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# Studies on Silicic Acid Gels: Measurements on Surface Tension During Setting

Louis Werthman

*Union College - Schenectady, NY*

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STUDIES ON SILICIC ACID GELS

Measurements on Surface Tension During Setting

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STUDIES ON SILICIC ACID GELS

Measurements on Surface Tension During Setting

A thesis presented to the Department of Chemistry  
of Union College in partial fulfillment of the require-  
ments for the degree of Bachelor of Science in Chemistry.

by Louis Westman

Approved by Charles B. Hurd

June 1939

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## Introduction

Several theories have been advanced for the mechanism of formation of gels of hydrated silica or silicic acid gels, as they are commonly called. These theories have in common the idea of a thickening of the structure by an intermeshing of particles in the solution. No one theory has been universally accepted by the workers in this field. There is a need of more sufficiently complete data before any one theory can be selected above the rest.

In this paper, results will be presented to show the change in surface tension during gelation of silicic acid solution. This research was undertaken with the belief that the change in surface tension during gelation might give further insight into the process of gel formation.

## Historical

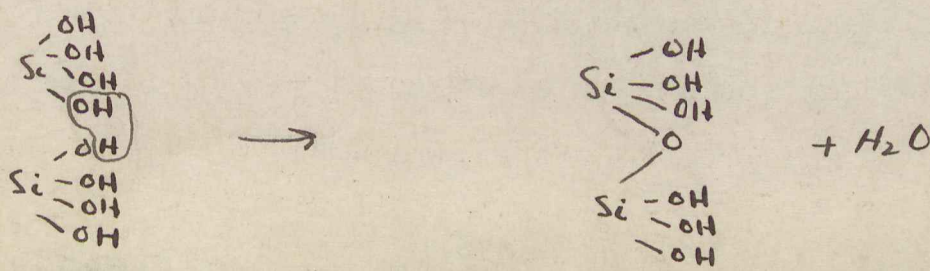
The gel mixtures were prepared by mixing solutions of sodium silicate and acetic acid. Many investigators have prepared silicic acid gel from a solution of a soluble silicate, usually water glass, and an acid. Walden (1) indicates that Pott had prepared colloidal silicic acid in this way before 1800.

Graham (2), a worker in this field, obtained the hydrogel of silicic acid by pouring concentrated hydrochloric acid on sodium silicate. Holmes (3) has described the results obtained

by mixing a solution of water glass with an acid.

The gel mixture prepared from solutions of sodium silicate and dilute acetic acid produces in the mixture sodium acetate together with excess acetic acid or silicate. Hurd and Letteron (4) pointed out a possible way of avoiding the presence of these soluble materials by starting with a pure suspension of colloidal silicic acid. Treadwell and Wieland (5) prepared pure silicic acid gels by electrolysis of sodium silicate. However, for the work carried out in this research, it was not absolutely necessary to deal with silicic acid free from the presence of these soluble materials. It undoubtedly does not make very much difference in studying the surface tension during gelation, when the interest is in the gelation process, whether the actual surface tension of silicic acid is being measured or whether it is a relative tension. Therefore, as a matter of convenience, the simpler method of gel preparation was used.

At the time of this writing, the theory of gelation most popular with the investigators in this field is the Fibrillar Theory. It is assumed that the fibrillar structure consists of condensed silicic acid, the molecules having formed chains and interconnected. The condensation takes place by water splitting off from two molecules of simple silicic acid. As this condensation continues, the chains grow larger. One of the condensations is shown in the following.



A number of the physical properties of silicic acid gel in relation to gelation have been studied. Prasad, Mehta, and Desai, (6) studied the scattering of light by the silicic acid solution during gelation. They plotted curves, extinction coefficient, which is a measure of the light scattering by the colloidal particles in the solution, against time. Their curves are similar to the ones obtained by the writer who plotted surface tension during gelation against time. Prasad, Mehta, and Desai concluded that the formation and enlarging of the particles in the solution was continuous, and showed the formation of definite structures.

The viscosity change during setting has been determined, showing a slow increase in viscosity followed by a very rapid increase as the gel sets. It has also been observed that the electrical conductivity does not change markedly as the gel sets. There is actually only about a two percent decrease in conductivity. (7)

Not very much has been done in the past with the determination of change in surface tension during gelation. Hurd and Letteron (8) measured the surface tension during setting, but they worked without accurate temperature control, and over a narrow range of solution concentrations. Fraser (8) also determined the surface tension, attempting to tie this up with results obtained from viscosity measurements. The curves presented by Fraser were unlike those obtained by Hurd and Letteron, and also unlike those obtained by the writer. Although Fraser did not note in his thesis what concentration silicic acid solutions he used; the results to be cited in this article, taken over a large range of concentrations,

and with use of good temperature control, seem to indicate that his curves are not accurate.

The previous work on the measurement of surface tension during gelation of silicic acid solution therefore indicated that more complete data might prove interesting.

#### Experimental

Measurements were made by means of a Du Nooy tensimeter.

This instrument measures the force necessary to tear a platinum ring from the surface of a liquid. The force is determined in terms of the torsion of a wire, and is read from a calibrated scale. This method of surface tension determination was used because of the rapidity in which readings can be taken. A container six inches in diameter, wall height about one centimeter was substituted for the regular watch glass in order to insure plenty of fresh surface, and to nullify as much as possible any side effects. It should be noted here that precautions must be taken against contamination. The surface tension is noticeably lowered by the presence of grease, soap, or impurities. This presents a problem in obtaining corresponding results. The ring must be carefully handled <sup>to</sup> insure a perfect, level circle. It is also necessary that the platinum ring be cleaned and fire flashed after every reading if surface tension and not adhesion tension is to be measured. If the ring is not cleaned, the readings will rise rapidly, and will not be coherent. Although the Du Nooy tensimeter is not the most accurate surface tension measuring instrument, it is the most practical for this kind of work, where not the actual surface tension but the change in surface tension is desired.

