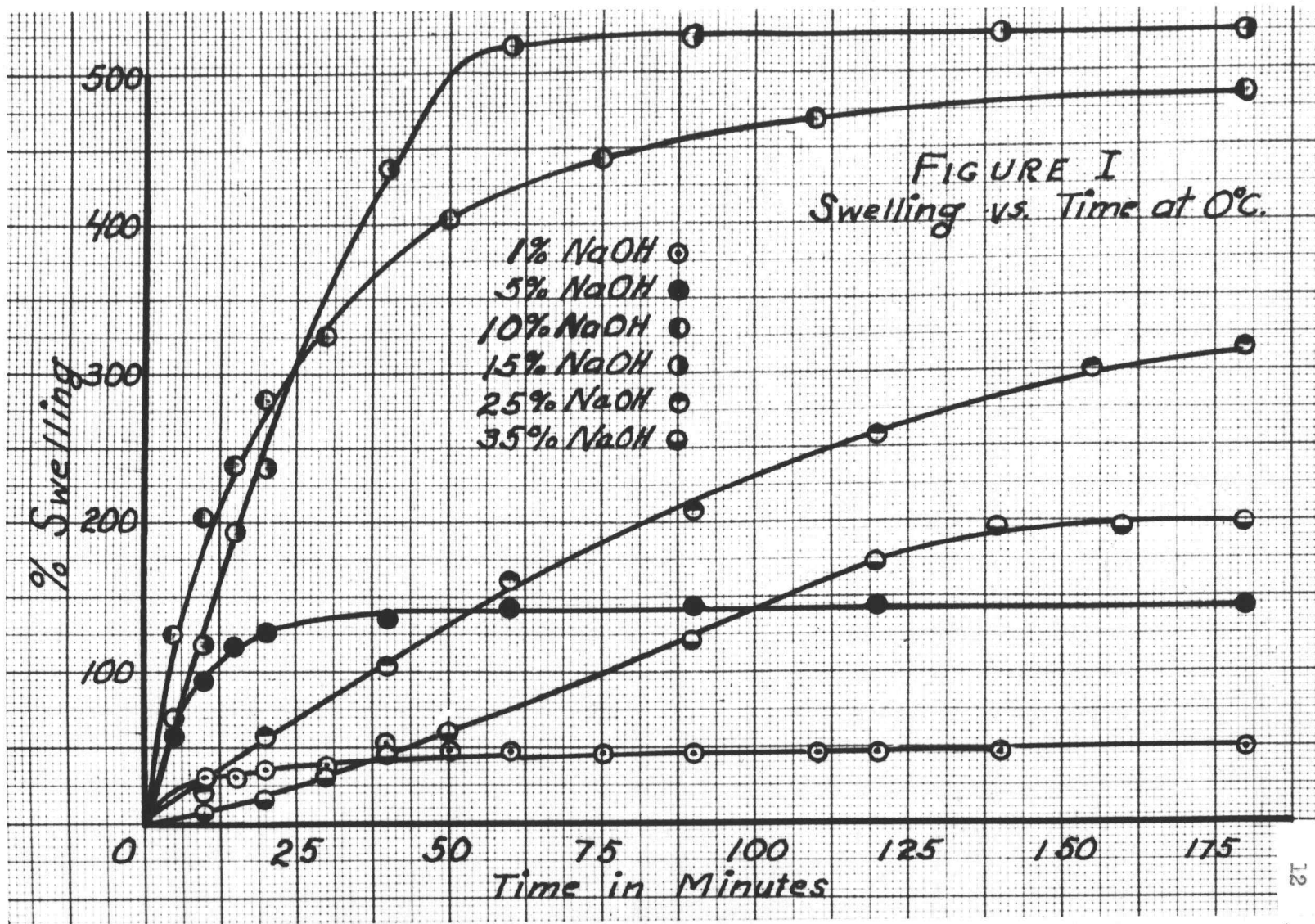


TABLE V

PER CENT SWELLING VERSUS TIME AT 15° CENTIGRADE

TIME IN MINUTES	PER CENT CONCENTRATION OF NaOH					
	1	5	10	15	25	35
5	31	100	374	389	286	58
10	33	102	382	411	322	160
15	38	107	382	420	335	206
20	40	109	387	432	335	220
25	42	111	387	434	333	240
30	45	113	389	434	340	256
40	47	111	391	432	340	264
50	45	113	393	429	340	276
60	45	111	398	429	340	278

TABLE VI

PER CENT SWELLING VERSUS TIME AT 45° CENTIGRADE

TIME IN MINUTES	PER CENT CONCENTRATION OF NaOH					
	1	5	10	15	25	35
5	31	63	102	298	189	---
10	31	56	102	278	187	---
15	33	65	109	300	187	---
20	33	67	111	300	184	---
30	31	65	111	304	193	---
40	33	63	109	302	196	---

FIGURE II
Swelling vs. Time at 15°C.

