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Dialysis of Silicic Acid

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A thesis presented to the Department of
Chemistry of Union College, in partial
fulfillment of the requirements for the
degree of Bachelor of Science in Chemistry,

by Paul L. Merz

Approved by Charles B Hurd

May 21 1940

INTRODUCTION

This research was a quantative study of the polymerization of silicic acid molecules which occurred during the process of gel formation by the means of dialysis.

The condensation of the silicic acid molecules, $Si(OH)_4$, to form larger molecules of colloidal size, as suggested by the polysilicic acid fibrillar theory, was investigated with membranes of known pore size at various stages of the reaction.

Although filter and membrane action is only to a limited extent comparable with the action of a sieve, and is much more dependent on the absorption in the capillaries than the size of the pores, still a close connection between the concentration of membranes and the size of particles held back by them has been reported (1) and it was hoped that by this means the mechanism of the condensation of polysilicic acids could be studied to some extent.

HISTORICAL

Many investigators before 1900 attempted to separate electrolytes present in a silicic gel mixture from silicic acid by the means of dialysis and observed that considerable amounts of the silicic acid,when first formed, dialized through the membrane with the electrolytes. This phenomenon was investigated qualitatively by Zigmondy, (2) who observed that the silicic acid passed through the membrane freely in the early part of the reaction and that as the reaction proceeded the amount of silicic acid dialyzing through decreased until by the time of gelation, the silicic acid had entirely ceased to pass through the membrane.

Zigmondy also observed that upon the addition of mineral acid to the gel mixture much less silicic acid would diffuse through the membrane.

With the exception of an even less complete investigation by Jardis (3) this phenomenon of the dialysis of silicic acid has not been further investigated and,as far as could be determined, the phenomenon had not been investigated quantatively.

EXPERIMENTAL PROCEDURE

Any study of the condensation mechanism of silicic acid must be carried out under uniform conditions throughout the entire experiment. Collodion was chosen as the membrane material for the dialysis because of its ease of preparation, its reproducibility and the possibility of controlled permeability variation. All dialysis will be carried out with 6" membrane sacks which will be filled with the substance to be dialyzed and placed in 8" test tubes containing 40 c.c. of water. All reactions and dialyses will be carried out at 25° C.

The collodion sacks were all prepared by the following procedure: U.S.P. collodion solution, General Chemical Co., code No.1611, was poured over the inside of 6" test tubes, the test tubes were inverted and allowed to drain and dry for a predetermined period of time. The test tubes were then placed upright, filled with distilled water and allowed to stand for about ten minutes, after which they could easily be removed. The membranes were preserved in distilled water for at least 48 hours before using. The permeability of these membranes depends on the period allowed for drying of the collodion film previous to filling with water. A number of such membranes were made each with a different time of drying, ranging from 5 to 85 minutes. The pore sizes of each of these membranes were then determined by the air pressure method (4,5 and 6). In this method the pores of the water saturated membrane are considered as capillary tubes wet with water. The air pressure, P, required to force the water from the tubes (pores) depends on the interfacial tension between the water, air and the membrane, and the radius of the pore, r. These are connected by the relation $r = \frac{2 S \cos \theta}{Pg}$ where S = surface tension of water

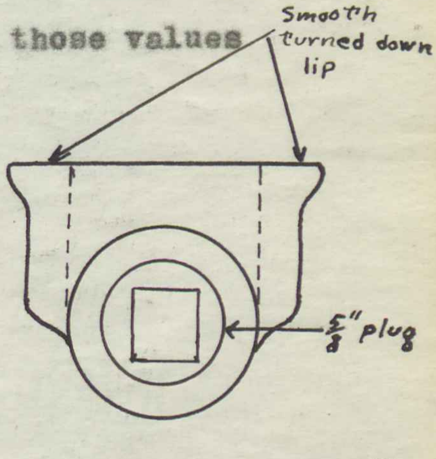
P = pressure in g/cm^2

g = gravitational constant = 980 dynes

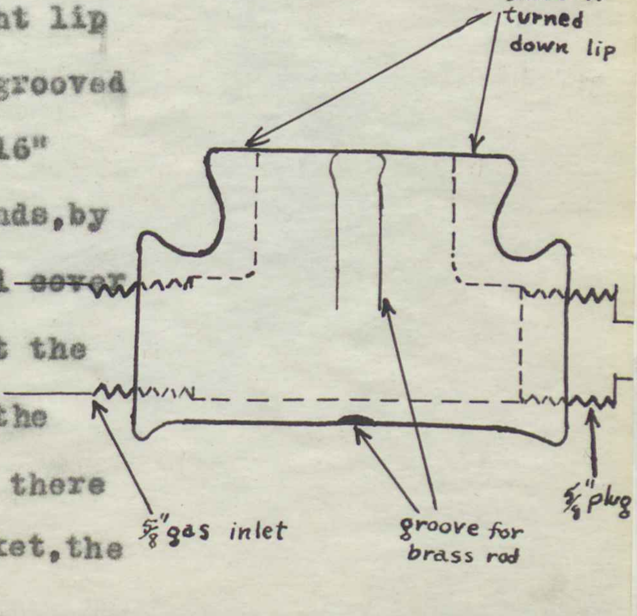
θ = contact angle between membrane and water = 53^0

For the collodion membranes under the conditions used the expression reduces to $r = \frac{1.26 \times 10^{-3}}{P}$ where P is in pounds and r measured in cm.

This formula is valid, according to Raleigh and Freundlich (7) for capillaries smaller than .01 cm down to those values which fall within the magnitude of molecular attraction; i.e., 50 Å.



The air pressure cell used to hold the membrane was made from an old 5/8" pipe "T", with a 3/4" side outlet. The edge of the 3/4" side outlet was turned down smooth on a lathe so as to provide an airtight lip ½" wide. The surface to the "T" was grooved to provide a "seat" for a piece of 3/16" diameter brass rod. threaded at both ends, by means of which a perforated 1/8" steel cover plate could be clamped tightly against the turned-down surface of the pipe T by the means of thumb screws. In the holder there was placed in order a thin rubber gasket, the



membrane out to fit the holder, a like shaped piece of linen cloth, a piece of 60 mesh copper gauze, a second rubber gasket, and finally the perforated steel cover plate. The cell was then connected with a tank of compressed nitrogen and a pressure gauge, a film of water was placed over the membrane and a magnifying glass focused on the copper gauze through the 1/5" holes in the steel plate. The gas pressure was applied gradually to the membrane, the number of bubbles which appeared at each successive pressure being recorded. The data obtained for the series of membranes is shown in the tables below:

Drying Time of Membrane	Pressure in lbs.per sq.in.	Number of bubbles	Pore Size in Angstrom
5 min.	5.0	5	24,750
	9.2	7	13,500
	11.5	14	10,730
	13.0	18	9,525
	15.55	22	8.250
	19.0	27	6,520
15 min.	11.5	3	10,730
	15.0	6	8.100
	17.5	11	7,200
	20,0	16	6,190
	22.5	18	5,500
	25.0	22	5,000
30 min.	22.5	9	5,500
	25.0	16	5,050
	27.5	19	4,580
	30.0	22	4,200
	32.5	25	3,880
	35.0	26	3,600
60 min.	27.5	2	4,580
	43.0	3	2,930
	52.5	5	2,400
	60.0	10	2,100
	65.0	12	1,940
	75.0	13	1,680
	85.0	16	1,470
	90.0	21	1,400
	95.0	24	1,310
	100.0	27	1,260
	110.0	30	1,150