Accurate temperature <sup>control</sup> was obtained by use of an air thermostat. The surface tension apparatus was placed in the insulated chamber of the thermostat, and all work was performed there. The thermostat was so constructed that the instrument could be operated through a small door in the side of the chamber. A glass window allowed adequate observation. The small door did not cause appreciable discrepancies in temperature control since it was open only during actual operation of the apparatus, and this was never more than 30 seconds at a time. The heating elements were operated by an adjustable thermo regulator, and circulation <sup>1</sup> was maintained by a fan driven from outside the chamber. It was necessary to stop the fan while taking readings, for the vibrations set up interfered with the surface of the solution. This again did not cause any serious trouble. By means of the thermostat, the temperature did not vary more than 0.5 degrees.

The pH measurements were made, in the case of the acid gel mixtures, using the quinhydrone method. Hurd and Carver (9) found this method the most satisfactory. For the alkaline gel mixtures, the pH determinations were made by means of a colorimetric method using buffer solutions.

The gel mixtures were prepared from sodium silicate, 1.26 N with respect to sodium hydroxide, and from C.P. glacial acetic acid diluted to 1.03 N. The amounts of sodium silicate and acetic acid were varied, although the total volume was fixed in all cases at 80 cc. The solutions of silicate and acid were thermostated in separate beakers at the desired temperature for at least five hours before mixing. Adjustment was made for the 1.5 degrees rise on mixing due to the neutralization of sodium hydroxide



by acetic acid. The silicate was poured into the acetic acid, and after thorough mixing, about 15cc of the solution was placed in the special container and the first surface tension reading was taken as quickly as possible. Readings were taken at frequent intervals until the gel had set. The gel was considered set when the platinum ring of the Du Nuoy tensimeter would no longer enter the mixture.

It must be noted at this point that the time of set obtained from the surface tension readings does not exactly correspond to the time of set obtained by test with the tilted rod method in a separate container. This may be explained by the fact that the gel tested with the glass rod resulted from about 75cc of mixture contained in a regular 100cc beaker. It would seem that amount of solution makes an appreciable difference in time of set. More accurately, from observations made, it seemed that height of solution caused a good part of the difference in time of set. However, this discrepancy does not affect the actual gelation process.

The following data contains the results of the series of tests. A number of surface tension determinations were made at different temperatures for each gel mixture. The figures are tabulated for scale readings on the Du Nuoy tensimeter. These may be converted to dynes per cm.

Curves were plotted showing Du Nuoy scale readings as ordinates against time after mixing in minutes as abscissae.

## Variation of surface tension during the process of Gelation

Table 1

sodium silicate 25cc.

pH - 4.65

acetic acid 55cc.

<u>Time</u>	<u>Reading</u>	<u>Temp.</u>	<u>Time</u>	<u>Reading</u>	<u>Temp.</u>
0'	-	25.2° C	0'	-	34.5° C
3	94.5	"	3	81.5	"
6	94.8	"	9	82.0	"
8	94.5	"	11	82.8	34.7
10	"	"	17	85.0	"
21	94.8	25	20	83.0	"
23	94.7	"	22	83.3	35
44	94.5	"	26	83.0	"
46	95.0	"	28	84.0	35.1
49	94.0	"	32	82.9	35
68	95.0	"	35	83.0	35.2
70	94.0	"	39	"	"
99	"	"	41	"	"
101	94.5	"	46	83.1	"
104	94.2	"	50	83.2	"
107	94.0	"	52	83.5	35.1
125	95.5	"	53	83.7	"
128	94.0	"	56	85.0	35.2
130	95.0	"	62	85.0	35.1
145	96.0	"	66	85.7	35.0
147	96.5	"	68	86.0	35.1
153	96.1	"	71	87.0	"
160	99.0	"	73	88.0	35.2
162	97.5	"	75	89.0	"

<u>Time</u>	<u>Reading</u>	<u>Temp/</u>	<u>Time</u>	<u>Reading</u>	<u>Temp.</u>
164'	97.9	25 C	77'	91.5	35.2 °C
165	98.5	"	81	115	35.1
168	101.5	"	83	120	35.2
169	100.5	"	<u>87</u>	<u>130</u>	<u>35.1</u>
170	101.5	"			
172	103	"	0'	-	45 C
176	115	"	4	68.0	"
178	116	"	7	"	44.8
180	119	"	10	"	44.9
183	130	"	13	"	44.9
184	134	"	16	"	45.
<u>187</u>	<u>141</u>	<u>"</u>	20	67.5	"
			23	68.0	"
			26	68.4	"
			28	69.5	44.9
			30	70/5	"
			31	70.0	"
			33	72.0	45
			35	72.5	"
			37	74.0	"
			39	75.0	"
			<u>42</u>	<u>120</u>	<u>"</u>

Plate I

pH = 4.65



Table 2

sodium silicate 20cc.

acetic acid 60cc.

pH - 4.502

<u>Time</u>	<u>Reading</u>	<u>Temp.</u>	<u>Time</u>	<u>Reading</u>	<u>Temp.</u>
0'	-	29° 0	0'	-	35° 0
4	87.0	"	4	84.0	35.5
6	86.5	"	10	83.0	"
10	86.0	"	15	82.0	"
15	85.5	29.2	22	81.0	"
20	85.0	28.8	28	80.0	35.3
35	84.0	29.0	33	"	35.4
45	"	29.1	43	80.5	35.9
54	"	28.5	50	80.0	36.0
62	"	29.3	62	"	"
124	"	29.0	79	"	"
132	"	"	84	"	"
158	"	29.5	93	"	"
167	"	29.0	105	"	"
180	"	"	115	"	"
195	"	"	128	"	"
213	85.0	"	142	80.2	"
217	85.5	29.3	150	80.0	"
225	86.0	29.2	157	81.5	"
233	"	29.0	161	84.0	"
235	87.0	"	164	86.0	"
242	87.3	29.3	165	87.0	36.1
253	87.0	29.5	168	88.0	36.0
261	88.0	29.3	175	96.0	"