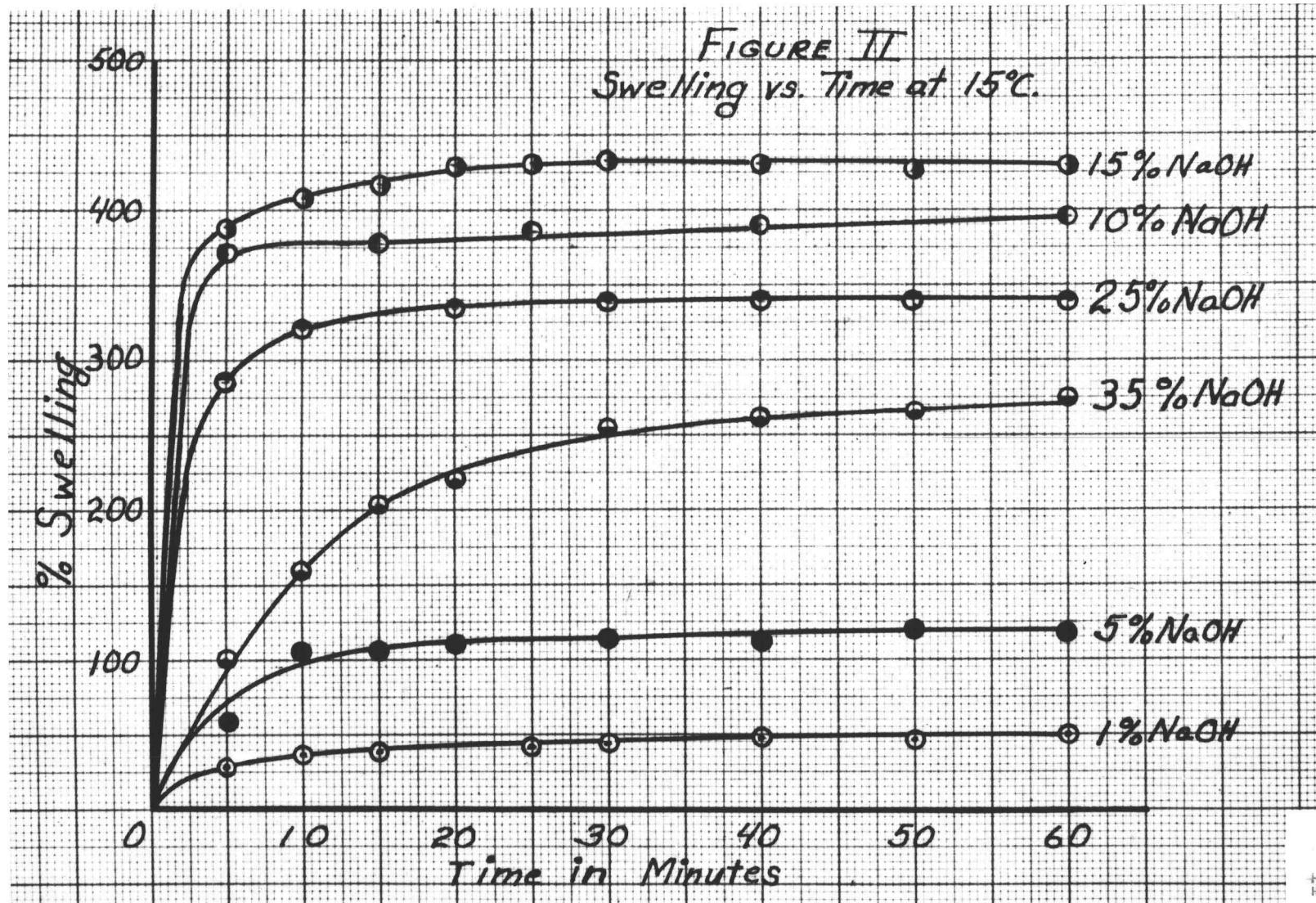


TABLE VII

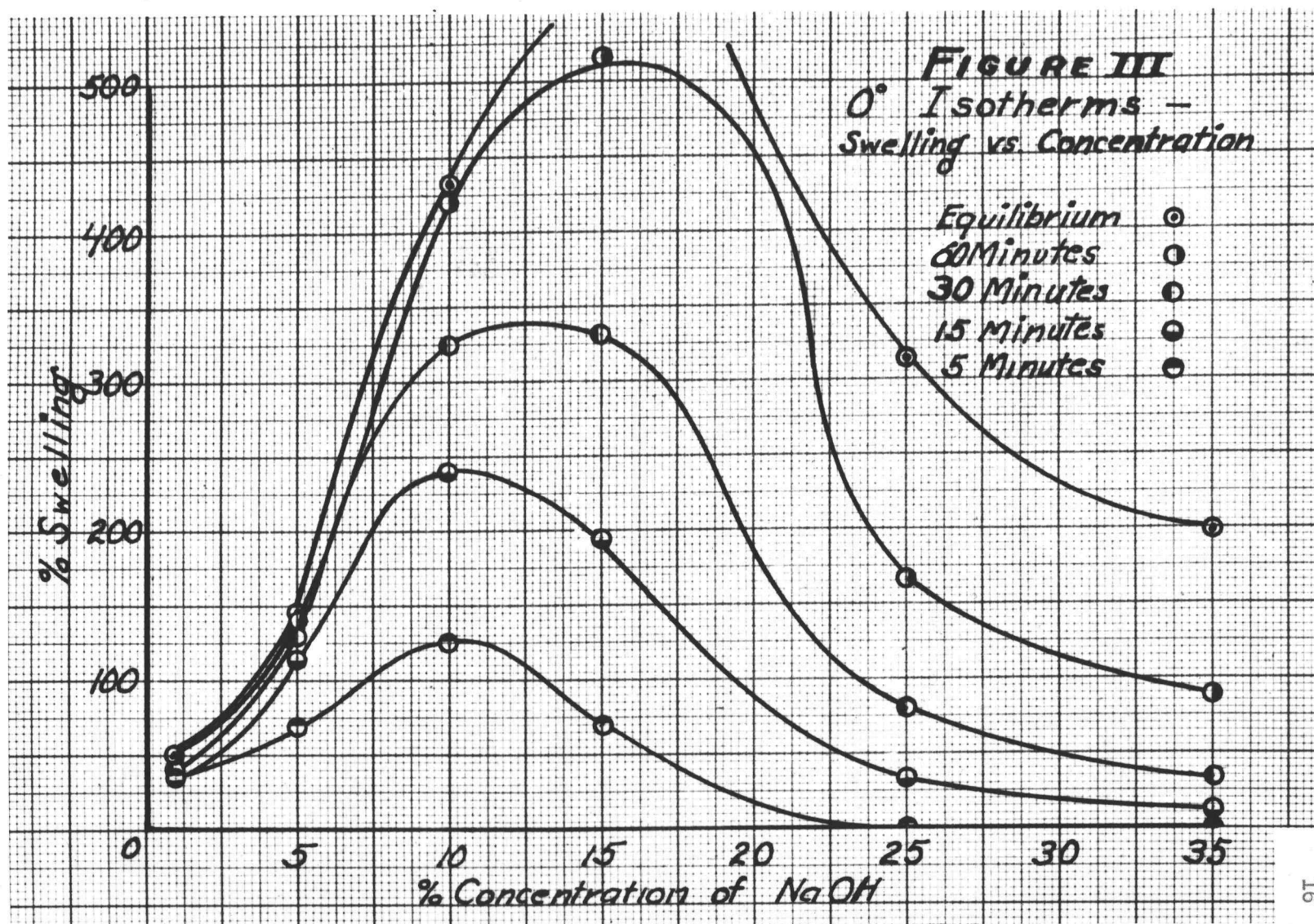
PER CENT SWELLING VERSUS TIME AT 65° CENTIGRADE

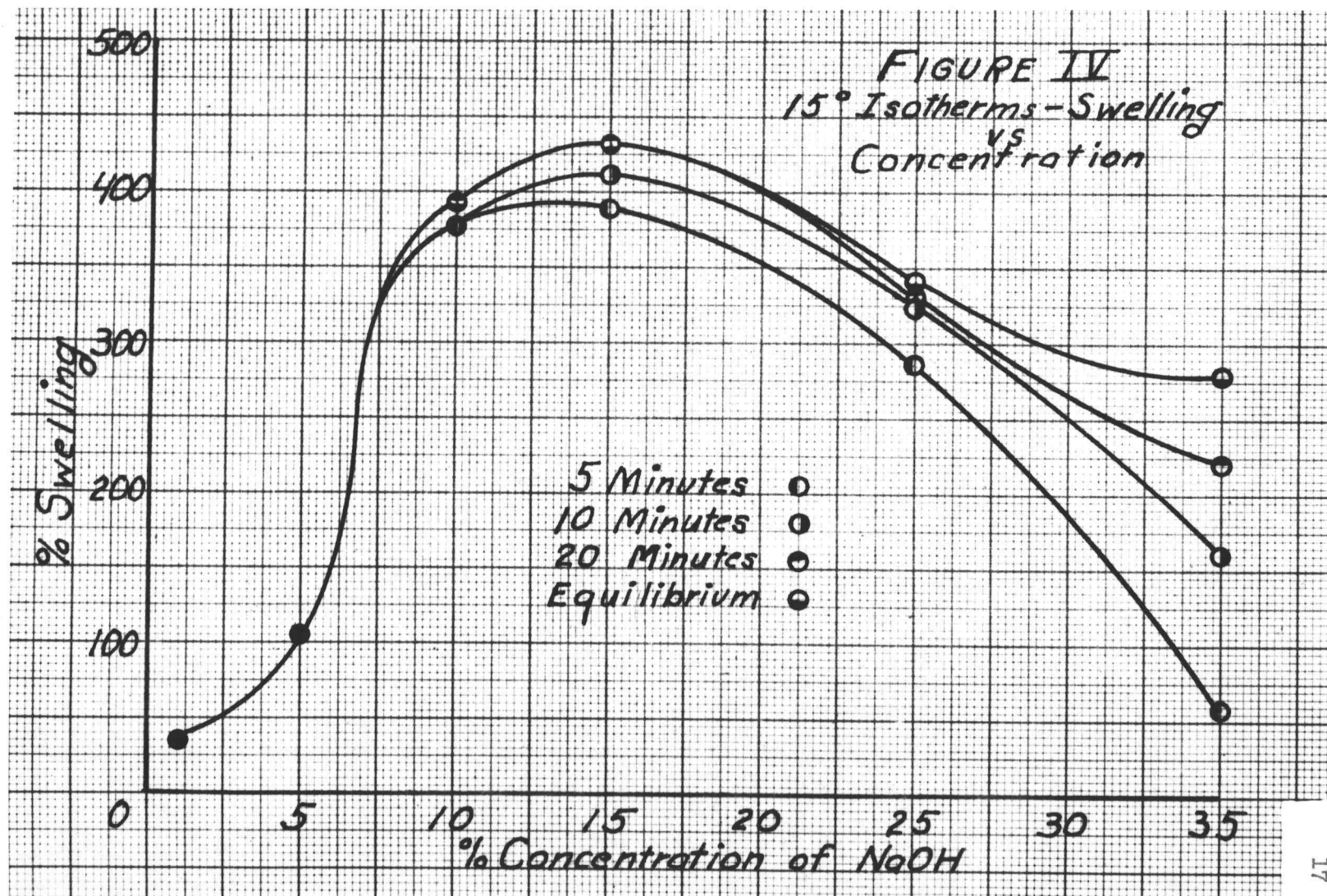
TIME IN MINUTES	PER CENT CONCENTRATION OF NaOH					
	1	5	10	15	25	35
5	24	58	58	162	200	129
10	22	56	65	156	200	129
15	22	58	67	158	198	129
25	27	56	67	162	198	134
40	24	56	71	162	200	131

TABLE VIII

PER CENT SWELLING VERSUS TIME AT 85° CENTIGRADE

TIME IN MINUTES	PER CENT CONCENTRATION OF NaOH					
	1	5	10	15	25	35
5	29	33	40	96	125	116
10	31	40	42	98	127	113
15	29	38	45	100	131	116
25	31	40	47	100	129	116
40	29	40	45	100	129	116





Rearrangement of the data in Tables IV to VIII inclusive so as to show the per cent swelling in various concentrations of sodium hydroxide and at various temperatures at the end of 5, 10, 15, 20, and 30 minutes, and after equilibrium swelling had been reached, makes more evident the effect of caustic concentrations and of temperature on the extent of swelling. This has been done in Tables IX to XIV inclusive. The data in these tables are shown graphically in Figures V to XVI inclusive in which the data from each table have been plotted first as isotherms showing per cent of swelling against concentrations of caustic and then as isoconcentrations showing per cent swelling against temperature.

The isotherms show best that swelling is greatest at sodium hydroxide concentration of 15 per cent and decreases as concentration becomes greater or smaller. The isoconcentration curves show clearly that greatest swelling is obtained at 0° C., although equilibrium is reached much more slowly and that amount of swelling becomes progressively smaller as temperature is increased.

TABLE IX

FIVE MINUTE SWELLING

PER CENT CONCENTRATION NaOH	PER CENT SWELLING				
	0°	15°	45°	65°	85°
1	33	31	31	24	29
5	67	100	63	58	33
10	127	374	102	58	40
15	71	389	298	162	96
25	0	286	189	200	125
35	0	58	---	129	116

TABLE X

TEN MINUTE SWELLING

PER CENT CONCENTRATION NaOH	PER CENT SWELLING				
	0°	15°	45°	65°	85°
1	33	33	31	22	31
5	96	102	56	56	40
10	204	382	102	65	42
15	116	411	278	156	98
25	18	322	187	200	127
35	7	160	---	129	113