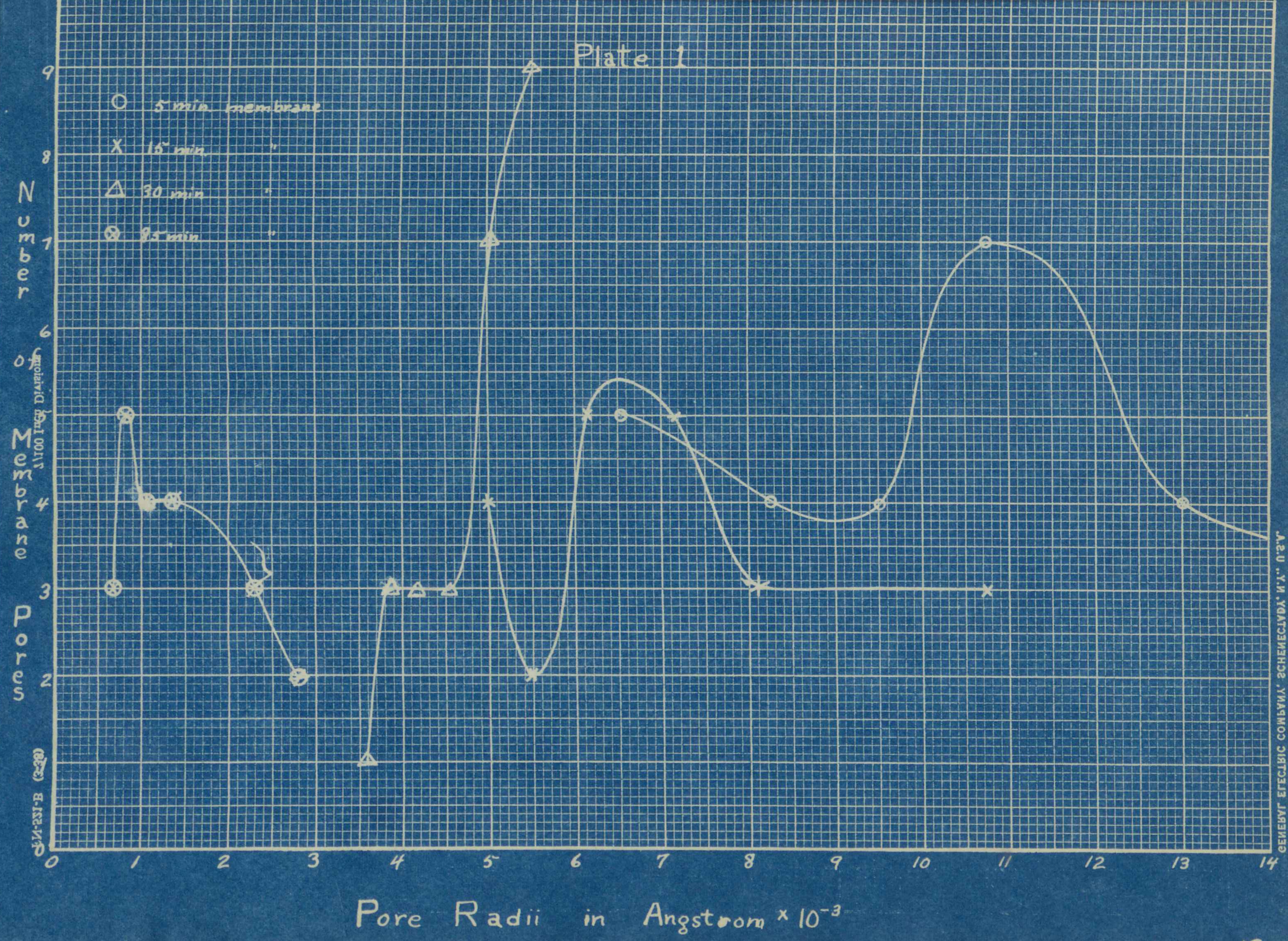
Drying Time of Membrane	Pressure in lbs.per sq.in.	Numder of Bubbles	Pore Size in Angstrom
85 min.	45.0	2	2,800
	55.0	5	2,290
	95.0	9	1,330
	120.0	13	1,050
	140.0	16	900
	150.0	20	840
	155.0	22	815
	180.0	25	700

The pressure indicated could be read from the pressure gauge to the nearest pound.

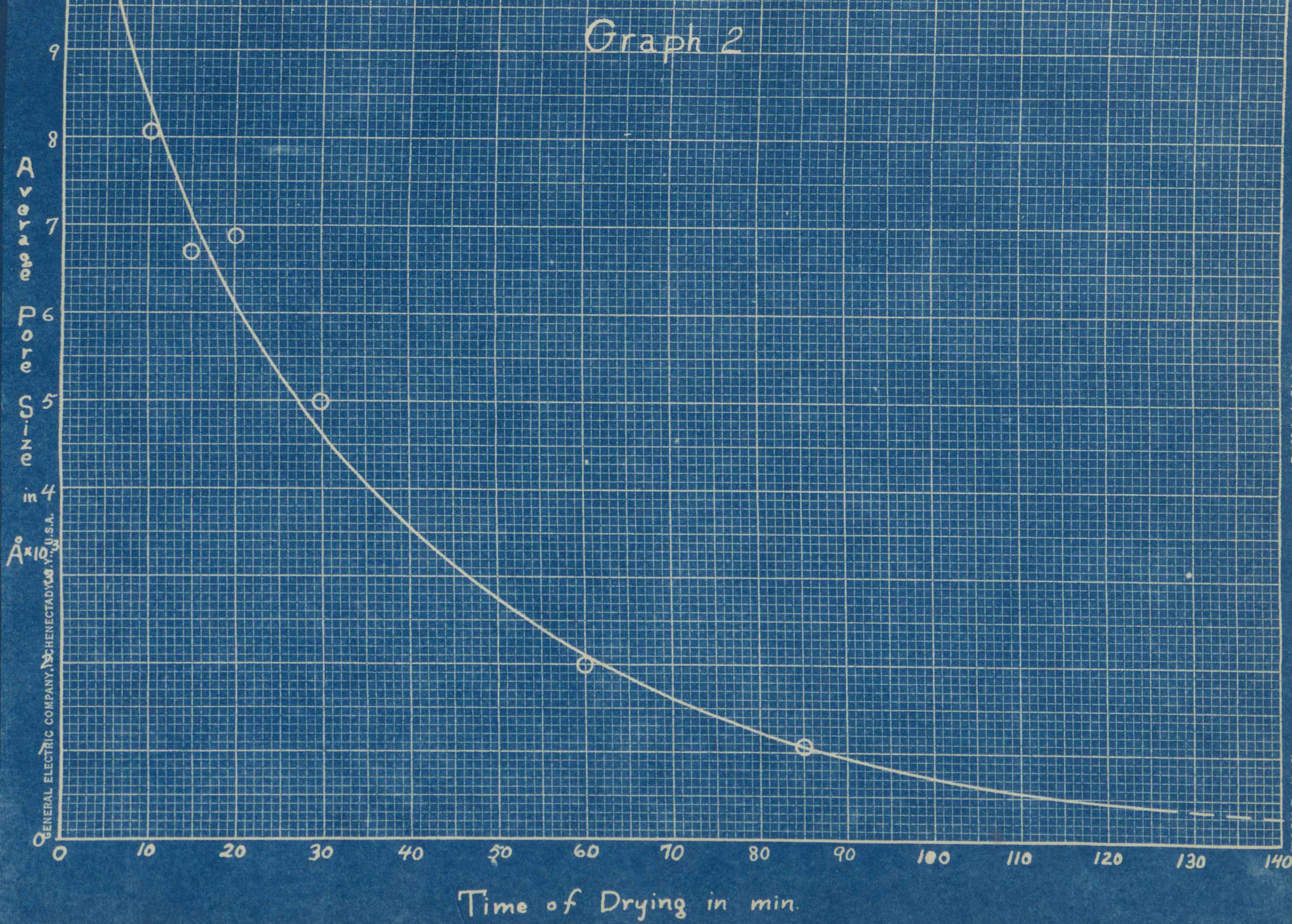
From this table it can be seen that the number of membrane capillaries does not vary with the time of drying and also that the pore size of each of the various membranes are extended over a considerable range or spread, but that the overall size as well as the average pore size between the various membranes is considerable, This is well illustrated in the following curves in plate 1, in which the number of pores are plotted against size of capillaries for the various membranes. If an "average" or "most probable" pore size value for each membrane is taken as the pore size of the 12th capillary, and this "most probable" pore size of each membrane is plotted against the drying time then a smooth curve results, as is shown in Graph 2. This curve can be extrapolated to give values of membranes whose pore size was too small to be determined by the available apparatus.