<u>Time</u>	<u>Reading</u>	<u>Temp.</u>	<u>Time</u>	<u>Reading</u>	<u>Temp.</u>
270'	87.5	29.0 °C	175'	96.0	36.0 °C
279	89.0	29.1	178	101.0	"
287	90.0	29.0	183	118.0	"
298	91.5	"	186	131.0	"
306	95.5	"			
310	101.0	"	0'	-	45.0 °C
314	109.0	29.1	4	78.0	"
317	115.0	29.0	10	77.0	45.2
322	118.0	"	15	76.5	45.3
326	129.0	"	20	76.0	45.0
330	136.0	"	25	"	"
334	140.0	"	30	"	45.1
340	145.0	"	37	"	45.0
			40	76.1	45.2
0'	-	56 °C	46	76.0	45.0
2	71.5	"	50	"	45.1
4	"	55.8	55	77.0	45.3
6	"	55.5	59	78.3	45.2
10	71.8	55.3	62	79.5	"
15	72.5	55.2	65	80.5	"
17	73.5	55.5	72	81.5	45.0
20	"	55.0	75	83.0	"
24	73.0	55.5	77	84.0	45.1
29	74.0	55.4	80.0	85.0	45.0
34	76.0	55.2	85	87.0	"
38	81.5	"	90	90.1	45.2
			94	102.0	45.3
			96	114	45.2
			100	135	45.0
44	127.0	"			

Du N v̄y

Scale

Readings

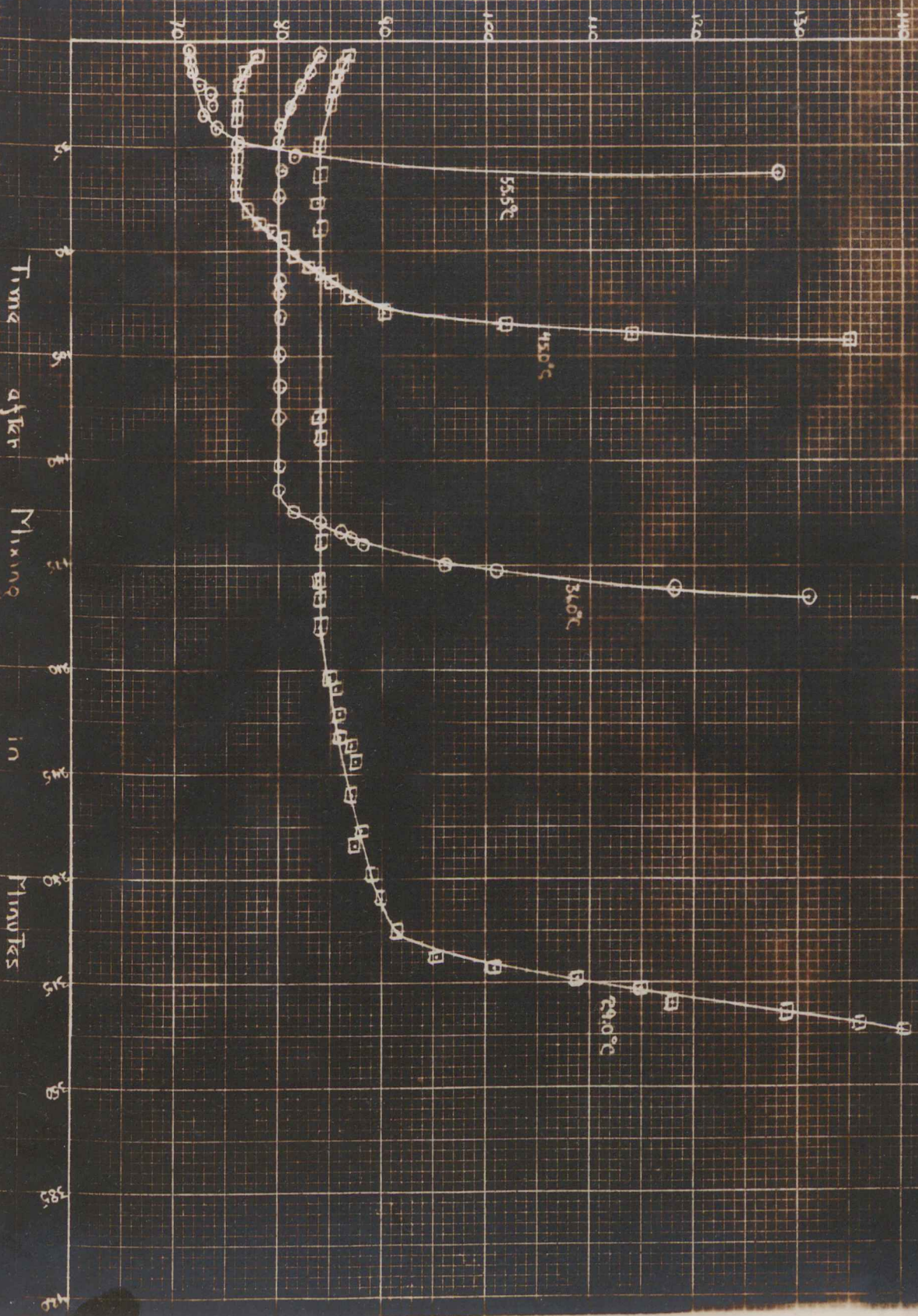


PLATE II  
PH = 4.502

Table 3

sodium silicate 15cc.

acetic acid 65cc.

pH - 4.23

<u>Time</u>	<u>Reading</u>	<u>Temp.</u>	<u>Time</u>	<u>Reading</u>	<u>Temp.</u>
0 min.	-	28°C	0 min.	-	40.5°C
3	91.5	28.5	3	86.0	40.0
5	90.0	"	6	84.5	40.3
10	87.5	"	12	85.0	40.1
15	86.5	28.0	21	83.0	40.5
23	85.0	"	27	"	"
31	"	"	35	"	"
43	"	"	110	82.9	"
64	84.5	"	117	"	40.3
77	84.8	"	133	83.0	40.5
173	84.5	"	140	85.0	"
192	85.0	28.3	151	85.8	"
206	84.5	28.3	162	86.0	"
300	"	28.0	174	"	"
327	"	"	183	"	"
346	"	"	190	"	"
367	85.0	"	197	86.2	40.7
370	84.7	"	204	86.8	40.5
393	84.5	"	212	87.5	"
415	85.0	"	221	88.0	"
430	"	"	229	89.0	"
443	"	28.5	239	89.5	41
450	"	28.0	245	90.0	"
463	85.5	28.2	251	91.0	40.5
491	86.0	28.5	258	99.0	"



Table 3 (cont'd)

Time	Reading	Temp.	Time	Reading	Temp.
525 min.	86.0	28.0	264 min.	107.0	40.5 °C
535	"	"	267	111.0	"
550	"	"	271	117.0	"
580	"	"	276	125.0	"
587	87.0	28.3	<u>285</u>	<u>140.0</u>	"
592	88.0	"			
600	"	"			
603	89.0	"			
<u>610</u>	"	"			

