INFLUENCE OF TEMPERATURE AND HYDROGEN ION CONCENTRATION ON TIME OF SET OF SILICIC ACID GELS IN THE BASIC REGION

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INTRODUCTION

The main purpose of this research was to determine the time of set of silicic acid gels as a function of temperature and hydrogen ion concentration expressed in pH units. The silicic acid gels were formed by the reaction between sodium silicate and acetic acid. The gels studied were mainly basic in nature, their pH's ranging from 6.8 to 10.75. Gels above this latter pH were found to take a very long time to set - a matter of days and even weeks. The gels were run at three different temperatures - 0°, 25.1° and 38.5° C. The pH's of the gels were obtained by means of the colorimetric method using standard buffer solutions. The values of these standard solutions were obtained by means of the Beckman pH meter which uses a glass electrode.

By means of the data obtained above, the energy of activation could be obtained. The pH drift was also investigated qualitatively.

HISTORICAL

Silicic acid gels have been known for over one hundred years. Early investigations consisted of determining different methods of preparation and studying the gel properties. More recent studies consist of determining the conditions under which the gel is formed, to try to find a mechanism for the S setting of a gel, and to determine the structure of silicic acid gel. Studies along this line have shown that the setting of silicic acid is dependent on the following factors:

1. Temperature
2. pH
3. Silica concentration
4. Presence of soluble organic and inorganic substances
5. Type of sodium silicate used
6. Type of acid used
7. Radiation

The higher the temperature, the shorter is the time of set of the gels. The higher the silica concentration, the more rapidly will the gel set. A minimum time of set was observed by Holmes[1] when the gel was slightly alkaline. Then as the pH was raised or lowered from this minimum point the time of set increased. Also very acid gel mixtures show a very short time of set. Prasad and Hattiangadi[2] discovered that gelation is affected by the presence of electrolytes and non-electrolytes. They found that ammonium acetate decreased the time of set and that alcohol hastened the time of set in basic gels, but delayed the time of acid gels. Hurd and Rothemich [3] found that sodium acetate also reduced the time of set, while sodium chloride gave no effect.

Other properties of these gels have also been studied - viscosity during setting, change of surface tension during setting, syneresis which is the slow exclusion of fluid from a gel as it is allowed to stand for some time, charge on the particles, elasticity, thixotropy which is the knitting together again after the gel has been stirred in the early stages of setting.

Hurd and Letteron[4] in studying the effect of temperature on the time of set found that the log time of set plotted against the reciprocal absolute temperature gave a linear relationship. They showed that the slope of the line obtained is equal to Arrhenius heat of activation, Q divided by R, i.e.,

$$\frac{d\ (\ln \text{time})}{d\ 1/T} = \frac{Q}{R}$$

This heat of activation came out to be about 16,600 calories for gels prepared from 1.25 N sodium silicate and 2.0 N acetic acid. This value of the heat of activation falls between the limits of the heat of activation of ordinary chemical reactions.

Other weak acids, e.g., citric, succinic or tartaric, gave practically the same value for this heat of activation.

Silicic acid gels are assumed to have an open structure through which ions can flow without obstruction. This is based on the fact that the electrical conductivity of the gels does not decrease very much as the gel sets.

There are several theories for explaining the setting of a silicic acid gel. The emulsion theory proposed by Ostwald assumes that the gel consists of a liquid-liquid system with an emulsoid structure. This theory fails in the light of viscosity and elasticity of the gels. Another one, the cellular theory proposed by Butschli[7] says that the liquid part of the gel is held in the form of small droplets in a cellular structure made up of the solid phase. This theory fails somewhat in the light of syneresis and electrical conductivity of the gels. The theory most generally accepted is the fibrillar or brush heap one proposed by Nageli. This pictures a solid and a liquid phase, each continuous with the solid forming a fibrous or brush heap structure composed of long threadlike chains and containing the liquid between the fibers or chains. The structure is believed to be formed by condensation, water splitting out between two silicic acid molecules to form a bigger molecule. This "molecule" gets longer and longer, branching out to form a complex structure.