The problem of the effect of the chemicals used upon collodion membranes was investigated next. The fact that NaOH solutions attack and eventually dissolve collodion membranes automatically limited the experiment to those silicic acid gels formed in acid solution. Although dilute solutions of acetic,

Plate 1


○ 5 min membrane
X 15 min "
△ 30 min "
⊗ 95 min "
Number of Membrane Pores
9
8
7
6
4
3
2
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Pore Radii in Angstrom × 10^{-3}
1/100 Inch Divisions
GN-521-B (3-38)
GENERAL ELECTRIC COMPANY, SCHENECTADY, N.Y., U.S.A.

MP



Graph 2

Average Pore Size in Å×10³
9
8
7
6
5
4
3
0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
Time of Drying in min.

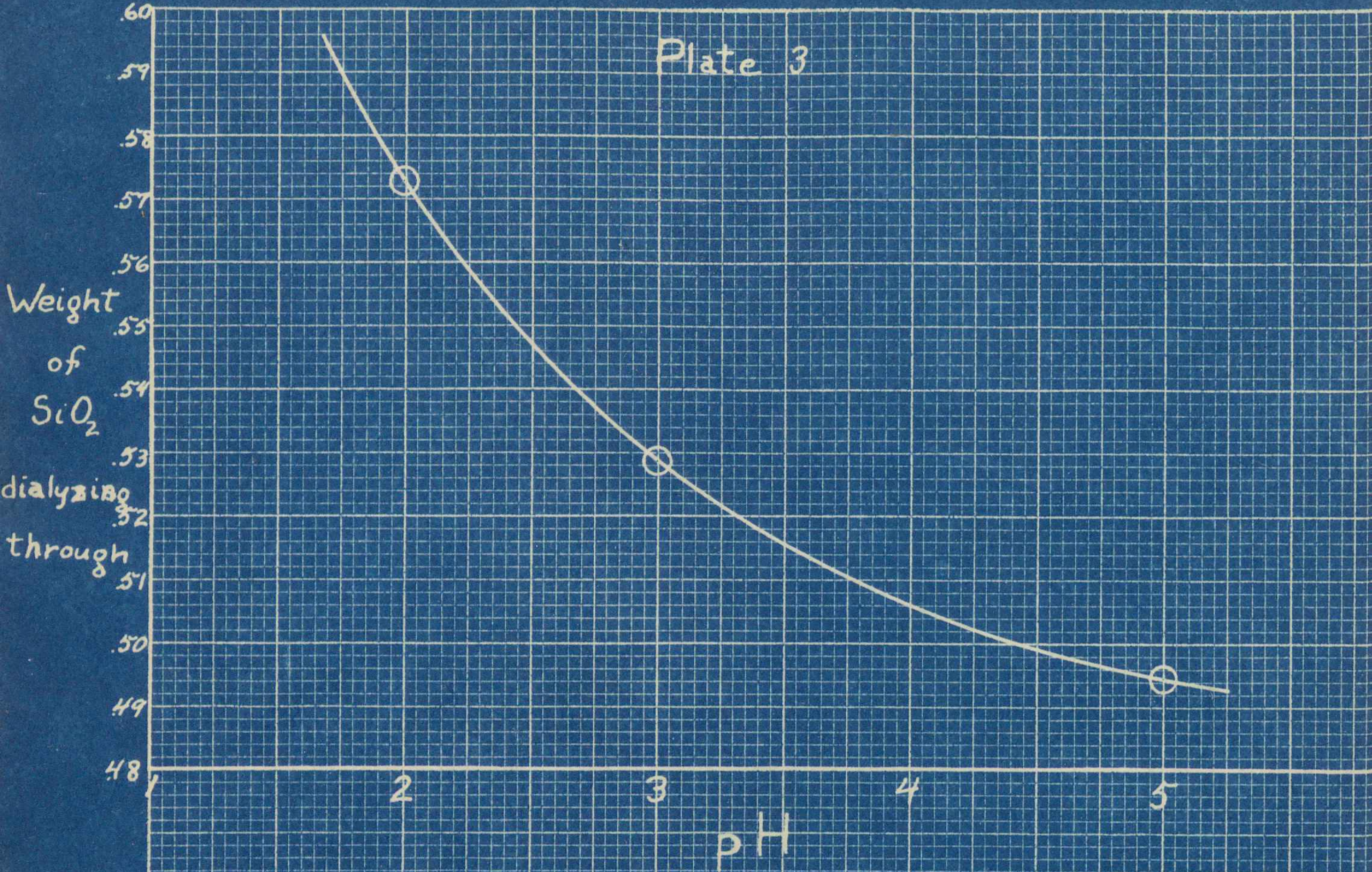


Plate 3

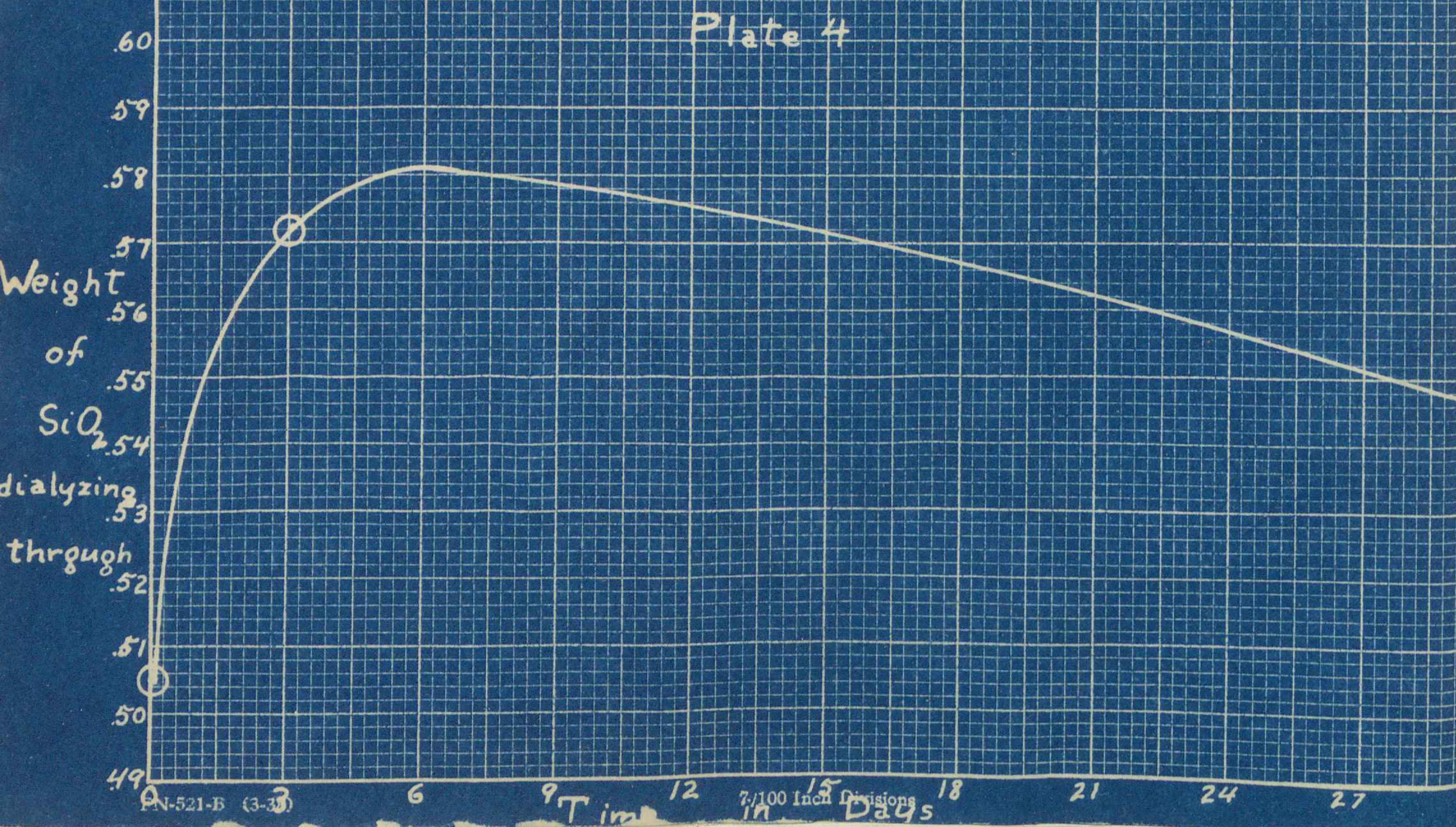


Plate 4

hydrochloric and sulphuric acids did not seem to have any physical effect upon the membranes even after standing several weeks, the effect of PH upon the permeabilities of the membranes was investigated. Several membranes, drying time 15 min., were placed in dilute H_2SO_4 solutions of three different pHs, and after being allowed to stand various lengths of time were taken