FIGURE V
Five Minute Swelling vs.
Concentration

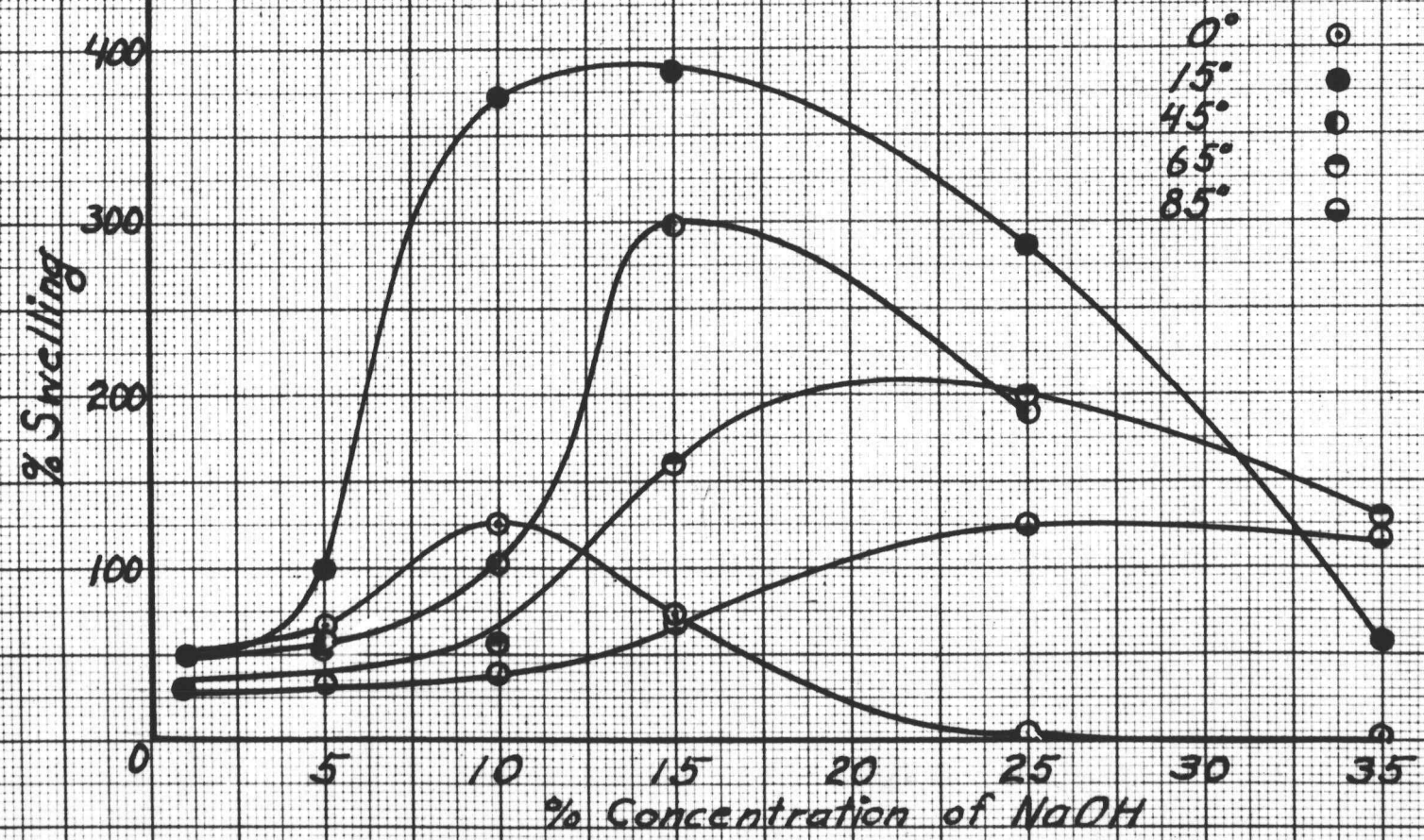


FIGURE VI
Five Minute Swelling
vs.
Temperature

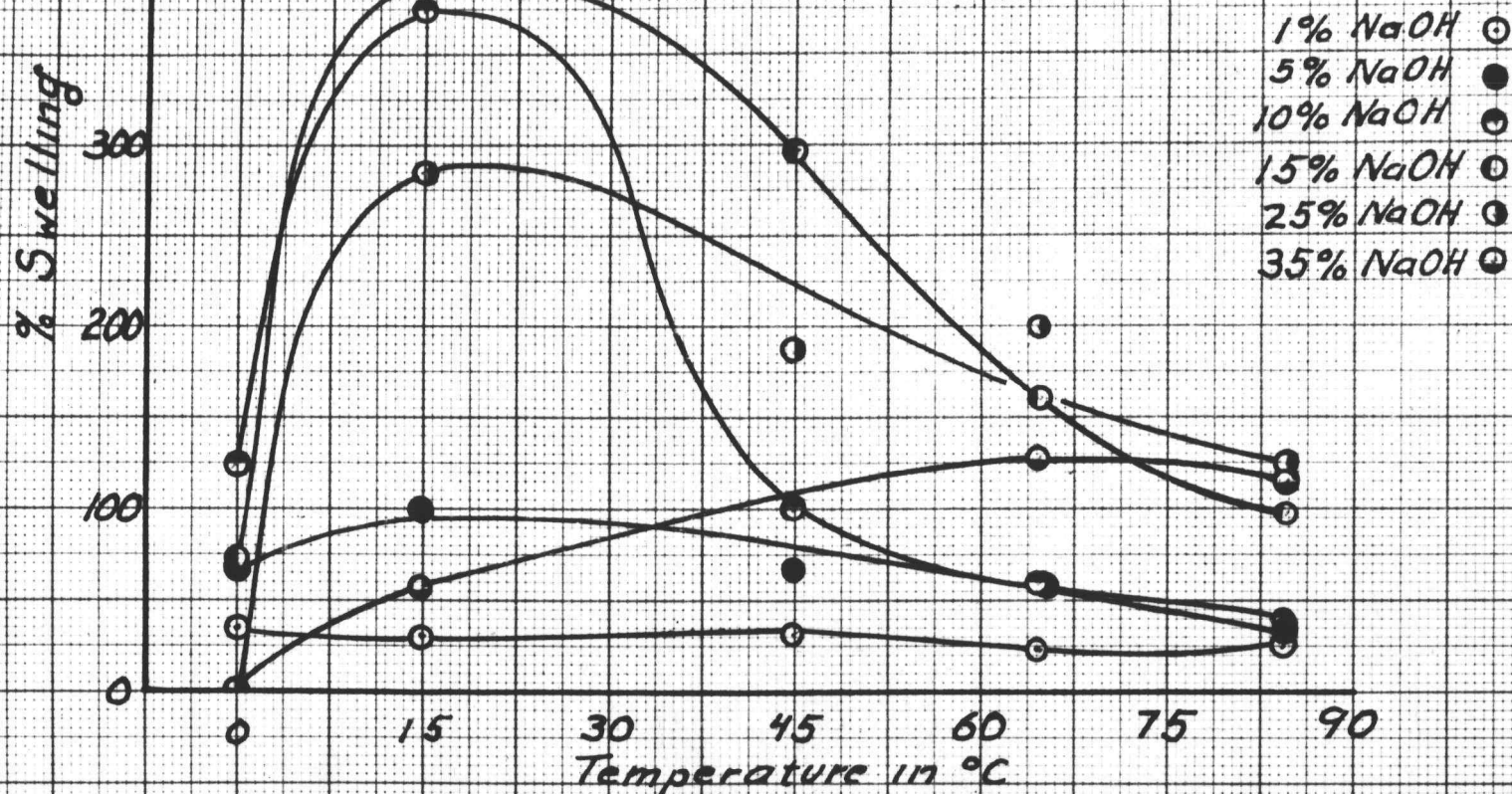


FIGURE VII
Ten Minute Swelling
vs.
Concentration

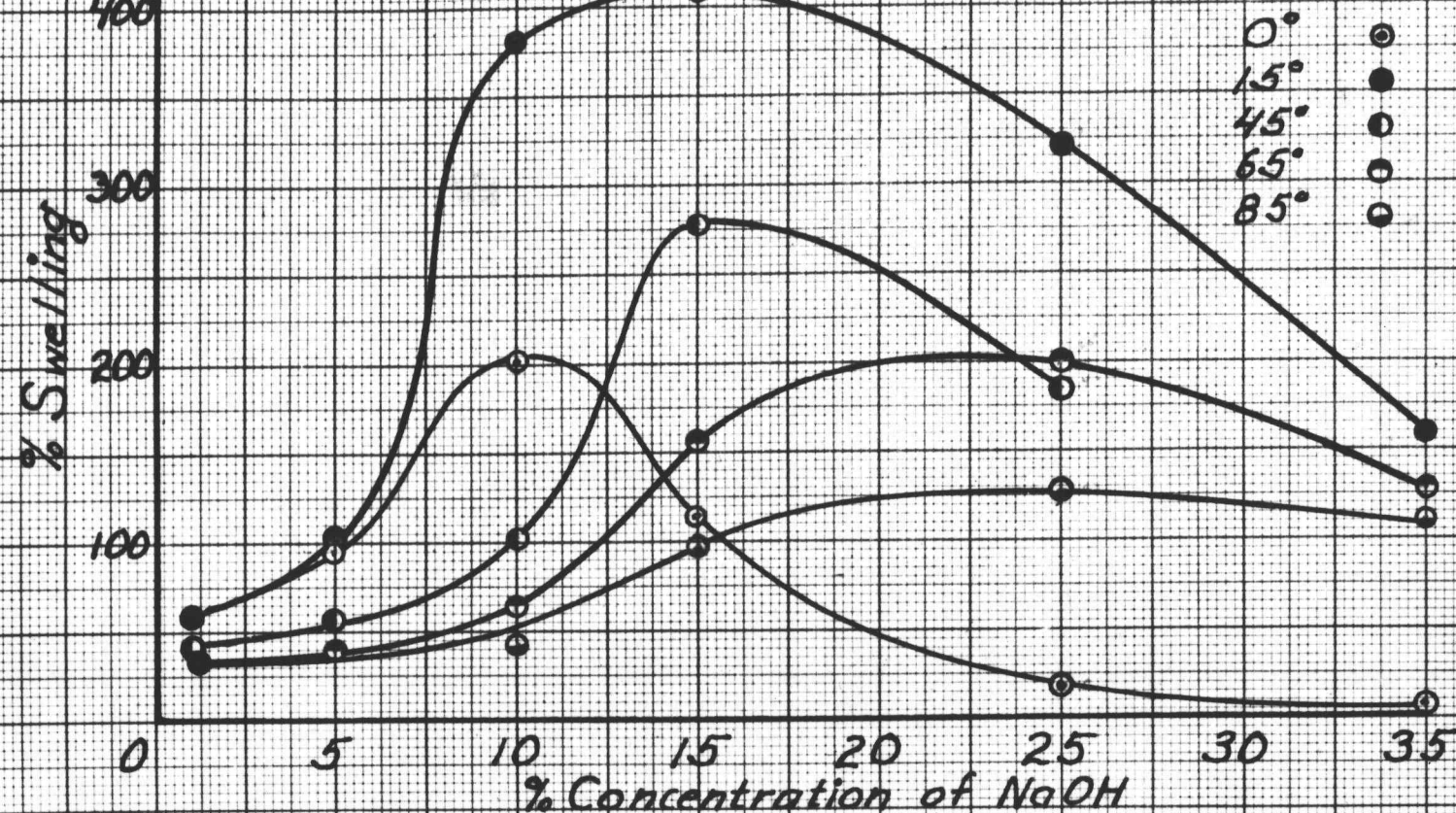


FIGURE VIII
Ten Minute Swelling
vs
Temperature

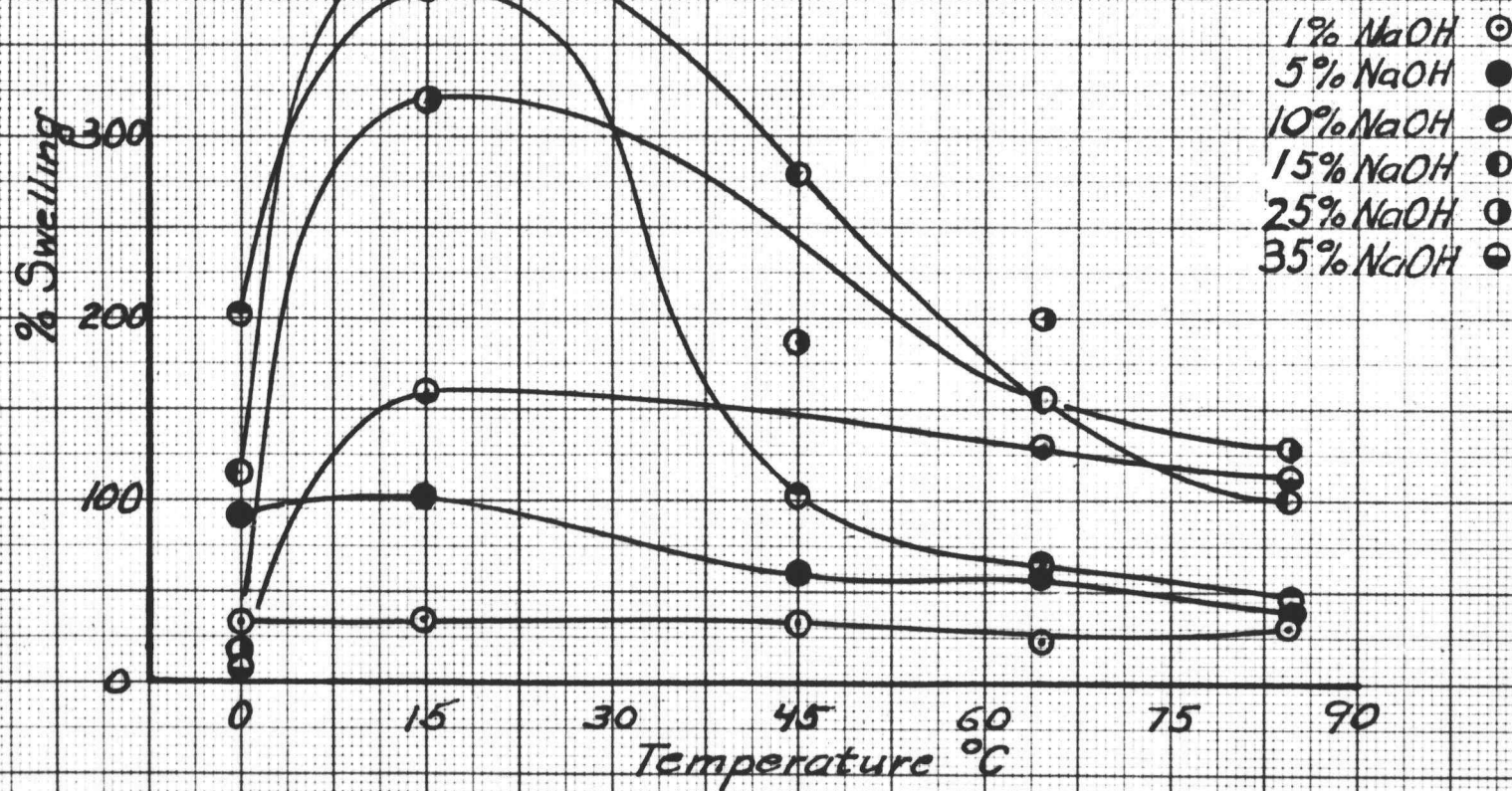


TABLE XI

FIFTEEN MINUTE SWELLING

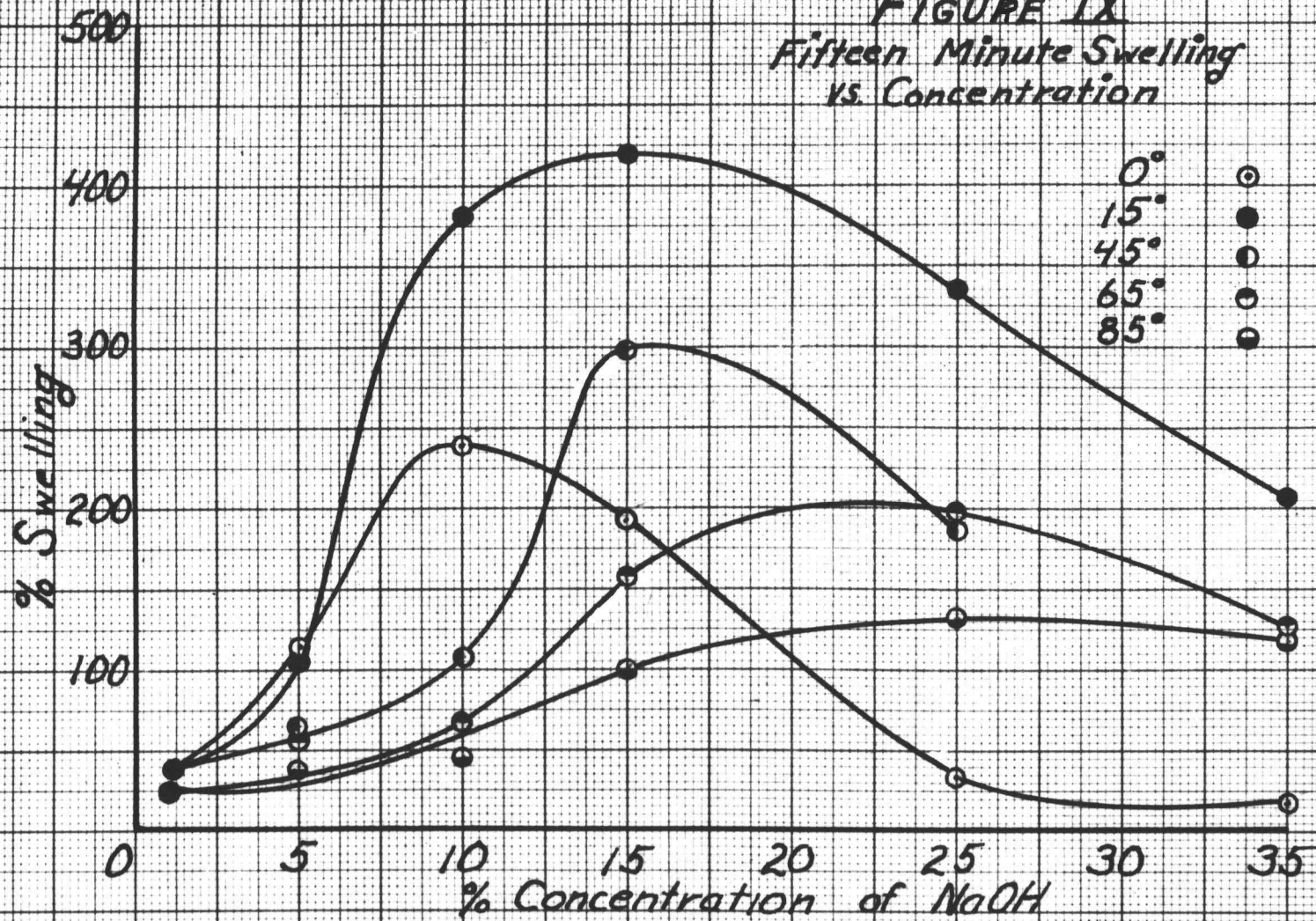
PER CENT CONCENTRATION NaOH	PER CENT SWELLING				
	0°	15°	45°	65°	85°
1	31	38	33	22	29
5	113	107	65	58	38
10	240	382	109	67	45
15	193	420	300	158	100
25	33	335	187	198	131
35	13	206	---	129	116

TABLE XII

TWENTY MINUTE SWELLING

PER CENT CONCENTRATION NaOH	PER CENT SWELLING				
	0°	15°	45°	65°	85°
1	38	40	33	25	30
5	127	109	67	57	39
10	284	387	111	67	46
15	238	432	300	160	100
25	63	335	184	198	130
35	15	220	---	132	116