APPARATUS AND EXPERIMENTAL

The reaction for the formation of silic acid gels is as follows:

$$Na_2SiO_3 + 2HAc \longrightarrow H_2SiO_3 + 2NaAc$$

The general formula for silicic acid is $(SiO_2)_m \cdot (H_2O)_n$, where m and n can have different integers. When m = 1 and n = 2, for example, we have orthomono silicic acid, H_4SiO_4. This is one of the simplest and as stated before, as the gel sets, long chains are formed by condensation. The sodium silicate used was the "E" Brand silicate manufactured by the Philadelphia Quartz Company. Five liters of the silicate were diluted to about 16 2/3 l. in a 20 liter bottle with freshly distilled water until a solution was obtained which was about 1.25 N with respect to standard NaOH. The silicate solution was titrated with standard sulfuric acid, using methyl orange as the indicator.

The HAc solution was made by diluting about 862 c.c. of 99.5% glacial HAc to 15 liters, using freshly distilled water again. The reason for using this water and not some that has been standing some time is that the latter would have CO_2 dissolved in it, which has a coagulating effect on the sol as it sets. The normality of the HAc was obtained by titrating with standard NaOH using phenolphthalein as the indicator. The NaOH was standardized against standard HCl which had been standardized against Na_2CO_3. Sodium silicate was 1.23 N; HAc was 1.008 N.

For the 25.1° and 38.5° runs, water bath thermostats were used to keep the temperature constant. These thermostats were electrically heated and stirred by a stirrer and motor arrangement to keep the temperature uniform throughout the bath. The temperature was controlled by means of a mercury regulator and a telephone relay. For the 0° runs, metal cans were placed in a large box and excelsior packed around them. Wet snow was then packed into the cans. Small 2 oz. bottles were used for the 0° runs. They were stoppered with paraffined corks and buried under the snow. Probably due to the thick walls of the bottles, thick corks and also that there was no stirring of the solutions in the bottles, the bottles had to be left in the snow bath a long time - a matter of two and even three hours before the solutions came down to 0° C. For the 25.1° and 38.5° runs, K beakers were used to hold the solutions. These only had to remain in the baths about 20 minutes before they came to temperature of the bath. A total volume of 80 c.c. of the solutions was used in each case. In one beaker was placed 25 c.c. of sodium silicate, and the other 55 c.c. in another beaker were made up of H_2O and HAc in varying amounts measured by pipettes and burettes.

For determining the time of set the tilted rod method was used. A gel was considered set when it could support a glass rod 10 cm. long and 5 mm. in diameter at an angle of about 15° - 20° to the vertical. After some experience, the opalescence of the sol near the setting time can enable one to approximate the time of set. This is advantageous because then one doesn't have to disturb the sol too many times as it sets with punctures of the glass rod. After the two beakers were properly thermostated, the sodium silicate in one beaker was poured into the other beaker which contained the HAc and H_2O and the resulting sol thoroughly mixed by pouring it back and forth several times. The time of set was started just as the silicate was poured into the acid solution.

For determining the pH's of these gels, standard buffer solutions with the proper indicators were used. Buffer solutions were made up according to directions given by Clark[5]. For the range 7.8 - 10, boric acid, KCl, NaOH solutions were used. One stock solution consisted of M/5 Boric acid plus M/5

KCl dissolved in one liter of solution, i.e., 12.4048 gms. boric acid and 14.912 gms. KCl. The other stock solution was N/5 NaOH. For the 9.2 - 11 range, sodium carbonate, borax buffers were used. One stock solution was 5.30 gms. of Na_2CO_3 dissolved in one liter of solution. The other was 19.10 gms. of $Na_2B_4O_7 \cdot 10\ H_2O$ per liter. For the range 7.8 - 8.4 the indicator used was phenol red; for the range 8.0 - 9.6 thymol blue was used; for the range 9.6 - 11.0 La Motte purple was used. This last indicator proved quite difficult to work with. In the first part of the range, i.e., from 9.6 to about 10.2, the color change from one buffer to the other was quite hard to distinguish. Also buffers in the higher pH's were prone to fade. An accuracy of about .1 - .15 pH unit is probably the best to be expected with this method.