out and thoroughly washed to remove all traces of acid. Ten cc. of $Na_2 SiO_3$ (1.355 N) was placed in each membrane sack and dialyzed in the usual way with the results shown below:

Number	pH	Time of Acid "Curing"	Time of Dialysis	Results as SiO_2, in g
1	2	72 hrs.	90 min.	0.5726
2	3	72 "	" "	0.5285
3	5	72 "	" "	0.4950
4	2	1 month	" "	0.5480
5	2	1 hour	" "	0.5044

The effect of the acid upon the membrane appears to be that of increased permeability with lower pH, as can be seen in curve III, this change in permeability amounting to about 9% between pH of 2 and pH of 3, and about 7% between pH of 3 and pH of 5. Curve IV showing the change of permeability with time, seems to indicate a chemical effect of the acids upon the membrane as well as an adsorption of the H^+ ions.

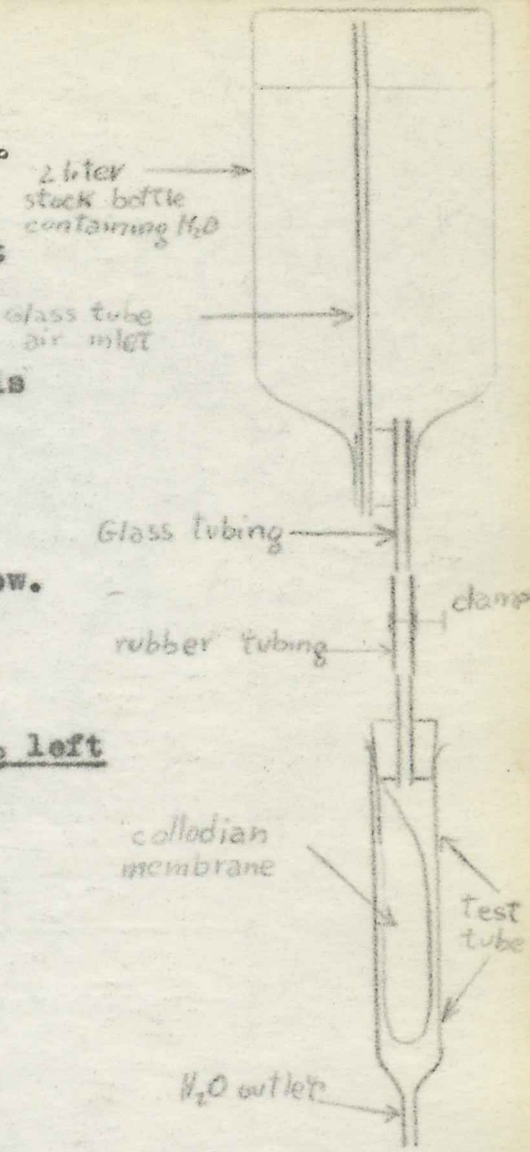
Before starting the actual dialysis of silicic acid it was thought well to investigate the silicate used throughout the experiment. This sodium silicate was commercial waterglass obtained from the Philadelphia Quartz Co., and diluted to 1.355 N with respect to the sodium. Each 10 cc. of solution contained 1.2570 g of SiO_2 when analyzed by the usual acid process.