FIGURE IX
*Fifteen Minute Swelling
 vs. Concentration*



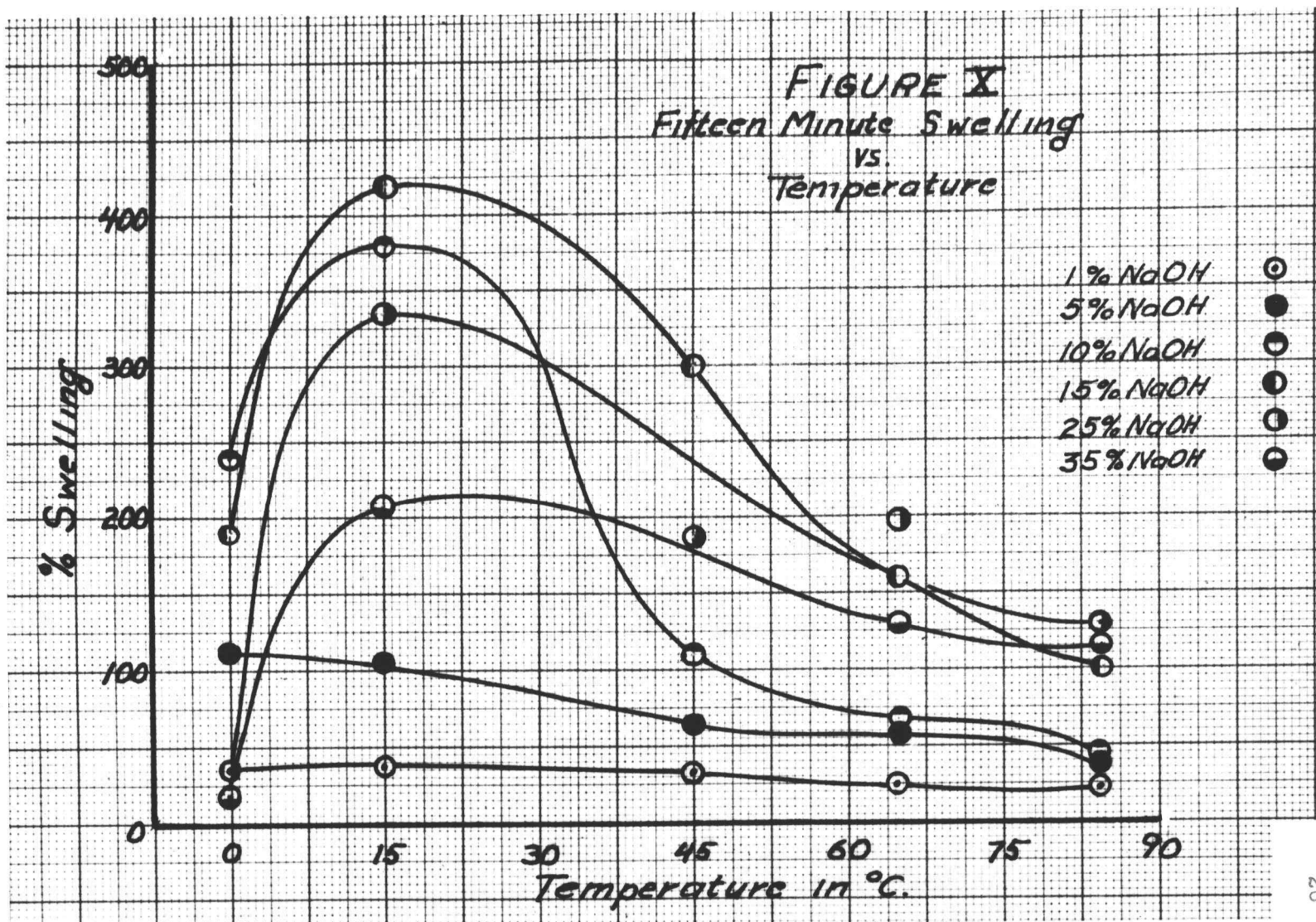


FIGURE XI
Twenty Minute Swelling vs.
Concentration

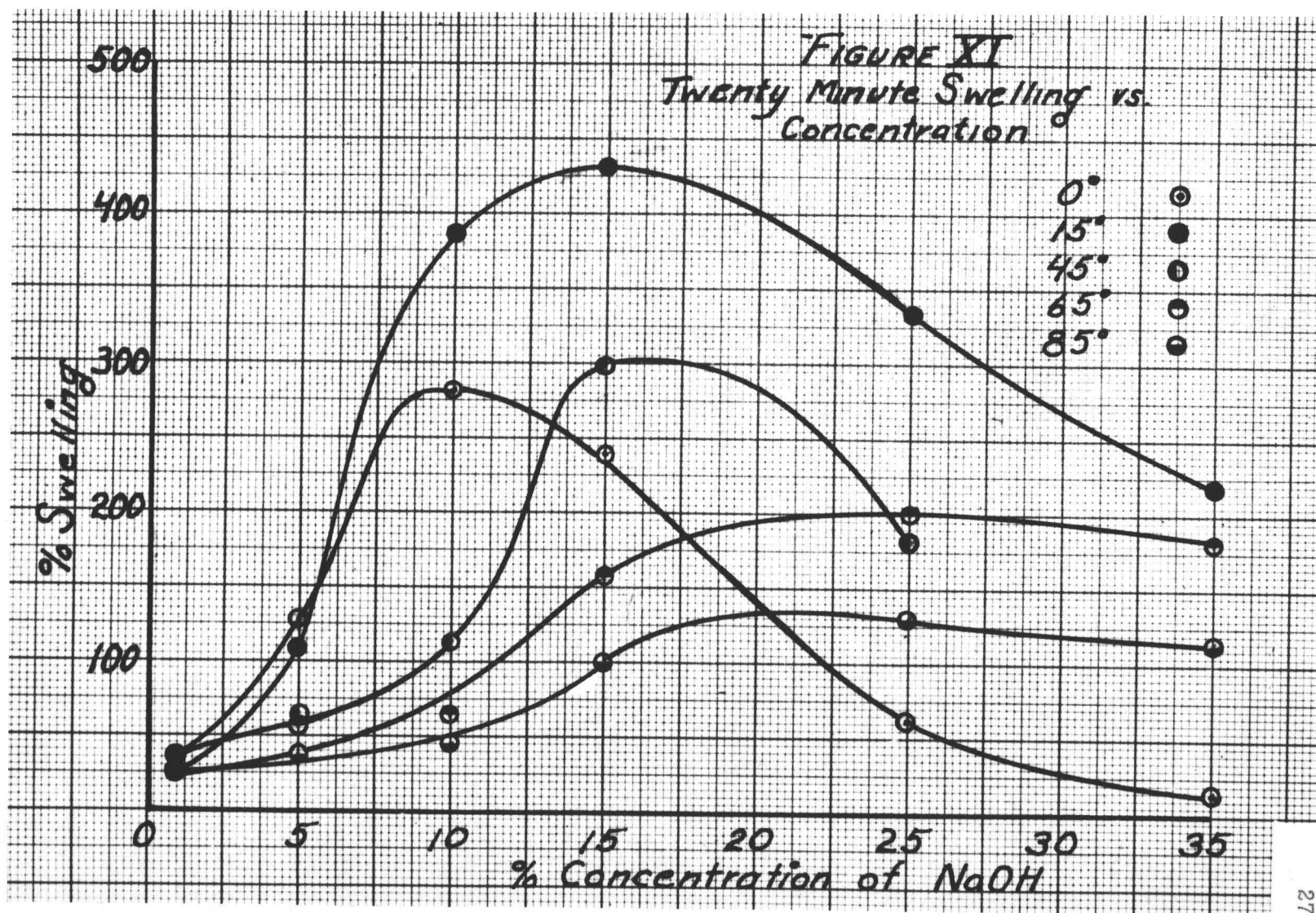


FIGURE XII
Twenty Minute Swelling
vs
Temperature

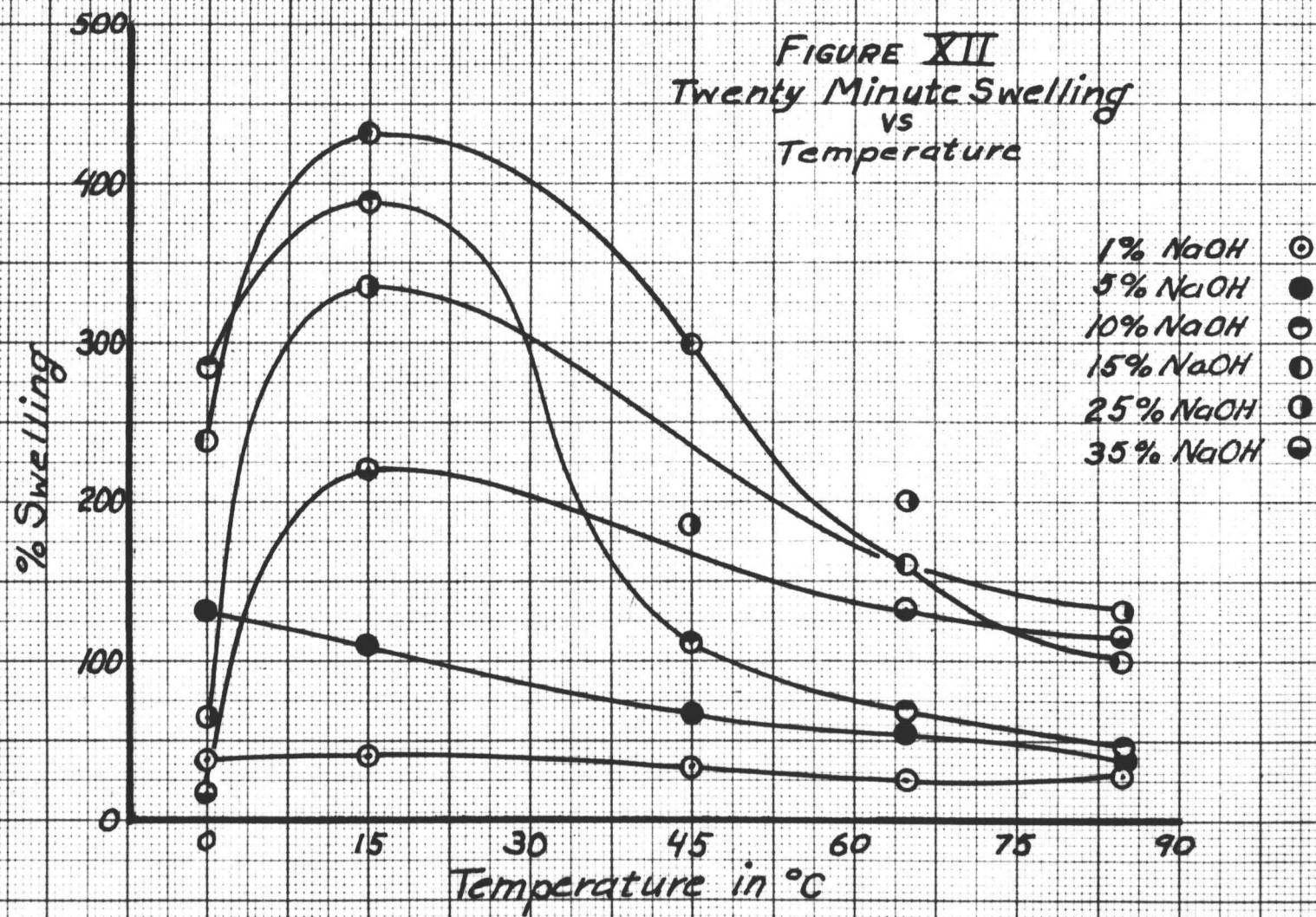


TABLE XIII
THIRTY MINUTE SWELLING

PER CENT CONCENTRATION NaOH	PER CENT SWELLING				
	0°	15°	45°	65°	85°
1	40	45	31	27	29
5	129	113	65	56	40
10	325	389	111	69	47
15	329	434	304	162	100
25	80	340	193	200	129
35	33	256	---	131	116

TABLE XIV
EQUILIBRIUM SWELLING

PER CENT CONCENTRATION NaOH	PER CENT SWELLING				
	0°	15°	45°	65°	85°
1	49	45	33	24	29
5	140	111	63	56	40
10	482	398	109	71	45
15	522	429	302	162	100
25	313	340	196	200	129
35	198	278		131	116