The pH's of the standard buffer solutions were obtained by means of the Beckman pH meter. This meter uses a glass electrode for determining pH's. The other electrode of the cell is a calomel electrode. This glass electrode works on the basis that a very thin membrane of glass separating two solutions gives potentials which depend directly on the hydrogen-ion concentrations. One solution, in side the small glass bulb, consists of .1 N HCl and a pinch of quinhydrone. The other solution is the one whose pH is to be determined. Apparently the hydrogen ions attach themselves to the glass membrane and the current is conducted by means of the Na ions present in the glass electrode. The voltage of the cell depends on the relative concentration of hydrogen ions on each side of the glass membrane. The instrument is calibrated to read directly in pH units. Before using the meter each time, a fresh calomel electrode was made and the instrument was calibrated against a known standard acetate buffer.

Buffers are solutions which possess the ability or property of resisting changes in hydrogen ion concentration on the addition of small amounts of acid or alkali. If an acid is added to a buffer consisting of a weak acid HA and one of its salts MA, the hydrogen ions of the acid added will react with the anions of the salt to form the undissociated weak acid, thus:

$$\overset{+}{H} + \overset{-}{A} = HA$$

If an alkali is added, little or no change in pH results because the hydroxyl ion is neutralized by the acid, thus:

$$\overset{-}{OH} + HA = H_2O + \overset{-}{A}$$

The method of obtaining the pH's of the gels is as follows: The holes of a spot plate are filled with the same amount of the different buffers. To these buffers is added one drop of the proper indicator, and the solution stirred to obtain a uniform color. Cleanliness is essential, Kleenex coming in very handy. Soon after mixing the solutions to form the gel at 25°, a hole of another spot plate which has in it the proper indicator if the range is known, is filled by means of an eye dropper, and the solution stirred. The color of this resulting solution is compared with the colors of the buffers. Where the two colors match or nearly match is the pH of the unknown solution. The buffers were about .2 of a pH unit apart, so that pH's in between these could be approximated. For the very fast setting gels, help was obtained in determining the time of set and the pH.

A glass electrode was used on these basic gels by Marotta[6] but proved to be an expensive as well as an ineffective method because the glass electrode became coated with silicate, which clogged up the porous membrane of the glass electrode and rendered it useless.

Much more work needs to be done in this field of determining pH's of the basic gels. Different indicators ought to be tried.

The pH drift was studied qualitatively by noting how the pH of the test solution which had the indicator in it changed. This was done by noting how its color changed.

RESULTS AND DISCUSSION

The times of set and the pH's of the gels at the three different temperatures are given in the tables. It is seen from the curves that the gels have a minimum time of set at all three temperatures in the slightly basic region - pH 8.4 - 8.7. This is in agreement with work done by Hurd and Letteron[4] and Prasad and Hattiangadi[2]. Below this minimum time of set the time of set increases with decreasing pH. Above the minimum point, the time of set increases with increasing pH. Plotting log time of set against the reciprocal absolute temperatures gave Graphs 4 and 5. Up to about a pH of 8.3 results were obtained which were in agreement, or nearly so, with previous work. The slopes of the curves on Graph 4 are positive, and nearly of the same value. But above a pH of 8.3 the slopes on Graph 5 are seen to decrease, become nearly zero, then even go on to negative values. Graph 6 was plotted with pH against values obtained by multiplying the slopes of Graphs 4 and 5 by 2.3 R, i.e., pH against effect of temperature on time of set. The curves of Graphs 4 and 5 show that above a certain pH, around 10.45, it takes a longer time for a gel to set at 38.5° C. than it does at 0° C. Due to this odd result, the times of set of the gels were checked and re-checked, especially in the higher pH range. The times given in the tables are the average of six and seven and sometimes even eight different runs, all the times of one individual run falling close together within experimental error. From Graph 5, where the slope of the curves changed from positive to negative, in particular in going from a pH of 10.43 to one of 10.5, or an acid volume of 20 c.c. to 19 c.c., it was predicted that there should be a gel with a pH between 10.43 and 10.5 that would give a horizontal curve with zero slope, or in other words a gel with acid volume between 19 and 20 that would set independent of temperature. A gel with 19.5 c.c. of HAc was tried. This was found to set nearly independent of temperature. At 0° it took 12.64 minutes; at 7.5° it took 12.25 minutes; at 25° - 12.33 minutes; at 38.5° - 12 minutes; at 42° - 11.42 minutes. From Graph 6 it can be seen by noting the pH where the curve crosses the pH axis, that a gel having a pH of about 10.48, or an acid volume of 19.4 or 19.45 c.c., should set independent of the temperature. At this pH of 10.48, a curve of zero slope should be obtained. It would have been very interesting to run a gel with this pH. It is [redacted] highly probable that this gel would have set independent of temperature because of the curves on Graph 5, i.e., it can be safely assumed that in passing from a curve of positive slope to a curve of negative slope, a curve should be obtained with a zero slope. This is further strengthened by the fact that a gel with a pH of 10.45 or an acid volume of 19.5 c.c. was found which gave a curve with a nearly zero slope.