Two experiments were performed, the first being a complete dialysis of 10 cc. of the waterglass to determine the amount of colloidal SiO_2 present, and the second experiment, the rate of dialysis of waterglass. Membranes air dried for 15 minutes were used in both cases.

In the first case the 10 cc. of waterglass was allowed to dialyze into amounts of 40 cc. of distilled water at 25°C., the time of dialysis in all cases being more than 4 hours. The results are indicated below:

No. of Dialysis	Time of Dialysis	Results in g
1	4.5 hours	.9270
2	16.5 "	.2583
3	48 "	.0450
4	7 "	.0157
5	17 "	.0069
7	17 "	.0020
6	8.5 "	.0022
Silica remaining in sack -		.0034

It can be seen that the amount of silica still contained in the membrane after eight dialyses was less than .3% of the original amount of silica. In order to see whether the waterglass could not be further dialyzed the constant dialyzer shown in the diagram on the next page was used. A controlable flow of distilled water from a 2 liter stock bottle ran in a thin film



outside of the membrane contained in a test tube, whose inside diameter was slightly larger than that of a 6" test tube. By this means the contents of 1 membrane could be conveniently dialyzed as desired. Some results obtained in this way are shown below.

Length of Time Dialyzed	Wt. of SiO_2 Between Membranes	% of SiO_2 left
48 hrs.	.0108 g	0.8%
60 "	.0089	0.6%
36 "	.0121	0.9%
1 week	.0052	0.4%
2 weeks	.0029	0.2%

Thus an almost negligible part, 0.2% of the silica present in the waterglass is present as colloidal particles larger than 10,000 Å.

In the determination of the rate of dialysis of the sodium silicate 10 cc. samples were dialyzed in the usual way for successive periods of time. The results obtained are shown below:

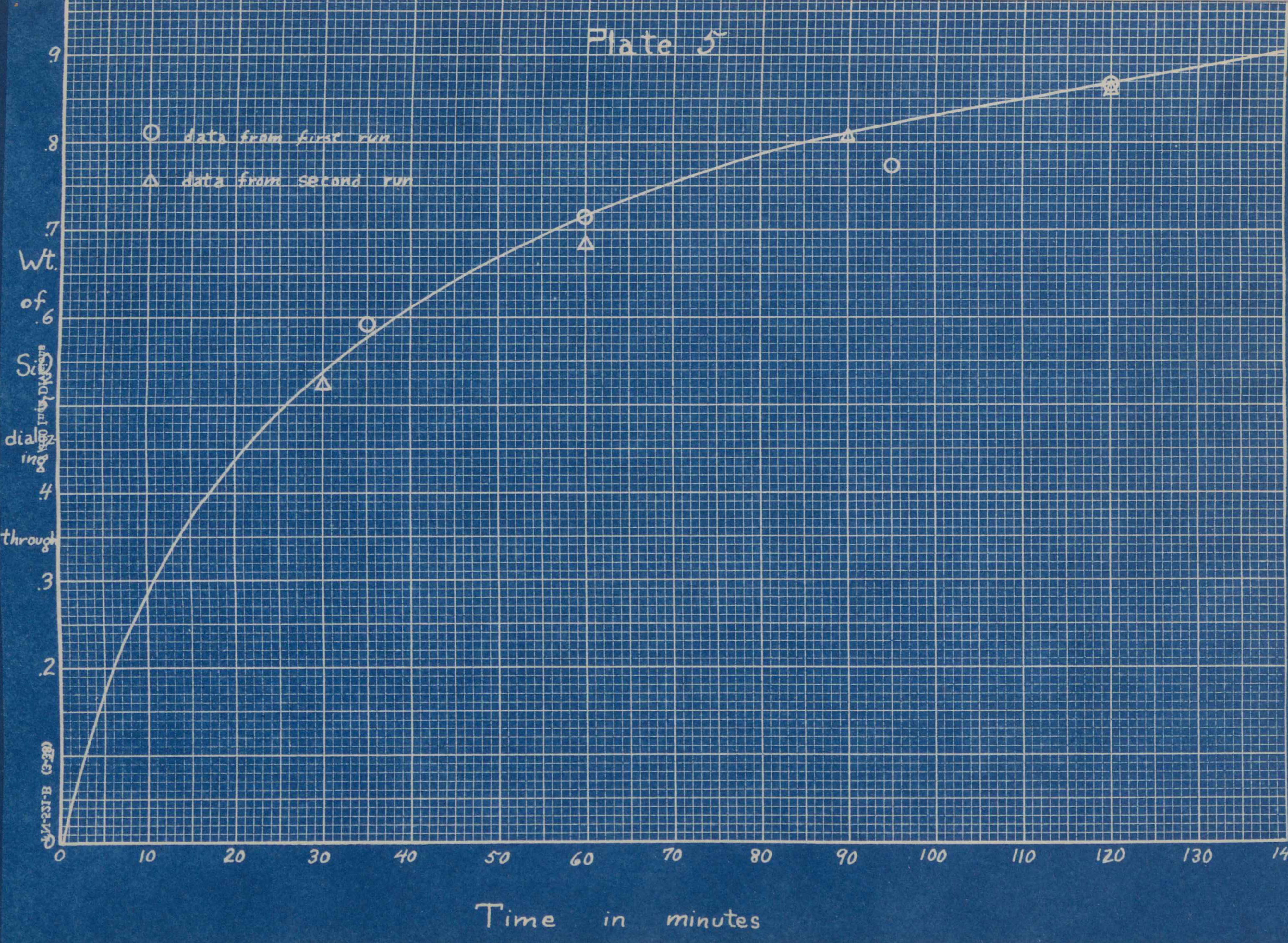
No. of Dialysis	Time of Dialysis	Amount of SiO_2 dialyzing through
1	35 mins.	0.5931 g
2	60 "	0.7147 g
3	95 "	0.7750
4	120 "	0.8667
5	150 "	0.9508

No.of Dialysis	Time of Dialysis	Amount of SiO_2 dialyzing thru
1	30 mins.	0.5210 g
2	60 "	0.6819 g
3	90 "	0.8050 g
4	120 "	0.8688 g

This data is shown in Plate 5 where the amount of SiO_2 dialyzing through the membrane is plotted against the time of the dialysis. This curve resembles that obtained for a first order reaction,but upon analysis does not yield either activity constants which are in agreement,or a straight line when the log of the amount of SiO_2 is plotted against the time. This curve will,however,be used later to determine the amount of SiO_2 dialyzing through any desired time for the gelling reaction at zero time; i.e.,for the SiO_2 dialyzing through the moment before condensation commences.