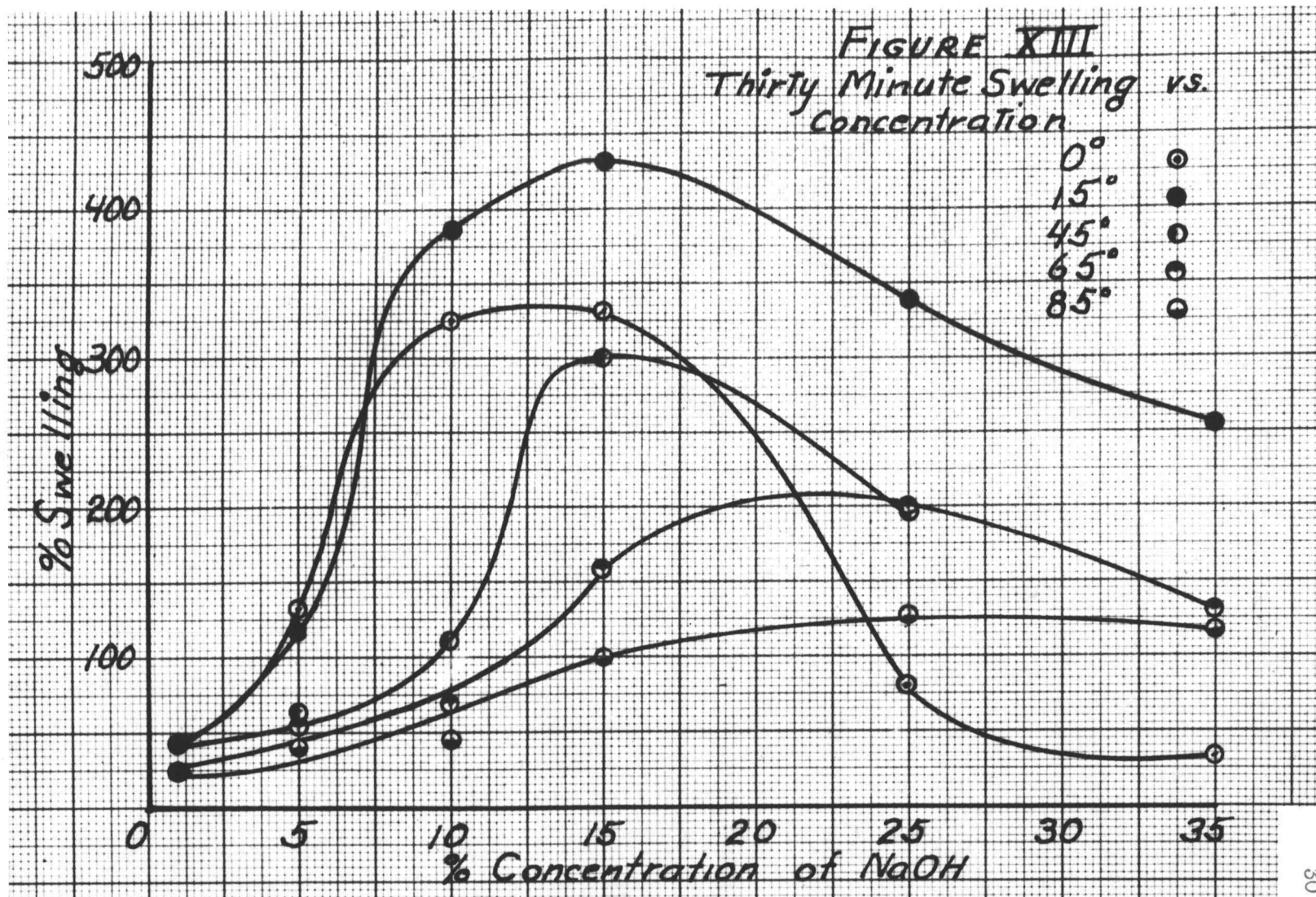
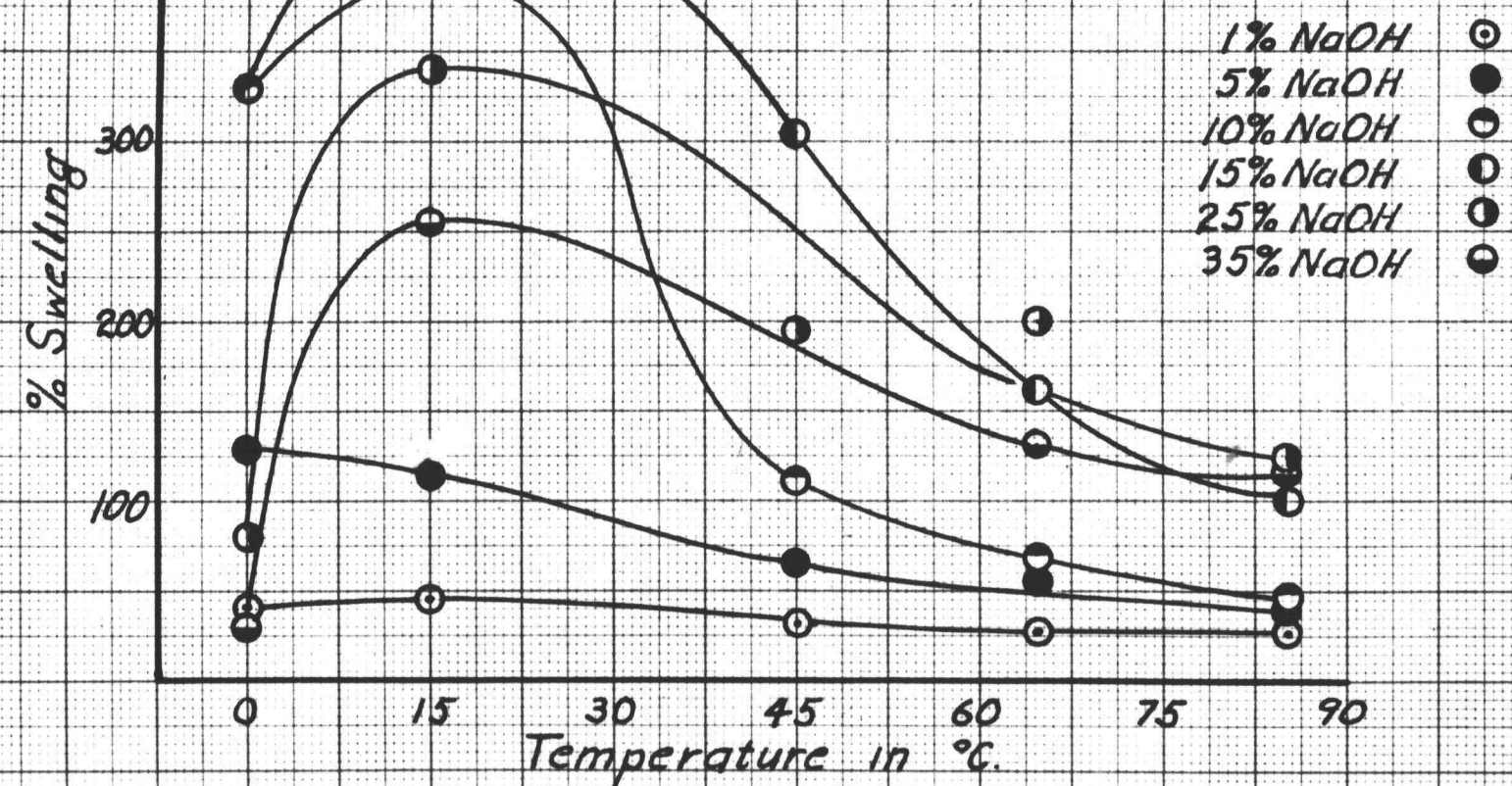


FIGURE XIV
Thirty Minute Swelling
vs
Temperature



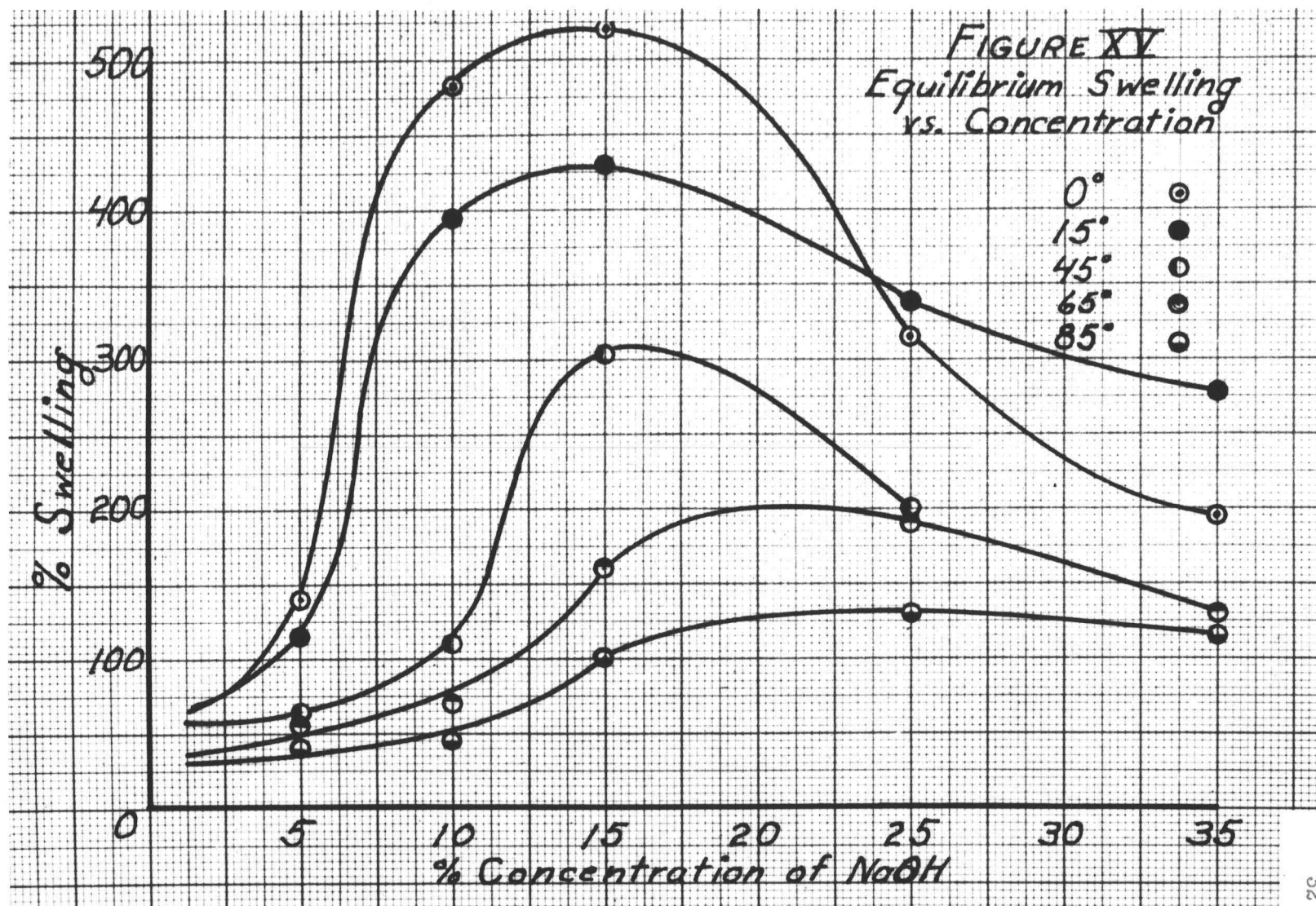
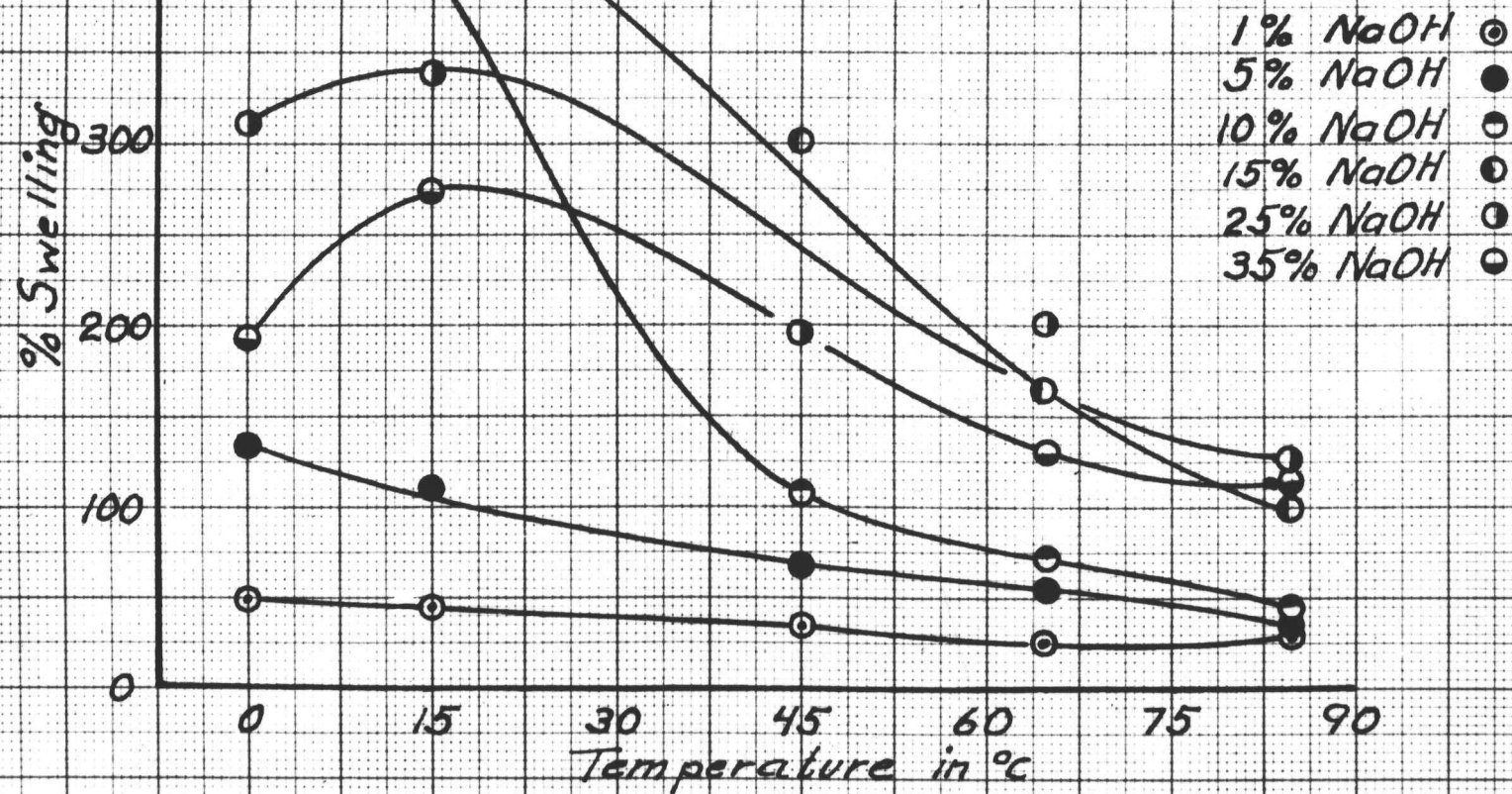
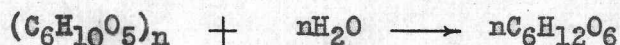


FIGURE XVI
Equilibrium Swelling
vs.
Temperature

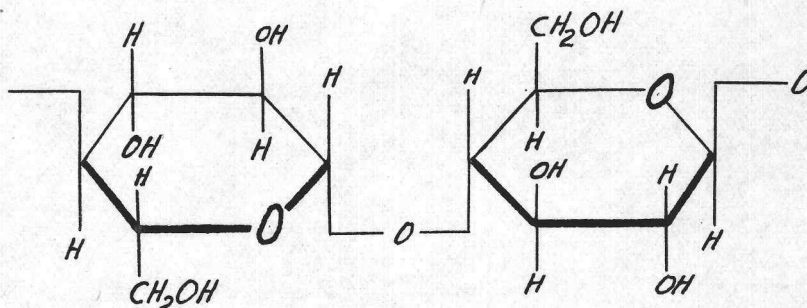


DISCUSSION OF THE SWELLING OF CELLULOSE. Cellulose was first defined by Payen (10) over 125 years ago as the fibrous residue that resists the attack of nitric acid and alkalis on woody tissue. He proposed the empirical formula $C_6H_{10}O_5$ (corrected on the basis of modern atomic weights) which is still considered correct today. Bracconot (1) was the first to publish the relationship between glucose and cellulose as represented by the equation:



This was later proved to be quantitative.