The values obtained by multiplying the slopes of the curves on Graphs 4 and 5 by 2.3 R can be looked upon as representing the effect of the temperature on the time of set. To explain the changing of the slopes on Graphs 4 and 5 it was suggested by Dr. Langmuir that in the process of a gel setting, there are probably two reactions going on - one tending to form the gel and one tending to destroy the gel or prevent its formation. As all the gels did set except those of extremely high pH, we can say that the reaction tending to form the gel is stronger than the other one. However, above a certain pH, about 10.48, the reaction tending to destroy the gel at the higher temperatures is stronger than the same reaction at 0° C. But the resultant reaction is still in favor of the formation of the gel; therefore, one does form although it takes a longer time at 38.5° than it does at 0° C.

Much more work should be done along this line to try to work out a mechanism for this gel setting in high pH's. The pH's can and should be expanded, i.e., gels with higher pH's should be studied. The temperature range should also be extended. Probably a lower temperature range, although harder to obtain, would be better to work with,because at higher temperatures the evaporation of the solutions would be quite appreciable. Of course, when working at low temperatures, the danger of freezing or salts crystallizing out should be looked for.

A slight pH drift was observed as the gels set. It was studied only qualitatively. Each gel as it was mixed went up about .2 - .25 pH units within a half hour after it was mixed. This drift toward a higher pH is probably due to the fact that the more complex acids that are formed due to the condensation of the simpler acids are not as highly ionized as the simpler acids present at the beginning, and therefore the solution becomes more and more basic as these less ionized acids are formed. Another way of looking at this pH drift is as follows. For simplicity, let us say at the beginning there are ortho-mono silicic acid molecules $Si(OH)_4$. In other words, for every Si atom there are 4 OH groups from which the H ion can ionize. As these molecules condense to form the more complex acids, there are less and less OH groups for each Si atom. For example, when two $Si(OH)_4$ molecules condense, the acid $H_6Si_2O_7$ can be formed. When three $Si(OH)_4$ molecules condense, the acid $H_8Si_3O_{10}$ can be formed. The hydrogen "lost" when these acids are formed goes to form practically undissociated water.

Such a small pH drift is seen probably due to the buffering effect of the sodium acetate formed.

In order to pursue a quantitative study of the pH drift, a more accurate method of determining pH's on the basic side than the colorimetric method used will have to be devised.

SUMMARY

The effect of temperature and pH on the time of set of silicic acid gels made by mixing solutions of HAc and sodium silicate was studied. The basic region was covered, using three different temperatures.

The pH's at the minimum time of set for these gels are on the alkaline side.

Above a pH of 10.45, the gels at 0° C. took a shorter time to set than those at 25.1° and 58.5° C. Below this pH, the opposite was found.

A gel having a pH of 10.45 was found to set nearly independent of the temperature.

The change of pH from time of mixing was noticed. It was seen to increase about .2 - .25 pH units.

TABLE I. (for Graph 1)

Temperature 25.1° C. $1/T = .00335$

25 c.c. of sodium silicate

c.c. HAc	c.c. H_2O	Time (min.)	Log Time	pH
30	25	1.52	.1818	6.8
29	26	.815	-.0888	7.4
28	27	.550	-.2596	8.0
27	28	.483	-.316	8.3
26	29	.574	-.241	8.6
25	30	.630	-.200	8.9
24	31	.810	-.0915	9.3
23	32	1.10	.0414	9.8
22	33	2.16	.3345	10.1
21	34	3.53	.5477	10.3
20	35	8.11	.9089	10.43
19.5	35.5	12.33	1.0909	10.45
19	36	23.85	1.377	10.5
18	37	67.5	1.829	10.55
17	38	154.	2.188	10.63
16	39	329.	2.517	10.7
15	40	700.	2.845	10.73
14	41	1215.	3.085	10.75