The actual dialysis of silicic acid was now undertaken. The procedure will be as follows: The reactants sodium silicate and acetic acid,after being brought to constant temperature at 25°C. in separate containers are mixed by pouring the mixture from one beeker to another. After allowing the reaction to proceed for 15 minutes,10 cc. of the mixture was removed,placed in a membrane and allowed to dialyze for 10 minutes into a solution containing the same concentration of sodium acetate,and having the same pH as the gel mixture. Thirty minutes after the time of mixing another 10 cc.of the gel solution was removed, and likewise dialyzed for 10 minutes. This procedure was repeated at successive intervals of 15 minutes. The gel mixture must all

Plate 5


○ data from first run
△ data from second run
Wt. of SiO2 dializing through
.9
.8
.7
.6
.4
.3
.2
0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
Time in minutes

have a time of set greater than one hour. The data of such a dialysis is given below and a graph of the reaction on the following page.

DATA

15 min.membrane used- average pore size = 6,700 Å.

Gel mixture - (25 cc. $Na_2 SiO_3$ sol.
(50 cc. H c_2 H_3O (0.999N)
pH = 5.00 (5 cc. H_2O

Time of set 1 hour 25 minutes.

Dialyzing medium (12.5 cc.NaO4 (1,350N)
(25.0 cc.H c_2 H_3O (0.990N)
pH = 4.85 (2.5 cc. H_2O

Gel mixed 3:36

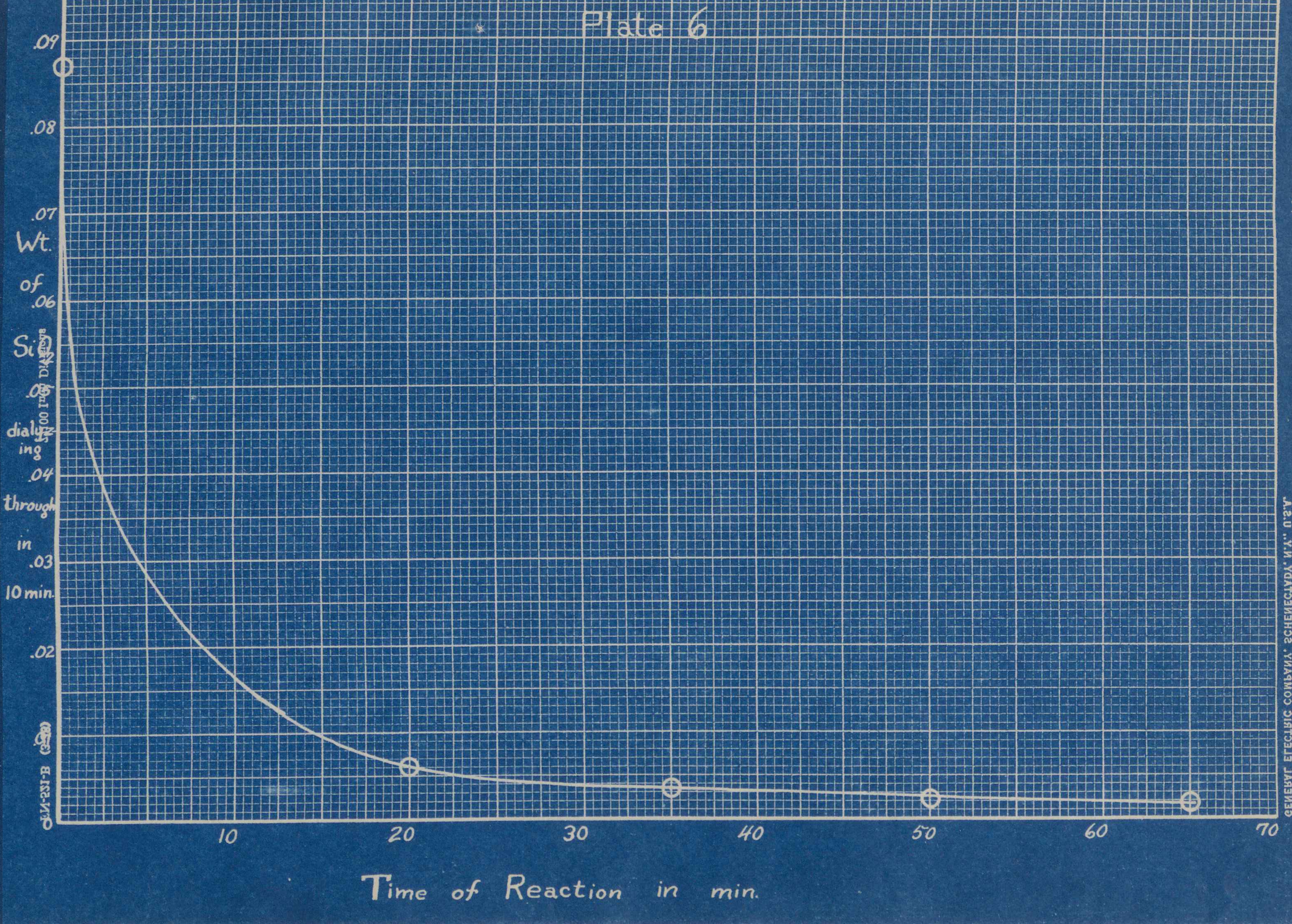
No.of Sample	10 cc Sample Removed at	Dialysis Started	Ended	Amount of SiO Dialyzing Through
1	3:51	3:52	4:02	0.0062 g
2	4:06	4:07	4:17	0.0033 g
3	4:21	4:22	4:32	0.0014 g
4	4:36	4:37	4:47	0.0014 g
5	4:51 gel was partly set and much too hard to be pipetted			

Same gel as above.

Gel mixed 12:00

No. of Sample	10 cc Sample Removed at	Dialysis Started	Ended	Amount of SiO_2 Dialyzing through
1	12:15	12:16	12:26	0.0065 g
2	12:30	12:31	12:41	.0030 g
3	12:45	12:46	12:56	.0024 g

Plate 6


.09
.08
.07
Wt. of SiO2 dialyzing through in 10 min.
.06
.05
.04
.03
.02
.01
0
10
20
30
40
50
60
70
Time of Reaction in min.

The experiment on the previous page (p.9) was obtained with longer setting gels and the use of 2 membranes of different pore size.

DATA

(a) parts - 35 min.membranes,-average pore size 1,050 Å

(b) parts - 5 min,membranes,- " " " 10,250 Å

Gel mixture (25 cc. Na_2SiO_3 (1.355 N)
pH = 4.7 (55 cc. H C_2 H_3O_2 (0.990 N)