The presence of three alcoholic hydroxyl groups, one primary and two secondary, for each glucose residue has been repeatedly established by esterification and etherification. On the basis of known facts, cellulose is now generally accepted to be a condensation polymer of glucose. It appears to take the form of glucopyranose units linked together in all cases as beta glucosides. This structure is shown schematically for two glucose residues.



Five such pairs of glucopyranose units are grouped in the monoclinic unit cell of cellulose. The minimum length for a cellulose molecule probably represents a length of twenty times that of the unit

cells, while the average molecular length of the cellulose molecules of cotton has been reported to be five times this amount. Because of the great length of the cellulose molecule, the unit cells are oriented more in one direction than in others, giving rise to long threadlike chains. A large number of these chains are, in turn, bundled together to form the crystallite or micelle, the building block of the cellulose fiber. Since not all the cellulose molecules are of the same length some bridge the gap and tie adjacent micelles together end to end. The chains of micelles in the cellulose fiber are arranged in a helix at a slight angle to the axis with an outside layer which spirals about the fiber at an angle which in some cases approaches ninety degrees. Wood fibers supply a striking example of such orientation.

X-ray evidence indicated that, when the cell walls of cellulose materials swell, water is taken up between the crystallites and within zones of less perfect orientation to add its volume to that of the cell walls. The spreading apart of the micelles is thus almost entirely at right angles to the direction of orientation of the threadlike units. The fact that only a limited amount of water can be taken up within the cell wall is probably due to the fact that the molecules that pass from one bundle to another do so in such a random manner as to tie them all together through chemical bonds. The micelles are thought to be further held together by the secondary valence forces of hydrogen bonds between hydroxyl groups on adjacent molecules. (18)

THEORIES ON SWELLING. A great many attempts have been made to explain the taking up of a swelling medium by a swelling solid. A few which have received rather wide support will be mentioned here.

Pauli and Handovsky (9) believe that certain ions are strongly adsorbed on the surface of cellulose and in order to maintain electrical neutrality, the oppositely charged ions become immobilized near the surface bringing their sphere of water with them. These authors believed that it is this water of hydration that is responsible for swelling.

Tolman and Stearn (15) believe that the adsorption of ions on the surface of the cellulose creates a surface charge that repels like surfaces allowing water to enter mechanically.

Proctor and Wilson (11) thought swelling to be due to the setting up of a Donnan membrane equilibrium that results in a higher concentration of ions within the membrane than on the outside which results in the taking up of water by osmosis because of the concentration difference.

Because of the many sided aspect of the problem of swelling none of the above theories is able to explain the swelling of cellulose under all conditions of temperature and concentration (17).

Of interest is the explanation offered by Stamm (14) for the swelling of wood in concentrated aqueous salt solutions. He offers a combined sorption-solution pressure-structural resistance equilibrium theory. He showed that the swelling of wood in saturated salt solutions increases with an increase in the partial specific

volume of the salt in solution. The swelling in all cases was less than the volume of the salt taken up, indicating that some water had been displaced. He observed a lag between the beginning of sorption of the salt and the commencement of swelling. As more salt enters the swelling structure, more water must be displaced or the material has to swell. As more and more water is displaced, its removal becomes more and more difficult. The force necessary to displace the water soon exceeds the structural resistance force so that swelling, rather than water displacement, results.

THE VARIATION OF SWELLING WITH CONCENTRATION AND TEMPERATURE. During the course of this investigation several factors which warrant discussion were observed.

I. Swelling of pulp was found to be much greater in caustic than in water. This is rather easily explained on the basis of the setting up of a Donnan equilibrium with the cellulose acting as its own membrane in the sodium hydroxide solution. There is no possibility of this occurring in pure water because of the absence of electrolytes.

II. Swelling was observed to be greatest at lower temperatures. This observation might be explained from two standpoints:

A. It has been repeatedly found that the amount of adsorption of one material by another decreases with increasing temperature. Since all attempts to explain swelling that have enjoyed any amount

of popularity have done so on the basis of adsorbed ions or molecules, one would expect swelling to decrease with increasing temperature.

B. It has been found that the degree of hydration of the sodium ion is lower at higher temperatures. This would lend credence to the theory of Pauli and Handovsky (9) since they explain swelling on the basis of water of hydration of the ion charged oppositely to the one highly adsorbed.

III. Data obtained in this study indicate that swelling is slowest at low temperatures. X-ray evidence (18) indicates that when marked swelling takes place there is an alteration in the x-ray lattice of cellulose. This would indicate that the swelling medium is actually entering and swelling the micelles. In cases of slight swelling, no evidence of intramicellar swelling has been found. Since at low temperatures swelling is marked as well as slow, one would be led to the conclusion that the low rate of swelling at temperatures near zero degrees is due to the fact that the swelling medium must penetrate more profoundly into the structure of the cellulose fiber. Also to be considered is the known fact that diffusion rates decrease with decreasing temperature. In order to swell cellulose, sodium hydroxide must first diffuse into it.

IV. The rate of swelling was also observed to decrease with increasing concentration of caustic. This author believes that this is readily accounted for by consideration of the fact that as concentration of alkali solution increases, its viscosity also increases.

This is accompanied by a corresponding decrease in the rate of diffusion of caustic through the solution and consequently into the fiber. The rate of penetration of the pulp sheet by a solution would obviously decrease with increasing viscosity. This lower rate of swelling may also be due in part to the necessity for penetration of the sodium hydroxide into the cellulose micelles, as pointed out in the following paragraph.

V. Swelling was observed to be maximum in fifteen per cent caustic solution. In order to discuss this finding two considerations should be stated.

A. The degree of hydration of the sodium ion has been found by many workers to decrease with increasing concentration.

B. X-ray data indicate that intramicellar swelling does not take place in concentrations of caustic below ten per cent. As has been mentioned above, swelling can be considered a function of ionic hydration. The x-ray evidence indicates that swelling below ten per cent caustic can be considered a purely adsorption phenomenon while above this concentration the internal surface of the micelle becomes more and more available for chemical combination between the cellulose and sodium hydroxide (18). When all the internal surface becomes available, then and only then can the addition of alkali be considered as a true stoichiometric chemical reaction. This may be the case only under conditions of optimum swelling.

THE EFFECT OF WETTING AGENTS. In order to ascertain whether or not wetting agents would have any effect upon the swelling of pulp as measured by this method, several experiments were carried out in which the swelling of pulp was studied in 5 and 15 per cent caustic solutions to which 0.03 per cent of various wetting agents had been added. 5 and 15 per cent sodium hydroxide solutions were chosen for these experiments because they had been found to cause near minimum and near maximum swelling respectively. 0.03 per cent wetting agents was chosen because literature supplied with them indicated that at this concentration surface tension lowering is about as great as can be obtained. Swelling measurements were made at temperatures of 0, 8, 15, 25, 45, 65, and 85° C.

The wetting agents used were Triton N-100, Triton K-60, Triton 770 and Kreecon 4-D. These particular wetting agents were chosen because among them are two anionic, one non-ionic and one cationic type. Triton N-100 is a non-ionic wetting agent consisting of a poly ether alcohol supplied in 100 per cent strength. Triton K-60 is cationic supplied as an aqueous dispersion of stearyl dimethyl benzyl ammonium chloride in the form of a paste containing 25 per cent active ingredient. Triton 770 is anionic containing 30 per cent sodium salt of an aryl poly ether sulfate and 30 per cent isopropanol in water. Kreecon 4-D is an anionic wetting agent supplied as a powder consisting of 40 per cent organic sulfonates and 60 per cent inorganic salts.

The results of these experiments are given in tabular form in Tables XV through XXI. The values for equilibrium swelling at various temperatures have been summarized in Table XXII and are shown graphically in Figures XVII to XX inclusive.

For the sake of easy comparison the corresponding curves for swelling in sodium hydroxide solutions without wetting agents are plotted in the same figures.

It should be noted that wetting agents were found to have only a negligible effect regardless of what type of wetting agent was used.

TABLE XV

SWELLING WITH WETTING AGENTS AT 0° CENTIGRADE

TIME IN MINUTES	PER CENT SWELLING							
	5 PER CENT NaOH				15 PER CENT NaOH			
	N-100	K-60	770	4-D	N-100	K-60	770	4-D
5	78	71	78	69	33	56	67	38
10	107	91	104	100	127	125	127	122
15	120	116	118	122	169	178	200	173
20	122	118	116	122	224	234	260	251
30	125	120	116	122	331	333	362	378
40	127	120	118	122	427	422	446	454
50	127	122	120	122	489	482	495	478
60	129	127	120	122	520	516	511	522
70	131	127	127	122	529	524	518	522
80	129	127	127	122	536	534	526	522
90	129	127	127	122	540	540	531	522

TABLE XVI

SWELLING WITH WETTING AGENTS AT 8° CENTIGRADE

TIME IN MINUTES	PER CENT SWELLING							
	5 PER CENT NaOH				15 PER CENT NaOH			
	N-100	K-60	770	4-D	N-100	K-60	770	4-D
5	91	78	78	87	300	325	322	273
10	94	85	80	98	356	371	380	387
15	96	89	87	100	427	415	436	414
25	100	94	100	104	474	472	474	484
35	100	100	94	104	489	489	478	507
45	100	98	94	104	484	489	486	507
60	100	100	94	104	486	486	486	507

TABLE XVII

SWELLING WITH WETTING AGENTS AT 15° CENTIGRADE

TIME IN MINUTES	PER CENT SWELLING							
	5 PER CENT NaOH				15 PER CENT NaOH			
	N-100	K-60	770	4-D	N-100	K-60	770	4-D
5	82	87	87	87	456	469	422	434
10	89	94	100	94	478	472	456	434
15	94	94	94	94	478	474	465	442
20	94	94	94	94	478	472	469	440
30	94	96	96	94	478	472	469	442

TABLE XVIII

SWELLING WITH WETTING AGENTS AT 25° CENTIGRADE

TIME IN MINUTES	PER CENT SWELLING							
	5 PER CENT NaOH				15 PER CENT NaOH			
	N-100	K-60	770	4-D	N-100	K-60	770	4-D
2	63	67	67	67	400	400	393	411
5	78	73	71	71	413	427	411	411
10	89	73	73	78	411	422	411	411
20	89	78	73	78	413	422	413	411

TABLE XIX

SWELLING WITH WETTING AGENTS AT 45° CENTIGRADE

TIME IN MINUTES	PER CENT SWELLING							
	5 PER CENT NaOH				15 PER CENT NaOH			
	N-100	K-60	770	4-D	N-100	K-60	770	4-D
2	53	53	53	56	273	278	278	282
5	58	58	56	56	276	278	278	289
10	56	56	56	56	278	278	278	289
20	56	56	56	56	278	278	278	289

TABLE XX

SWELLING WITH WETTING AGENTS AT 65° CENTIGRADE

TIME IN MINUTES	PER CENT SWELLING							
	5 PER CENT NaOH				15 PER CENT NaOH			
	N-100	K-60	770	4-D	N-100	K-60	770	4-D
2	49	49	47	38	158	156	149	151
5	49	49	47	38	160	158	151	151
10	51	49	47	38	160	156	149	151
15	49	49	49	38	158	158	149	151

TABLE XXI

SWELLING WITH WETTING AGENTS AT 85° CENTIGRADE

TIME IN MINUTES	PER CENT SWELLING							
	5 PER CENT NaOH				15 PER CENT NaOH			
	N-100	K-60	770	4-D	N-100	K-60	770	4-D
2	35	35	33	31	89	85	98	98
5	38	35	33	33	89	85	98	96
10	38	38	33	38	89	85	98	96
15	38	35	35	38	89	85	98	96

TABLE XXII

EQUILIBRIUM SWELLING WITH WETTING AGENTS

TIME IN MINUTES	PER CENT SWELLING							
	5 PER CENT NaOH				15 PER CENT NaOH			
	N-100	K-60	770	4-D	N-100	K-60	770	4-D
0	136	127	125	122	538	540	531	522
8	100	100	94	104	486	486	486	507
15	94	96	96	94	478	472	469	442
25	89	78	73	78	413	422	413	411
45	56	56	56	56	278	278	278	289
65	49	49	49	38	158	158	149	151