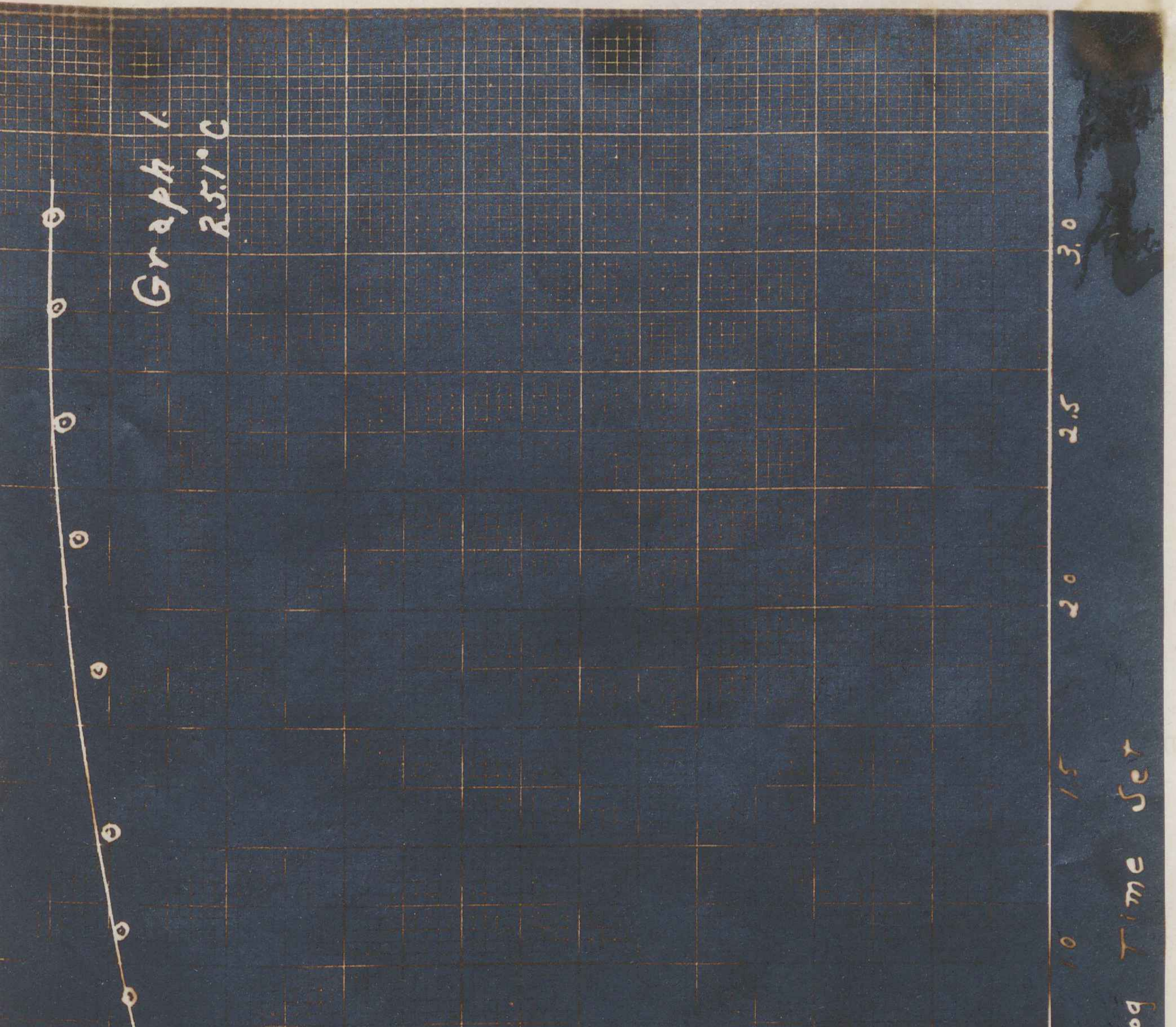