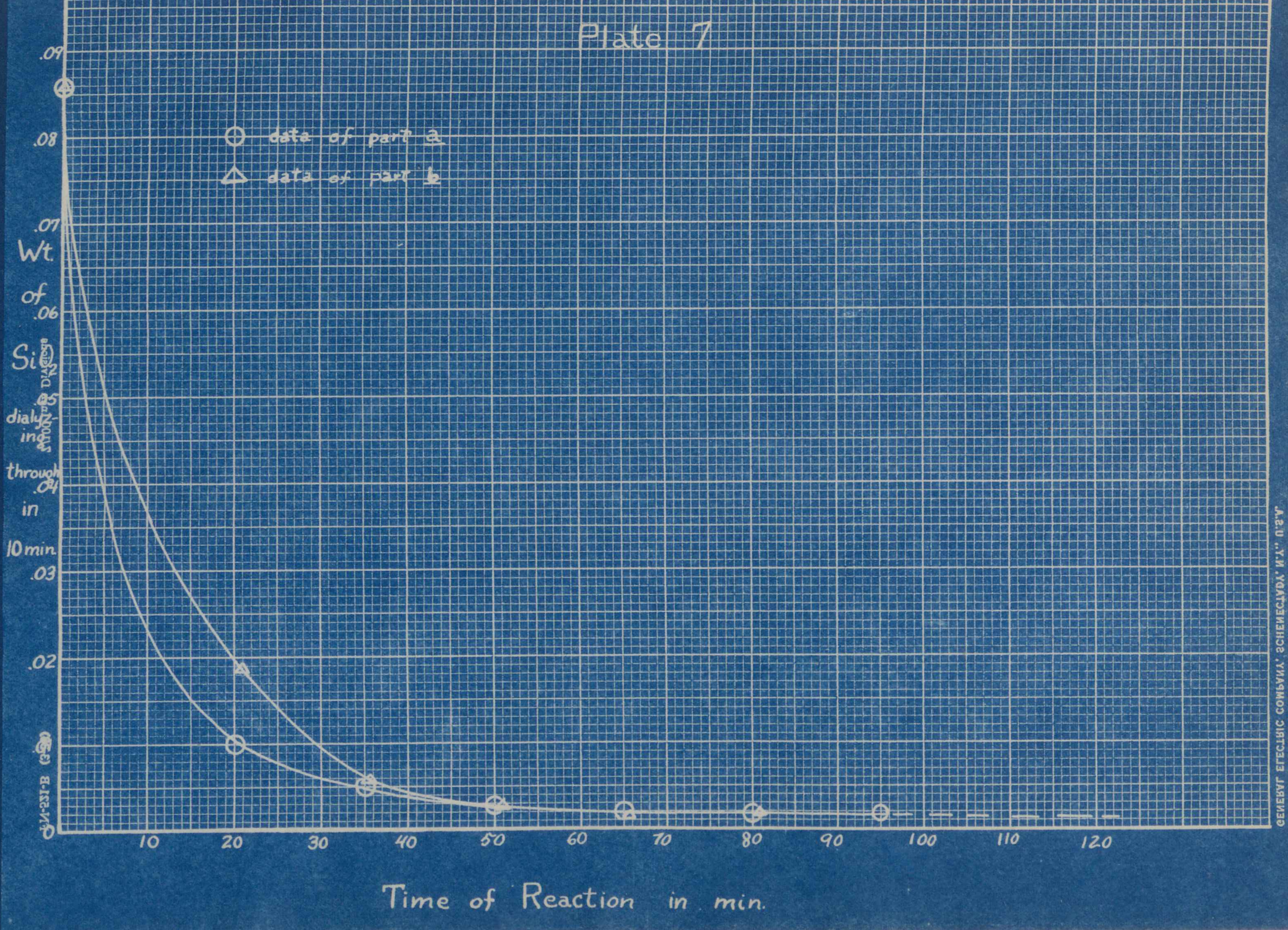
Time of set 1 hour 50 minutes.

Dialyzing mixture (25 cc. Na_2 SiO_3 (1.350 N)
pH = 4.7 (55 cc. H C_2 H_3O_2 (0.990 N)

Gel mixed 2:15

No.of Sample	10 cc.Sample Removed at	Dialysis Started	Dialysis Ended	Amount of SiO_2 Dialyzing Through
1 a	2:30	2:31	2:41	0.0094 g
b	2:31	2:32	2:42	0.0186 g
2 a	2:45	2:46	2:56	0.0048 g
b	2:46	2:47	2:57	0.0053 g
3 a	3:00	3:01	3:11	0.0023 g
b	3:01	3:02	3:12	0.0028 g
4 a	3:15	3:16	3:26	0.0018 g
b	3:16	3:17	3:27	0.0013 g
5 a	3:30	3:31	3:41	0.0016 g
b	3:31	3:32	3:42	0.0017 g
6 a	3:45	3:47	3:57	0.0018 g

Plate 7


○ data of part a
△ data of part b
Wt. of SiO_2 dialyzing through in 10 min.
.09
.08
.07
.06
.05
.04
.03
.02
.01
0
10
20
30
40
50
60
70
80
90
100
110
120
Time of Reaction in min.

(a) Parts - 5 min.membranes,average pore size 10,250 Å
(b) " -135 " " " " " 650 Å

Gel mixture (20 cc.of Na_2SiO_3 (1.355 N)
pH = 4.4 (50 cc.of H $C_2H_3O_2$(0.990 N)

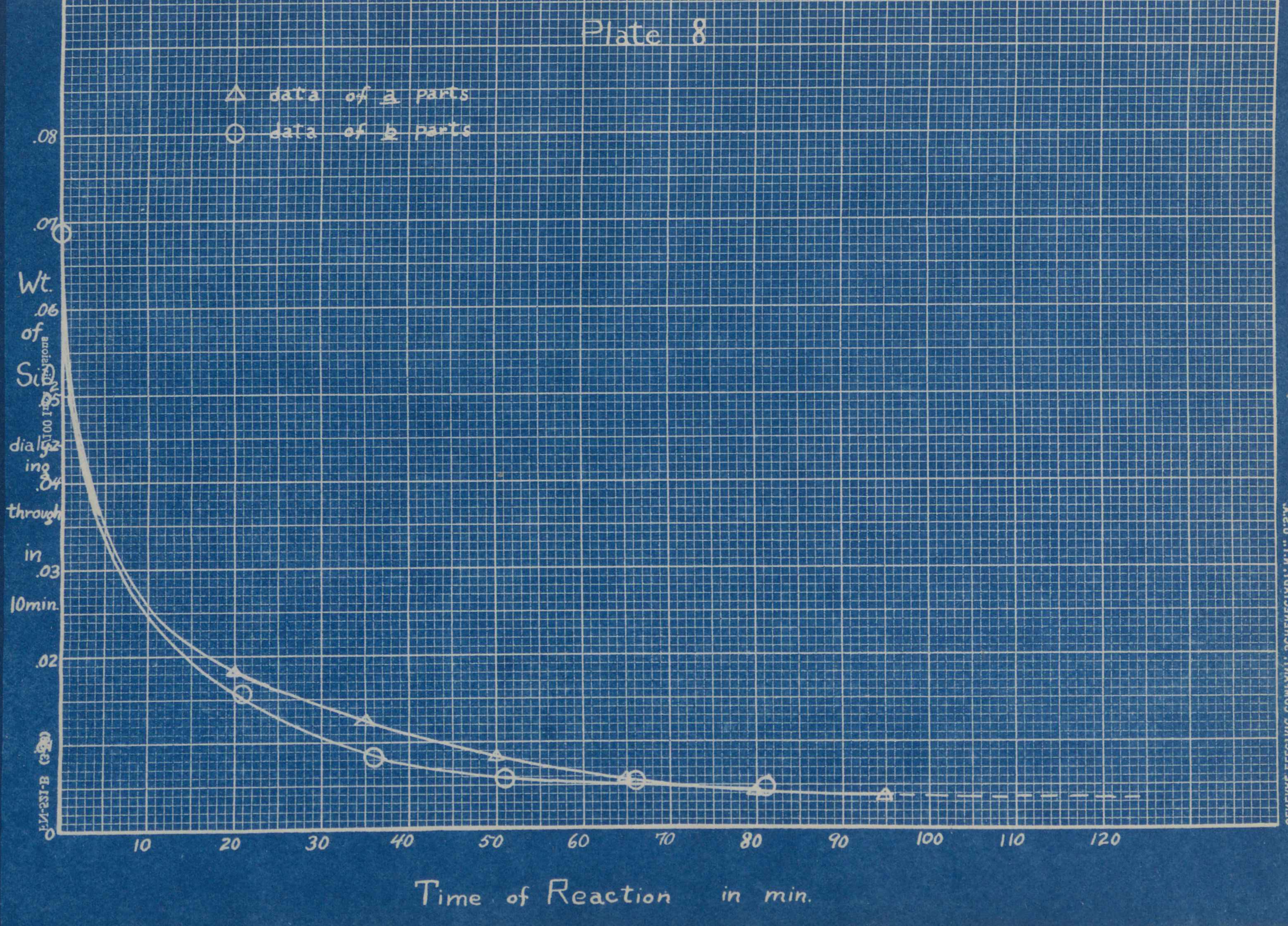
Time of set 4 hours 30 minutes.