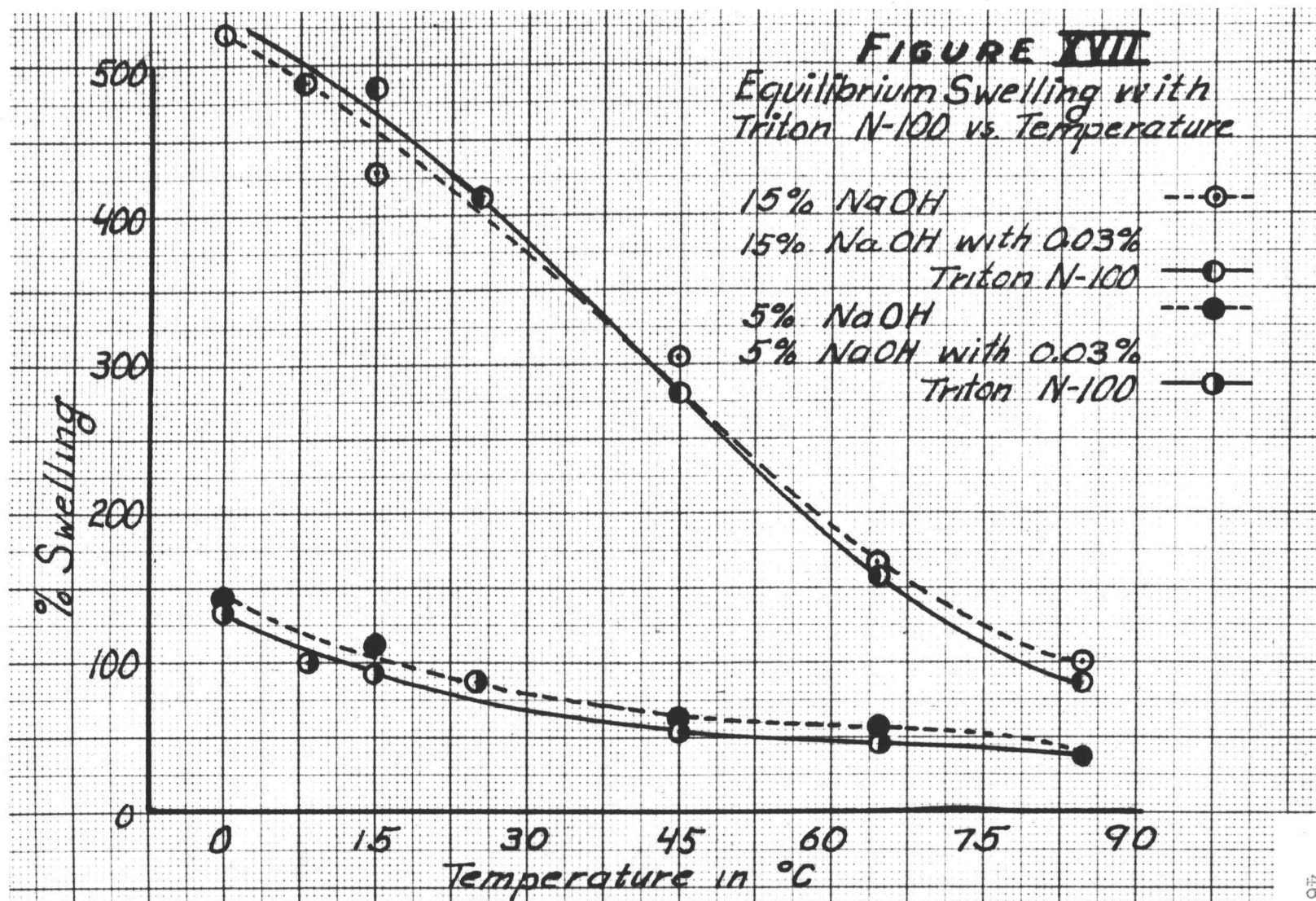


FIGURE XVIII
EQUILIBRIUM SWELLING WITH
TRITON K-60 vs TEMPERATURE

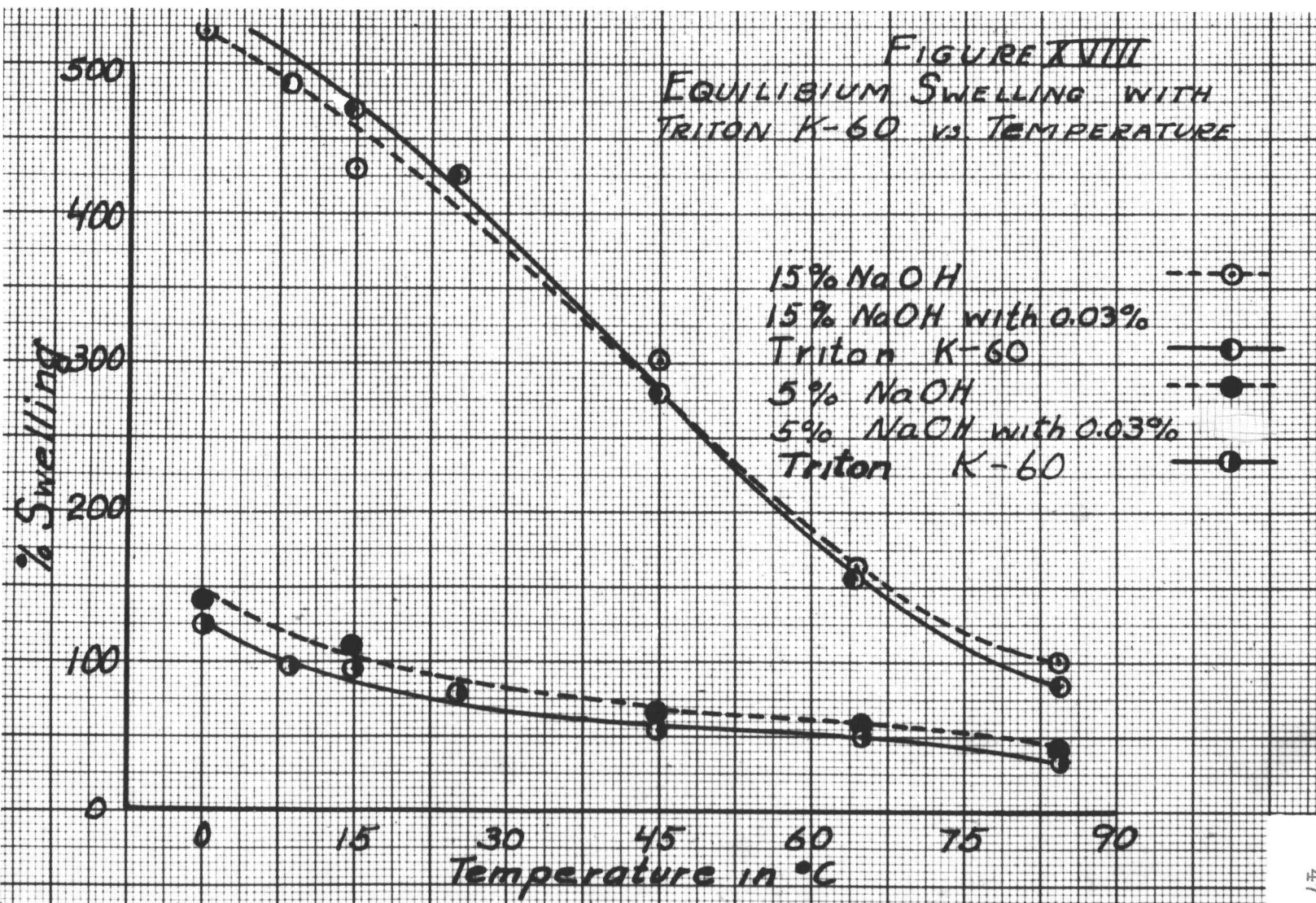
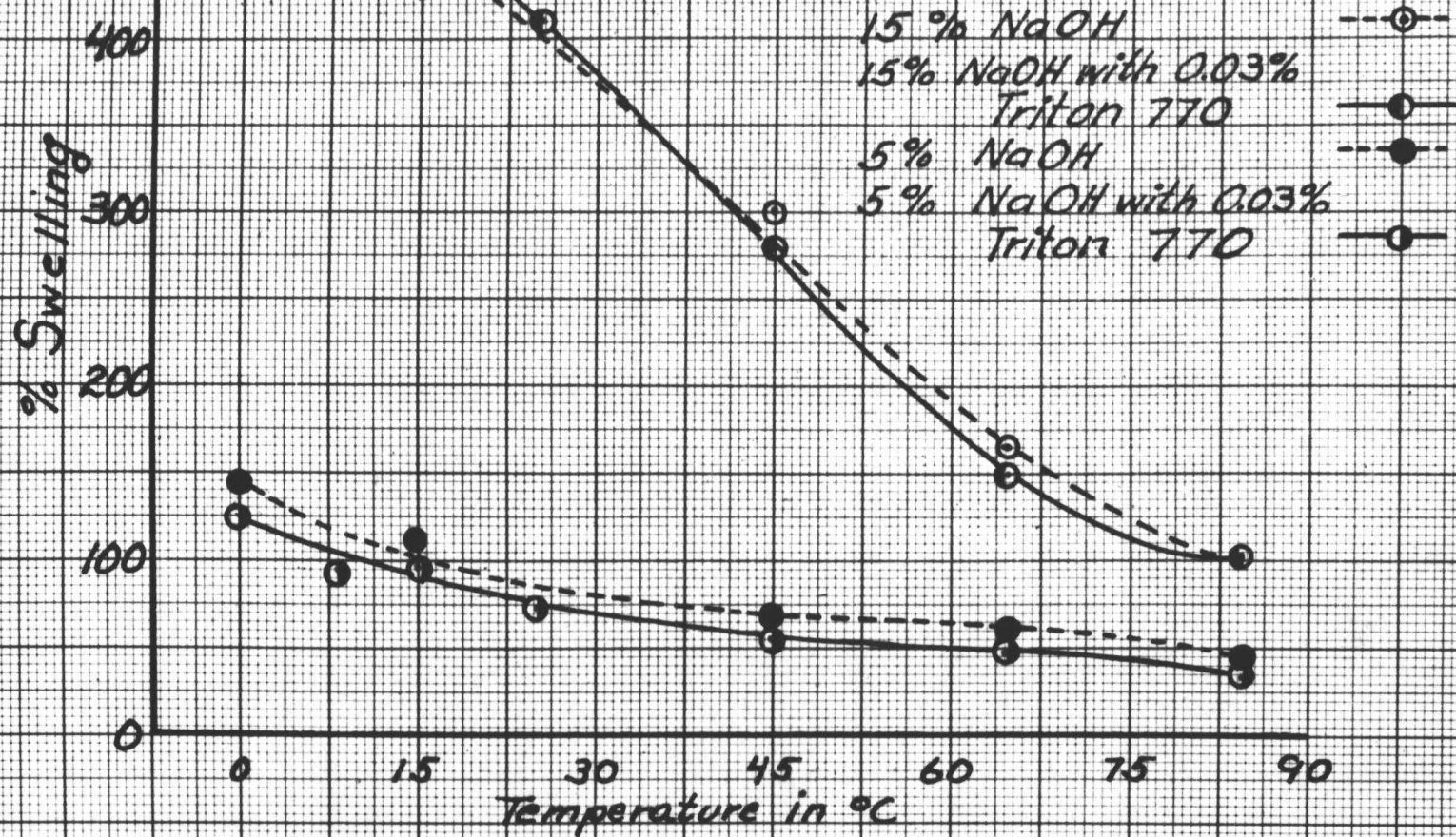
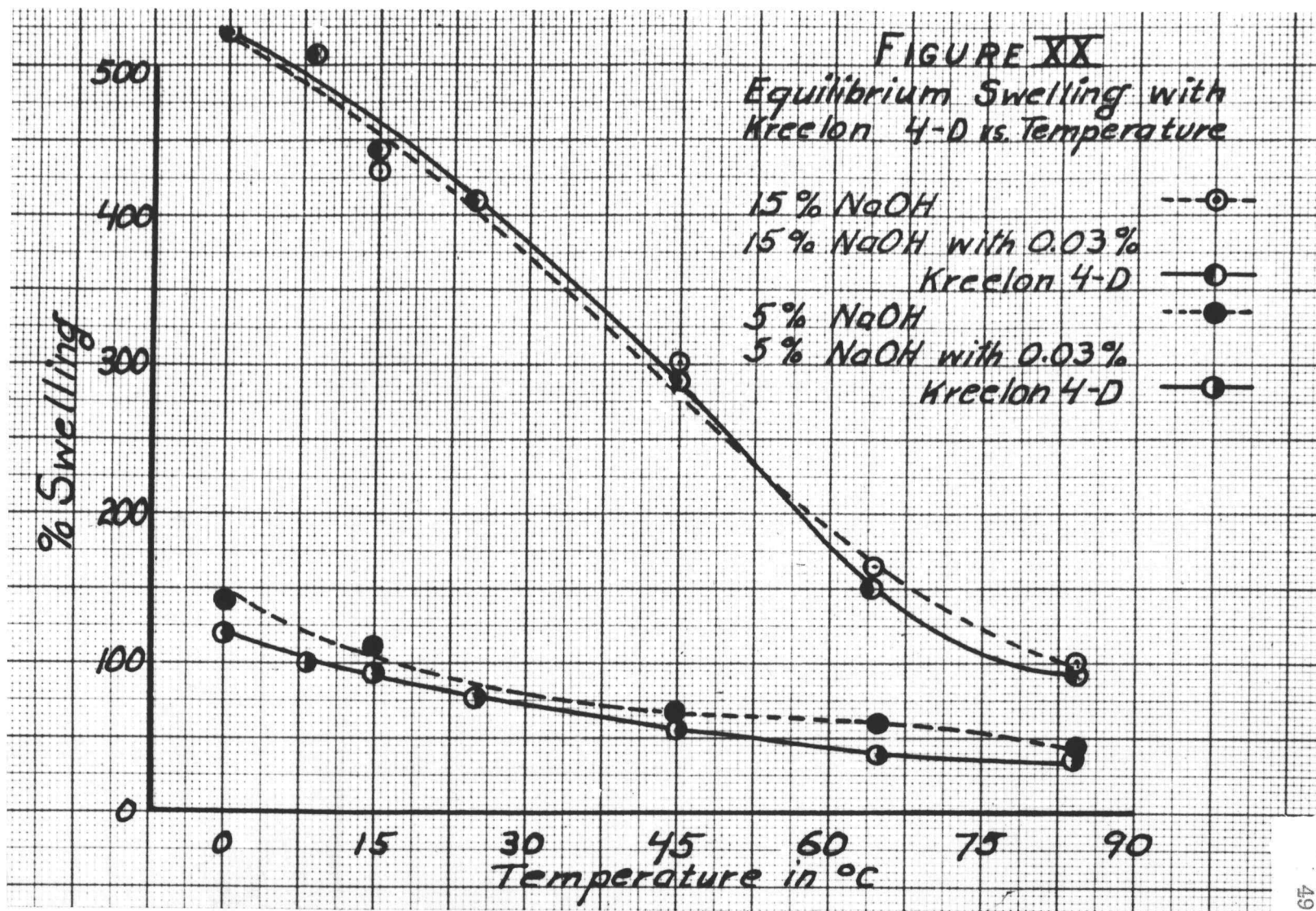