<u>Time</u>	<u>Reading</u>	<u>Temp.</u>	<u>Time</u>	<u>Reading</u>	<u>Temp.</u>
0 min.	-	51.0	75 min.	83.5	51.5 °C
2	81.5	"	83	84.0	51.0
7	79.0	50.5	92	"	"
11	"	51.0	100	85.0	"
15	"	"	110	87.0	"
26	80.0	51.4	115	87.5	"
30	81.0	51.0	121	89.0	"
35	80.5	"	126	91.0	"
44	81.2	51.5	133	98.0	"
50	81.5	"	140	113	"
56	82.0	"	147	142	"
65	83.5	"	155	155	"

DuNoüy Scale Readings



Plate III  
pH = 4.23

28.0°C

Table 4

sodium silicate 15cc.  
acetic acid 60cc.  
water 5cc.

pH - 4.16

<u>Time</u>	<u>Reading</u>	<u>Temp.</u>	<u>Time</u>	<u>Reading</u>	<u>Temp.</u>
0 min.	-	36.5 °C	0 min.	-	45.0 °C
2	85.5	"	2	86.0	"
6	86.0	36.8	5	84.0	"
10	87.5	36.5	10	83.0	"
13	86.8	"	12	82.5	"
18	85.8	36.8	16	82.5	45.2
23	85.4	36.5	30	82.0	45
28	85.2	36.2	38	83.0	"
34	85.0	36.5	42	82.5	45.3
40	"	"	50	83.5	45.2
85	85.5	"	57	84.0	"
92	85.2	36.3	61	83.0	"
101	85.5	"	67	"	45.0
115	"	"	77	84.0	"
125	87.0	36.5	82	83.5	"
140	"	"	88	83.0	"
150	"	"	95	83.5	45.1
158	"	36.3	104	83.5	45.0
165	"	"	108	"	"
183	87.5	36.5	121	"	"
188	"	"	126	"	"
194	88.5	36.3	138	85.0	"
196	"	36.5	146	85.5	"
201	88.5	"	154	"	"
213	89.0	"	161	86.0	45.2

Table 4 (cont'd)

<u>Time</u>	<u>Reading</u>	<u>Temp.</u>	<u>Time</u>	<u>Reading</u>	<u>Temp.</u>
228 min.	89.4	36.5 C.	173 min.	90.0 C	45.0 C.
235	89.0	"	178	90.0	"
242	89.5	36.0	183	105.0	"
251	89.8	36.5	186	120.0	"
258	89.5	"	188	130.0	"
266	89.8	"			
277	90.5	"	0 min.	-	55.5 C.
292	"	36.3	2	85.0	55.4
302	91.0	36.5	5	83.5	55.5
308	91.5	"	8	83.0	"
315	92.0	"	13	82.0	"
322	92.5	36.6	20	81.2	55.4
331	93.2	36.7	25	81.0	56.0
339	97.0	36.5	30	"	"
342	111	"	45	81.2	"
345	116	"	53	82.0	55.8
348	120	"	60	82.5	"
353	135	"	65	82.0	56.0
			70	"	"
			76	83.0	"
			82	84.0	55.9
			87	85.5	"
			91	86.5	56.0
			95	98.5	"
			100	130	"
			105	140	"

Du Noüy Scale Readings



PLATE IV  
PH = 4.16

Table 5

sodium silicate 25cc  
acetic acid 15cc  
water 40cc

pH - 9.6

<u>Time</u>	<u>Reading</u>	<u>Temp.</u>	<u>Time</u>	<u>Reading</u>	<u>Temp.</u>
0 min.	-	36.8 C	0 min.	-	55.0 C
4	96.0	38.5	2	89.5	"
7	"	"	5	91.5	"
11	95.0	"	9	91.0	55.1
15	95.5	"	12	"	55.3
22	96.0	38.3	17	"	55.2
25	95.5	"	19.5	"	55.1
29	95.0	"	24	97.0	"
32	"	"	31	98.0	"
39	94.9	38.5	35	95.0	55.2
43	95.0	"	38	"	55.0
48	95.2	"	44	104.0	55.3
55	95.0	38.7	50	115.0	"
66	"	38.5	55	115.0	"
75	95.2	"	64	125.0	55.6
80	95.8	38.8	<u>70</u>	<u>136.0</u>	<u>55.4</u>
82	95.5	"			
88	96.0	38.5			
90	"	"			
97	96.5	"			
105	97.0	38.8			
108	"	"			
115	98.0	38.5			
121	99.3	"			
123	100.2	38.3			

Table 5 (cont'd)

<u>Time</u>	<u>Reading</u>	<u>Temp.</u>	<u>Time</u>	<u>Reading</u>	<u>Temp.</u>
128min.	101.5	38.3 C			
133	102.0	38.5			
145	102.0	"			
150	103.0	"			
160	105.0	38.3			
170	118.0	38.5			
<u>175</u>	<u>135.0</u>	<u>"</u>			