Dialyzing mixture (20 cc.of NaOH (1.350 N)
pH = 4.4 (50 cc.of H $c_2H_3O_2$ (1.350 N)

Gel mixed 1:00

No. of Sample	10 cc.Sample Removed at	Dialysis		Amount of SiO_2 Dialyzing Through
		started	ended	
1 a	1:15	1:16	1:26	0.0185 g
b	1:16	1:17	1:27	0.0158 g
2 a	1:30	1:31	1:41	0.0125 g
b	1:31	1:32	1:42	0.0083 g
3 a	1:45	1:46	1:56	0.0082 g
b	1:46	1:47	1:57	0.0058 g
4 a	2:00	2:01	2:11	0.0059 g
b	2:01	2:02	2:12	0.0057 g
5a	2:15	2:16	2:26	0.0045 g
b	2:17	2:18	2:28	0.0049 g
6 a	2:30	2:31	2:41	0.0040 g

Plate 8


△ data of a parts
○ data of b parts
Wt. of SiO_2 dialyzing through in 10 min.
.08
.07
.06
.05
.04
.03
.02
0
10
20
30
40
50
60
70
80
90
100
110
120
Time of Reaction in min.

In all the curves obtained from the data given on the previous pages it appears that the rate of dialysis was approaching constant value as the reactions proceeded, and, moreover, that this small but definite value would extend through and beyond the point of setting of the gel. This fact was investigated in the acid gel which had already set for approximately 24 hours before being dialyzed. The data for this dialysis is given below.

15 min. membrane was used,- average pore size 6,700 Å
(24.32 cc. $NaC_2H_3O_2$ (3.607 N)
(74.5 cc. Na_2 SiO, (1.178 N)
Gel mixture (34.89 cc. H $C_2H_3O_2$ (2.446 N)
pH ≅ 7.00 (91.29 cc. H_2O
(Total volume 225 cc., total wt. 236 g.

Total weight of SiO_2 present in 225 cc. ≅ 8.55 g.

Time of set 14 min. 15 sec.

Dialyzing mixture (40 cc. of $NaC_2H_3O_2$ (0.7 N)
pH ≅ 7.05

Wt. of Gel Sample used	Time of Dialysis	SiO Dialyzing Through
6.533 g	30 min.	.0010 g

0.42% of total SiO_2 capable of being dialyzed.

DISCUSSION OF RESULTS

In the preliminary work the effect of the reactants upon the collodion membranes and the rate of dialysis of the sodium silicate was studied. It was found that for the range used; i.e., between pH = 5 and pH = 4.4, the change in membrane permeability as toward sodium silicate is about 1%. This was within the limits of the experimental error of the gels investigated in the latter sections and thus this correction was not required for the date on pages 9, 10 and 11. It was believed that the rate of dialysis of sodium silicate as given on Plate 5 did not represent a first order reaction as any dialysis phenomena should, because, firstly, the effect of basic solutions upon collodion membranes and, secondly, the gradual shift in pH during the dialysis which results in a change in the molecular weight of the sodium silicate (8). It was believed that this discrepancy was not very large during the first 10 minutes of the dialysis and that the use of this value as the zero time value for Plates 6.7 and 8, did not involve a great deal of error.

In the primary work silicic acids of various pH and with various times of setting were dialyzed at various stages of the reaction. For all gels a characteristic curve was obtained in which the amount of silica dialyzing through the membrane decreased very rapidly during the first few minutes of the reaction, and as the reaction proceeded, approached a constant value which was 7% to 1% of the amount of silica dialyzing through at the start of the reaction. This value remained constant even after the gels had already set for many hours. Although this is a direct contradiction of the result reported by Zigmondy (2) the result appears to be valid, as shown by the consistent results illustrated in all three Plates 6,7 and 8. The possibility that less than 10% of the silicic acid present is in a condition capable of being dialyzed; i.e., apparently of small molecular size, does not contradict the general polysilicic acid fibrillar theory as presented by C.B.Hurd (9).

The interpretation of the results of silicic acid dialysis depends upon the extent to which membrane action is analgeous to that of sieve mechanism. As previously indicated the two actions are comparable to a limited extent only, since the permeability is much more dependent upon adsorbability and electro-adsorbability than mere physical dimensions. Kruyt (10) states that the diffusibility of a substance is governed by physical-chemical properties which run more or less parallel with the size of the molecules but which also depend upon their chemical composition. This view is confirmed by the experiments of Biltz (11). In this experiment on silicic acid gels the mechanism studied does not involve any chemical reaction other than the splitting out of water from between the silicic acid molecules. Thus the variation noticed in the dialysis rate as the reaction proceeded can be considered as the result of the building up of the particle size of silicic acid molecules since the adsorbability probably in this case runs parallel to the particle size. The permeability differences obtained for membranes of different drying time, see Plates 7 and 8, are what might be expected on the basis of either adsorption or sieve phenomena.

CONCLUSION

From the experimental work accomplished on the dialysis of waterglass it can be definitely stated that the silicates contained in commercial waterglass are practically all in solution, and that less then two parts per thousand are present as colloidal silica. The results obtained on the acid-silicate reaction seem to indicate that there is a very rapid condensation of the simple silicic acid molecules in the early stages of the reaction to form larger non-dialyzing colloidal particles, but that this polymerization of simple silicic acid molecules is incomplete. In every gel examined regardless of its age there is some silica capable of diffusing through collodion membranes.

Further experiments of this type should be carried out particularly with more than one membrane having permeability differences which are greater than those used in the last two experiments. Gels with a longer time of setting may also be utilized to study the condensation occurring during the early stages of the reaction.

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