FIGURE XIX
Equilibrium Swelling with
Triton 770 vs Temperature





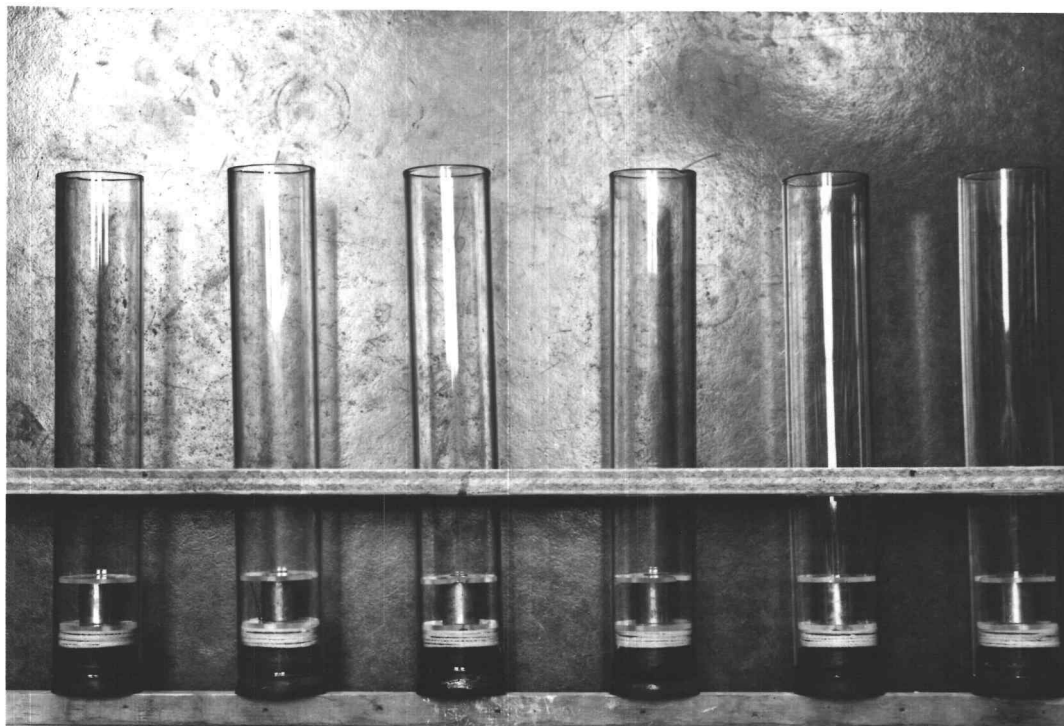
IV. SUMMARY

A method for the measurement of the swelling of cellulose pulp was devised and the swelling of pulp sheets in various concentrations of sodium hydroxide and at various temperatures was studied. The influence of wetting agents on pulp swelling was also investigated.

Swelling of cellulose in caustic solutions was found to be maximum at low temperatures and to pass through a maximum at 15 per cent concentration of sodium hydroxide. The rate of swelling was found to be slow in high concentrations of caustic and at low temperatures. Wetting agents were observed to have little or no effect on swelling as measured.

The data obtained in the investigation are presented in such a manner as to illustrate the above findings and these observations are discussed.

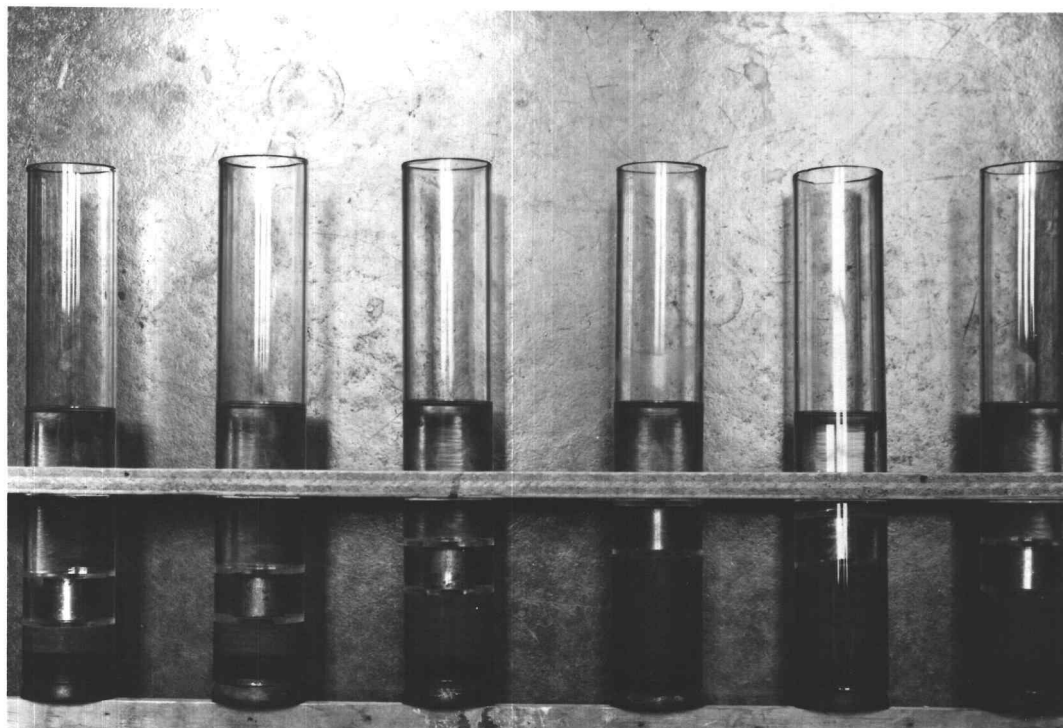
FIGURE XXI



PULP SAMPLES BEFORE SWELLING

Each cylinder contains 5 disks of pulp and
a weight as described in an earlier
section

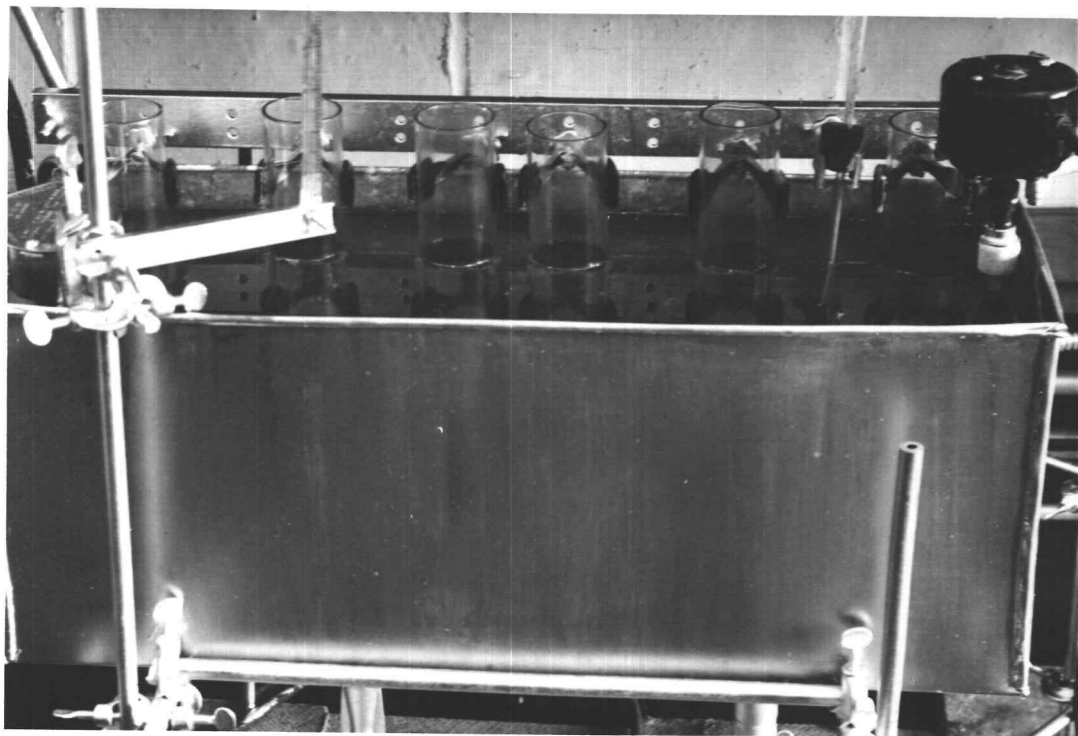
FIGURE XXII



PULP SAMPLES SWOLLEN AT 25° C.

Cylinders, from left to right, contain pulp samples swollen in 1, 5, 10, 15, 25 and 35 per cent sodium hydroxide solutions, respectively

FIGURE XXIII



CYLINDERS IMMERSED IN CONSTANT TEMPERATURE BATH

V. BIBLIOGRAPHY

1. Braconnot, Henri, Mémoire sur la conversion du corps ligneux, en gomme, en sucre et en un acide particulier. *Ann. chim. phys.* (2), 12, 172 (1819).
2. Collins, George E. and Williams, A.M., Studies on the swelling of cotton cellulose, I. Cotton hairs in solutions of sodium hydroxide. *J. Textile Inst.*, 14, 287 (1923).
3. Collins, George E., The length changes of cotton hairs in solutions of caustic soda. *J. Textile Inst.*, 21, 293 (1930).
4. Freudenburg, Karl, Tannin, Cellulose, Lignin. Berlin, Julius Springer, 1933, pp. 90-109.
5. Fujii, Mitsuo, The adsorption of alkali solution by rayon pulp. *Cellulose Ind. (Tokyo)*, 11, 184 (1935).
6. Hartman, Robert J., Colloid chemistry 2nd Ed., New York, N. Y., Houghton Mifflin Company, 1947, p. 424.
7. Mercer, J., British Patent 13, 296, (1850).
8. Noll, August, Criteria for the swelling of pulps. *Papier-Fabr.*, 29, Tech. Wiss. Teil, 114, (1931).
9. Pauli, W. and Handovsky, H., Investigations concerning changes in the physical state of colloids, IX Studies of alkali protein. *Biochem. Z.*, 24, 239, (1909).
10. Payen, Anselme, Mémoire sur la composition du tissu propre des plantes et du ligneux. *Compt. rend.*, 7, 1052 (1838).
11. Proctor, H.R. and Wilson, J.A., Acid-gelatin equilibrium. *J. Chem. Soc.*, 109, 307, (1916).
12. Richter, George A. and Glidden, Kenneth E., Cellulose sheet swelling - the effect of temperature and concentration of sodium hydroxide solutions. *Ind. Eng. Chem.*, 32, 480, (1940).
13. Stamm, Alfred J., Effect of inorganic salts on the swelling and shrinking of wood. *J. Am. Chem. Soc.*, 56, 1195, (1934).

14. Stamm Alfred J., Shrinking and swelling of wood. Ind. Eng. Chem., 27, 401, (1935).
15. Tolman, Richard C. and Stearn, Allan E., The molecular mechanism of colloidal behavior. J. Am. Chem. Soc., 40, 264, (1918).
16. Wise, Louis E., Editor, Wood chemistry, New York, N. Y., Reinhold Publishing Corp., 1944, p. 487.
17. Ibid., p. 489.
18. Ibid., p. 469.