Plate X  
pH = 9.6

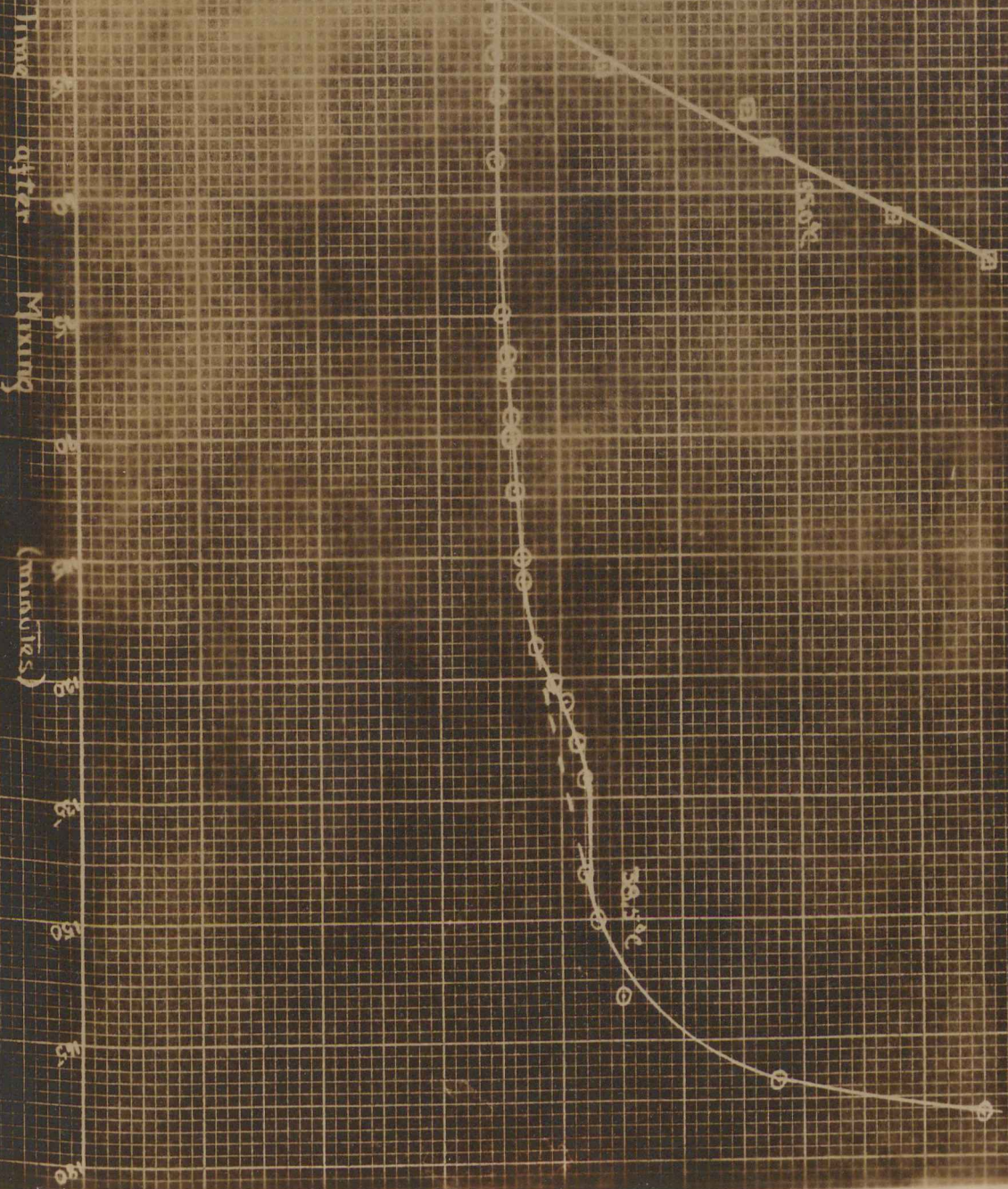




Table 6

sodium silicate 60cc.  
acetic acid 20cc.

pH - 10.8

<u>Time</u>	<u>Reading</u>	<u>Temp.</u>
0 min.	-	25.0 C
2	90.0	"
7	"	"
12	89.8	25.5
17	90.0	25.0
23	"	"
27	91.0	25.2
30	94.0	25.1
<u>34</u>	<u>132.0</u>	<u>25.1</u>

0 min.	-	43.5 C
3	75.0	"
8	"	43.0
12	"	"
20	"	"
25	77.0	43.1
29	78.0	43.0
33	80.0	"
<u>36</u>	<u>135.0</u>	<u>"</u>

<u>Time</u>	<u>Reading</u>	<u>Temp.</u>
0 min.	-	32.0 C
2	85.0	"
6	87.0	"
11	85.0	"
15	"	"
20	"	"
25	85.3	"
29	85.9	"
34	90.0	"
<u>37</u>	<u>132.0</u>	<u>"</u>

0 min	-	56.0 C
2	70.0	"
12	"	"
20	"	"
27	71.5	55.8
32	74.0	56.0
<u>36</u>	<u>130.0</u>	<u>"</u>