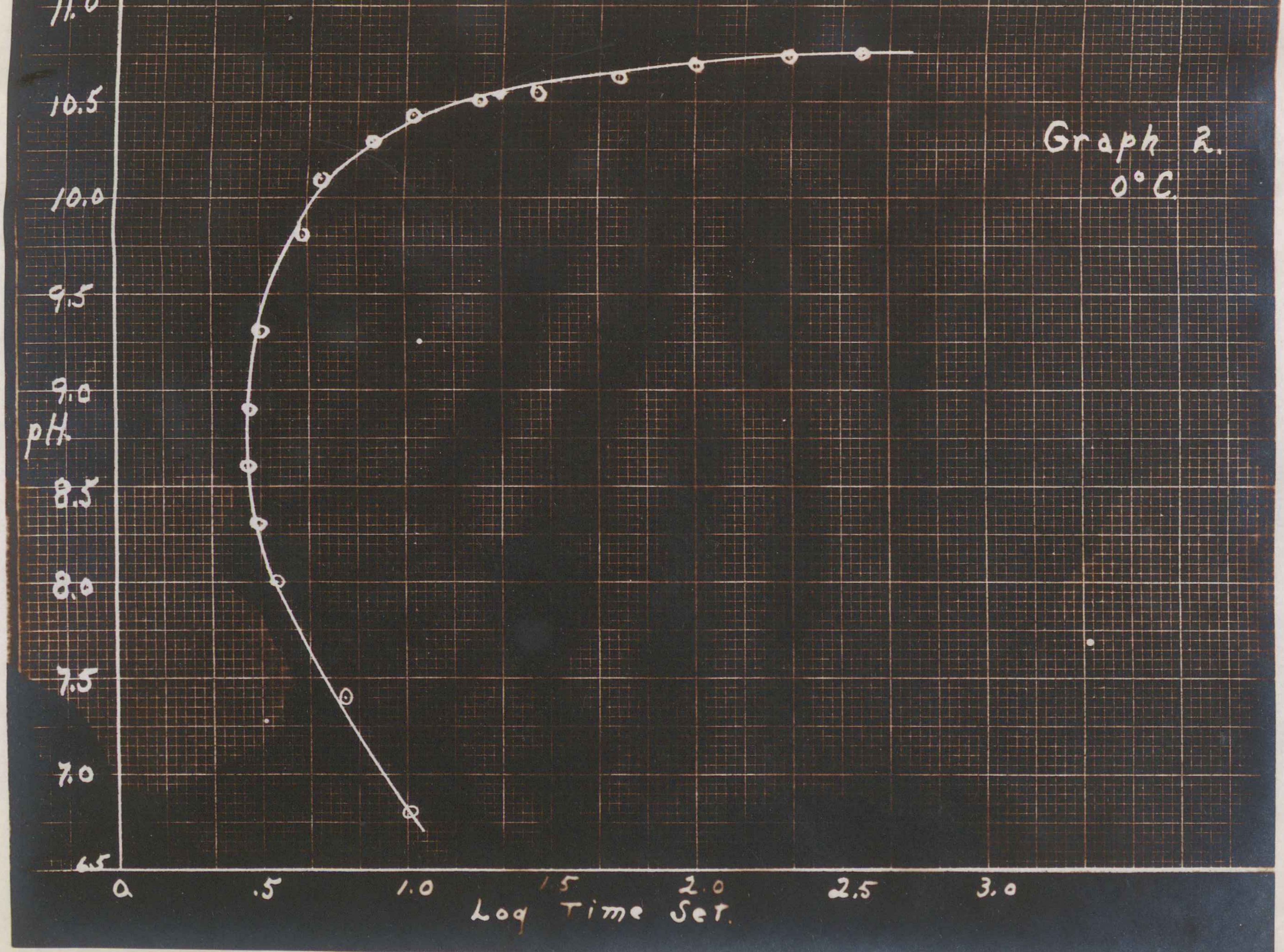