PLo-Ta VI  
pH = 10.8

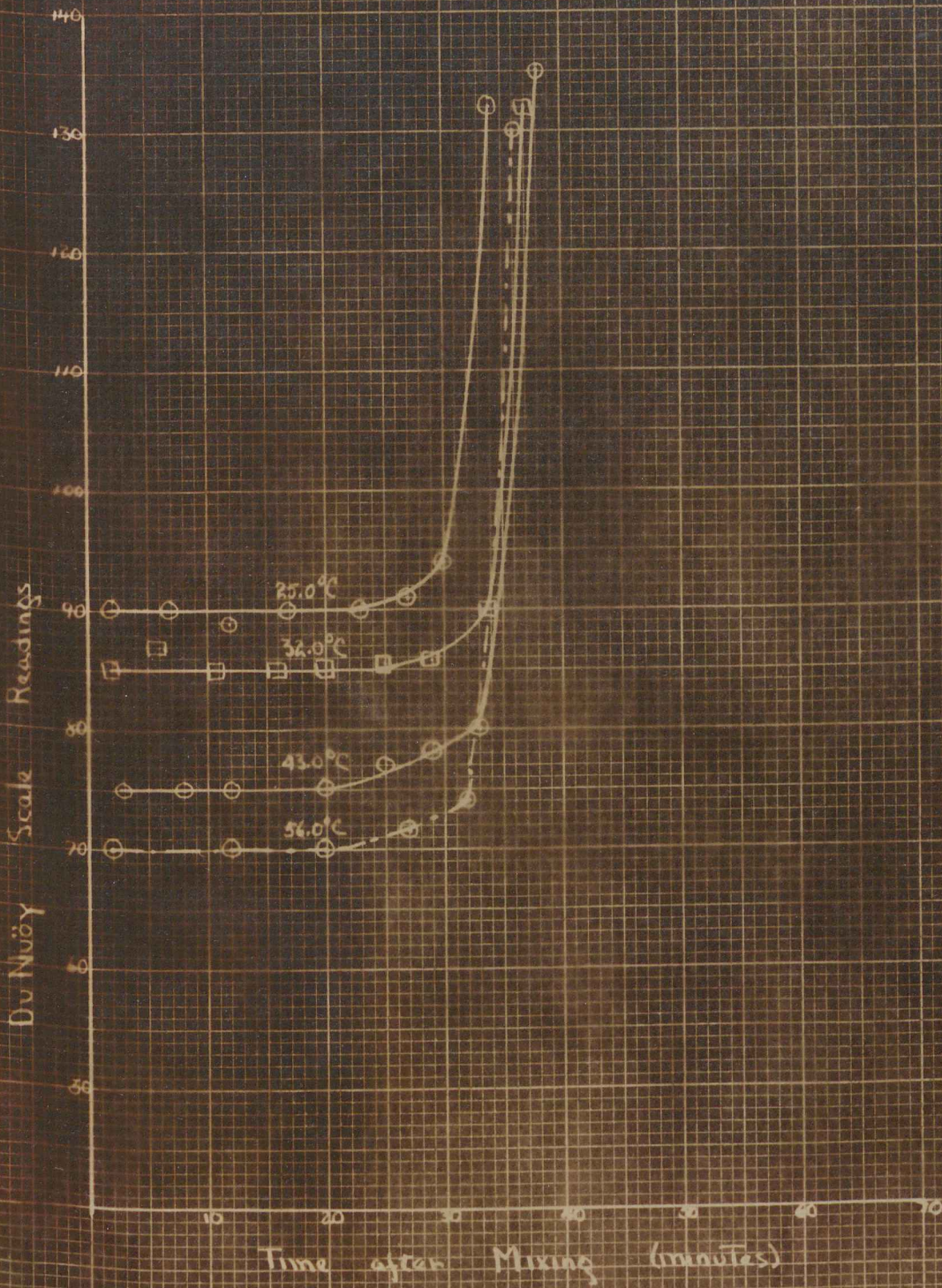


Table 7

sodium silicate 65cc.  
acetic acid 15cc.

pH -11.3

<u>Time</u>	<u>Reading</u>	<u>Temp.</u>	<u>Time</u>	<u>Reading</u>	<u>Temp.</u>
0 min.	-	32.0 C	0 min.	-	46.0 C
2	68.0	"	3	92.0	"
5	64.0	"	6	88.5	"
10	62.0	31.9	10	86.0	"
14	61.5	"	19	85.0	45.8
18	60.5	31.7	34	84.0	"
31	60.0	32.0	50	83.0	46.0
40	"	"	70	82.0	"
52	59.8	"	88	"	45.8
76	60.0	"	106	"	"
84	"	31.8	135	81.8	46.0
100	59.9	32.0	162	81.5	46.0
120	60.0	"	180	81.6	"
153	"	"	194	82.0	"
178	59.0	"	204	81.5	45.8
205	59.5	31.8	212	83.5	46.0
220	60.0	32.0	216	84.5	"
255	59.7	"	221	85.0	"
268	60.0	"	<u>330</u>	<u>130</u>	"
284	60/5	"			
292	61.5	"			
306	76.0	"			
309	88.0	"			
312	95.0	"			
316	120	"			

Table 7 (cont'd)

<u>Time</u>	<u>Reading</u>	<u>Temp.</u>
0 min.	-	52.0° C
2	95.0	"
5	91.0	51.8
10	88.0	"
16	86.5	52.0
24	85.5	"
31	85.0	"
45	84.5	52.1
60	"	52.0
82	"	"
105	84.0	"
124	"	"
160	"	51.8
172	"	"
176	84.5	51.9
180	87.0	52.0
182	92.0	"
<u>185</u>	<u>130.0</u>	"

Plate VII  
pH = 11.3

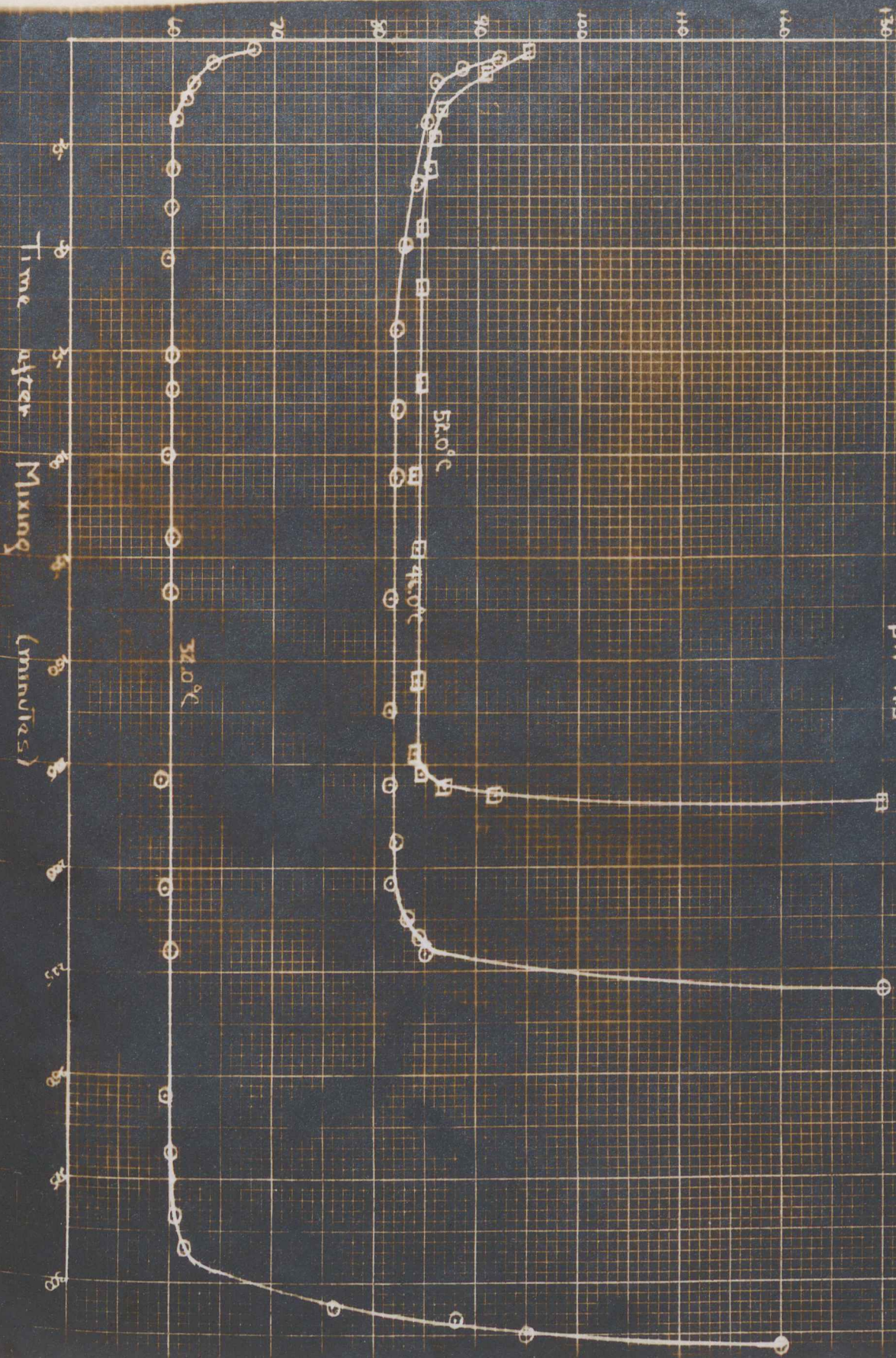
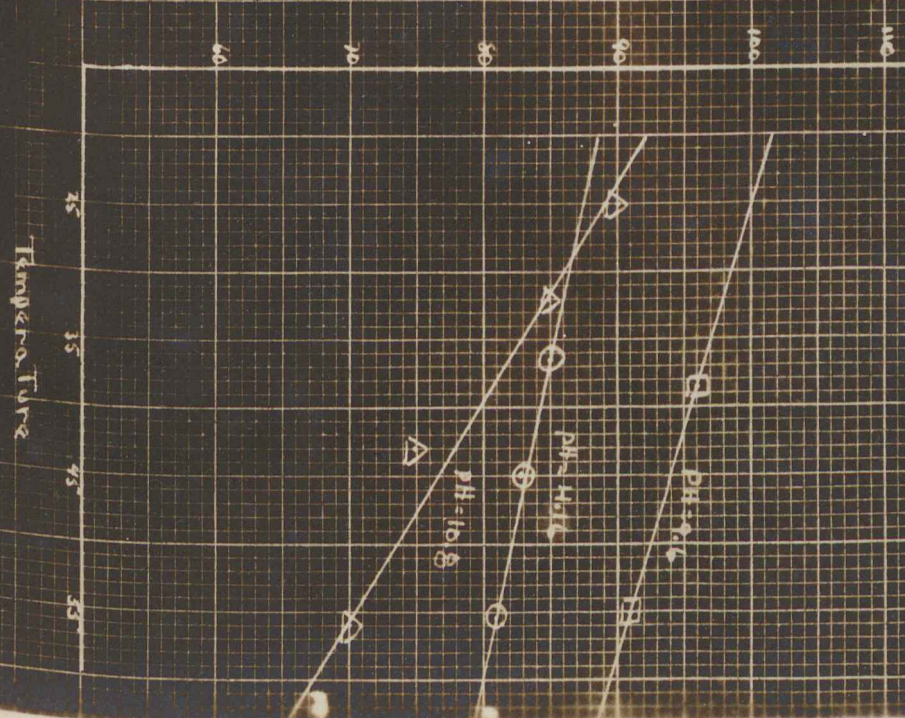
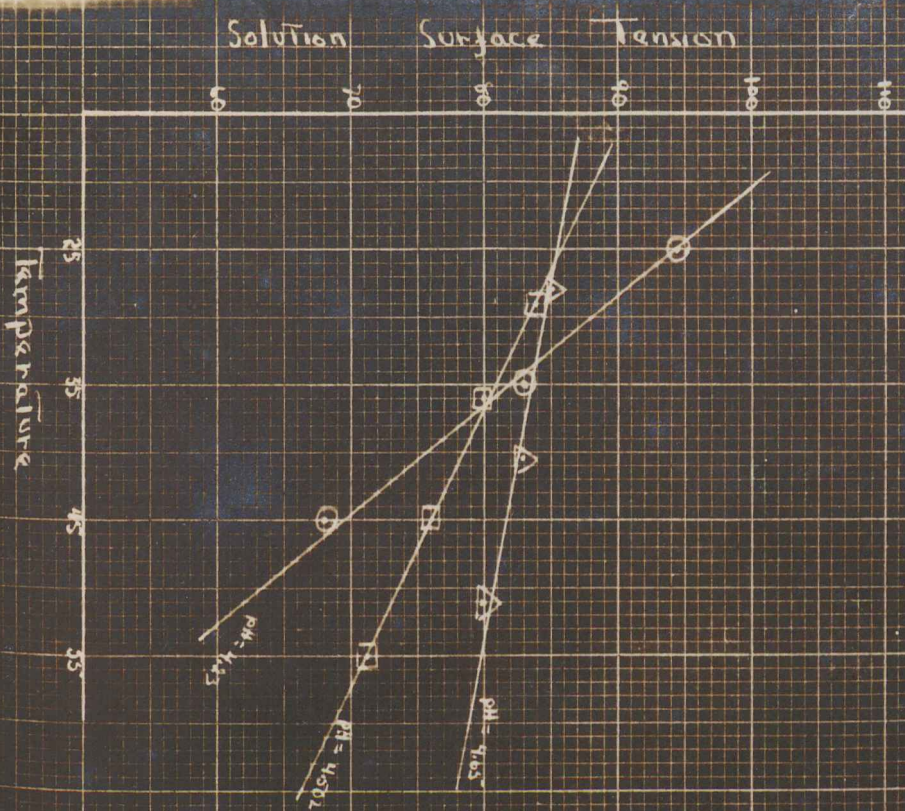


PLATE VIII

Variation of Surface Tension  
of Silicic acid solution  
with change in Temperature.



## Results

The curves are all quite similar and give a picture of the process of gelation. They indicate that gelation is the result of two actions: the first reaction or condensation, through which the surface tension remains about constant, and the second an intermeshing or like phenomenon, which is the actual setting, and which causes a large and abrupt change in surface tension. Increase in temperature causes no change in the process of gelation other than a change in the rate of setting.

It will be noticed that during the first phase of gelation, the solution follows the usual behavior in regard to surface tension, except for curve 7. There is a linear relationship between surface tension and temperature. The surface tension decreases as temperature increases. The slope of the surface tension-temperature curve decreases as the acidity increases, and the slope increases as the alkalinity increases. There is not, however, a continuity in passing from the acid to the basic region. It is doubtful in the second phase of gelation, setting, whether the surface tension is being measured. Likely here an adhesion effect comes in.

It was observed during gelation that though the solution when first prepared is transparent; after standing a faint opalescence becomes apparent. This opalescence increases markedly until the gel has set. It was noticeable, however, that the surface tension shows little or no increase until the solution attains its final degree of opalescence, at which time the solution starts to set. This phenomenon was also met in viscosity measurements as noted by Burd (10). The opalescence can be explained by the formation of

colloidal particles which become larger and finally coagulate to form the gel.

On close examination of the curves a number of peculiarities are noticed. These will be discussed in order.

1. For the gel mixture pH 4.65, the surface tension remains constant until setting starts. Higher temperatures only lower the starting surface tension. No doubt this regularity will hold for solutions of pH 4.5 to the limit pH=6.0. The mechanism in this case is likely an instantaneous reaction of the acetic acid with sodium silicate forming a simple silicic acid.

2. A new phenomenon was noticed when working with the gel mixtures of pH=4.50 to pH= 4.16. In each case there is an initial drop in surface tension to a constant reading. This drop seems to increase as acidity increases. It may be that in this case the reaction is not instantaneous, but requires a short time for completion. It appears that when the acetic acid is in large excess the reaction to silicic acid is slowed down, and that the reaction is complete when the surface tension arrives at a constant value.

Another explanation for the sharp drop may be in a statement by Moller (11). "When silicic acid is formed, it likely dissociates into water and silica. It is almost certain that in the hydrogel, the water is not chemically combined with the silica, and the so called silicic acids are to be regarded as adsorption products." The sharp drop in surface tension is common in cases of adsorption. Perhaps the drop in the surface tension of silicic acid solution may be due to an adsorption effect.

3. The curves for pH= 4.23 and 4.16 show small sharp rises in surface tension. These rises are too pronounced to be within the limit of experimental error.



Likely for gels of this acidity, which are long time setting gels, the setting process starts long before the gel actually appears set. In this case, the gelation process instead of being continuous may be said to proceed in spurts. There is evidently a difference in the gelation process of more acidic gels.

4. Curve 5, for gel solution  $\text{pH} = 9.6$ , shows the same gelation process as the acid gel solutions,  $\text{pH} = 4.6-6.0$ . There is no initial drop, and the surface tension remains constant until the setting takes place.

The alkaline gel solutions show a peculiarity that the acid do not exhibit. There is a tendency in the alkaline solutions for a thick film to form on the platinum ring. The ring does not pull away clean from the surface, but always has an adhering film. Unless the ring is cleaned after each reading, the cohesion between the film and the solution causes abnormal surface tension determinations. Prasad, Mehta, and Desai (6), found that the colloidal particles are larger in the alkaline gel solutions than in the acid.

5. A most unusual gel was obtained from a mixture of  $\text{pH} = 10.8$ . This solution is not unusual as far as surface tension is concerned, for with regard to this it is normal. The gel solution differs in that it has approximately the same time of set, no matter what the temperature. Actually the solution sets slightly faster at lower temperatures. This same peculiarity was met by Pomatti (12) in his investigations. Oddly, it seems that this phenomenon occurs only for a small pH limit. In working with a gel solution  $\text{pH} = 11.3$ , the usual temperature, time of set relationship was obtained.

The time of set of this gel solution,  $\text{pH} = 10.8$ , is also

unusually short. It does not correspond at all to the times of set for mixtures a little more or a little less alkaline. The action of this gel solution leads one to imagine that here there is not only a reaction toward gelation, but also a reaction opposing gelation. The net result is a gel only slightly affected by temperature. However, there is an inconsistency since a gel of higher alkalinity does not show a similar tendency. It is suggested that gel solutions of this pH be more thoroughly investigated.

6. Another unusual gel solution was obtained at a pH of 11.3. Here the peculiarity occurred of a rise in surface tension with a rise in temperature. This does not comply with the usual change of surface tension with temperature. Although time did not permit the careful checking of this gel solution, from checks made, this phenomenon does occur.

The gel resulting from this gel solution is of itself interesting. Although it set as usual in a small amount in the dish used in surface tension determinations; the setting was completely different in a beaker containing 80cc of solution. Only about a quarter of the solution actually set to a gel. The mass at the bottom of the beaker appeared to be a gel, though somewhat more solid. This of course arises from the fact that it contained far less water than the usual silicic acid gel. The solution above the gel was opalescent, and after standing a week, appeared as if it might clear up with time. This gel gives evidence of the formation of silicic acid gel by the coagulation of the silicic acid in the sol.

### Summary

The variation of surface tension during gelation of solutions of sodium silicate and acetic acid was studied. The reading on a Du Noüy tensimeter remains about constant until the solution starts to set, then rises rapidly. The mechanism of gelation is thought of consisting of two phases; a slow process followed by a rapid process.

The change of surface tension of silicic acid solution with temperature is linear.

An initial drop in the surface tension of gel solutions of pH under 4.5 denotes a difference in the gelation process in respect to solutions of pH above 4.5.

A gel of pH=10.8 has approximately the same time of set, no matter what the temperature.

The surface tension of a gel pH= 11.3 increases with increase in temperature. This gel seems to be formed by coagulation of colloidal silicic acid.

Further work on silicic acid gels in the high alkaline region should yield interesting results.

## References

- (1) Walden: Kolloid-Z., 9, 145(1911)
- (2) Graham: An. Physik 190, 187(1861)
- (3) Holmes: J. Phys. Chem. 22, 510(1918)
- (4) Hurd & Letteron: J. Phys. Chem. 36, 604(1932)
- (5) Treadwell & Wieland: Helv. Chim. Acta. 13, 842(1930)
- (6) Prasad, Mehta, & Desai: J. Phys. Chem. 36, 1324(1932)
- (7) Hurd & Swanker: J. Am. Chem. Soc. 55, 2607(1933)
- (8) Fraser: Thesis, 1937
- (9) Hurd & Carver: J. Phys. Chem. 37, 321(1933)
- (10) Hurd: Chemical Reviews, 22, 405(1938)
- (11) "Treatise on Inorganic & Theoretical Chem."  
Mellor: Vol. 6, pg. 293
- (12) Pomatti: Thesis, 1939