Graph 1.
25.1°C
pH.
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
0
.5
1.0
1.5
2.0
2.5
3.0
Log Time Sec

TABLE II. (for Graph 2)

Temperature 0° C. $1/T = .00366$

25 c.c. of sodium silicate

c.c. HAc	c.c. H_2O	Time (min.)	Log Time	pH
31	24	56.08	1.7488	
30	25	10.66	1.0277	6.8
29	26	6.08	.7839	7.4
28	27	3.87	.5877	8.0
27	28	3.0	.4771	8.3
26	29	2.66	.4248	8.6
25	30	2.75	.4393	8.9
24	31	3.17	.501	9.3
23	32	4.66	.6684	9.8
22	33	5.25	.7202	10.1
21	34	7.66	.8842	10.3
20	35	10.77	1.032	10.43
19.5	35.5	12.64	1.101	10.45
19	36	18.33	1.263	10.5
18	37	28.06	1.448	10.55
17	38	54.	1.732	10.63
16	39	103.	2.013	10.7
15	40	211.	2.324	10.73
14	41	369	2.567	10.75
13	42	720	2.857	



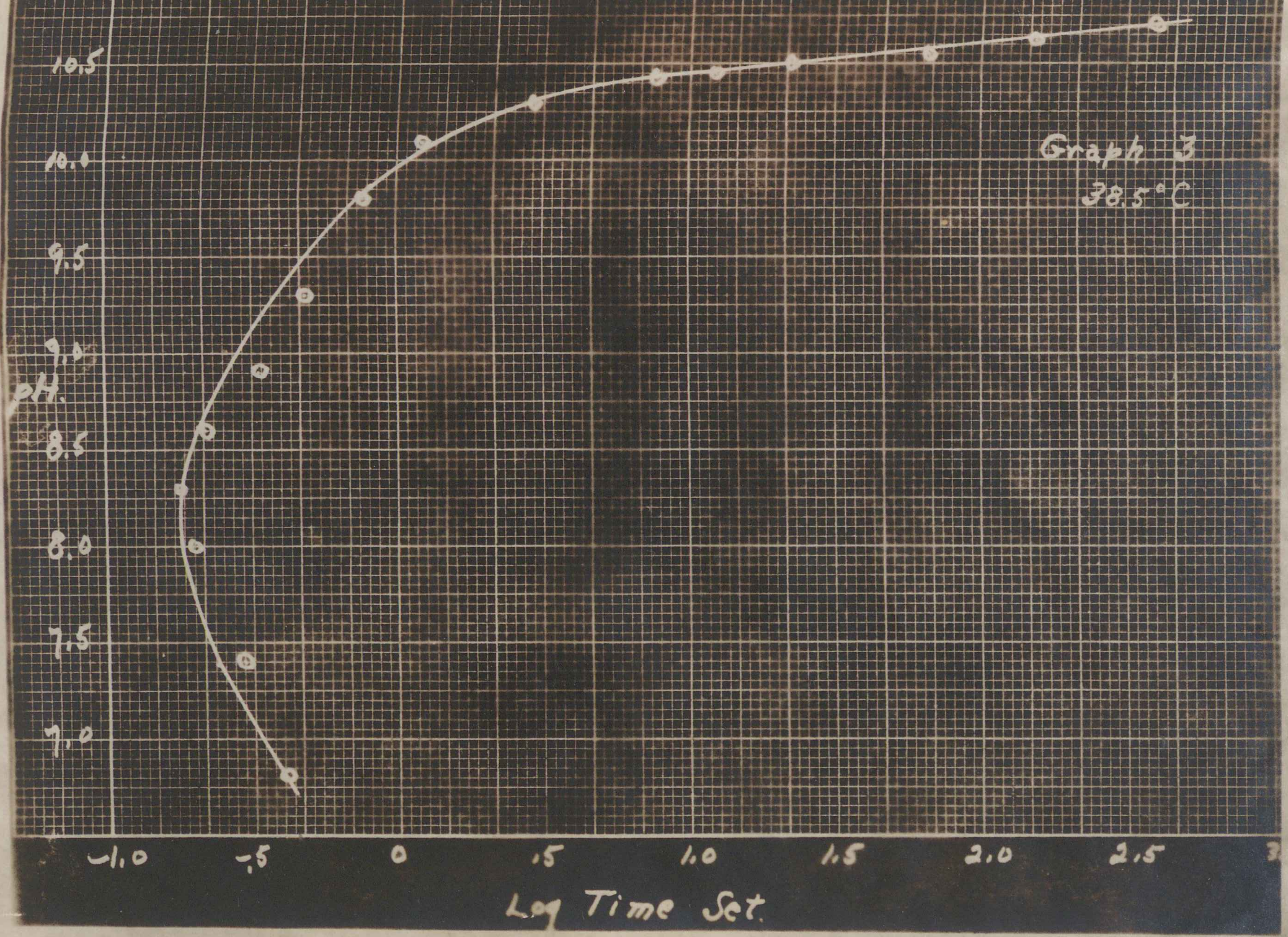
Graph 2.
0°C

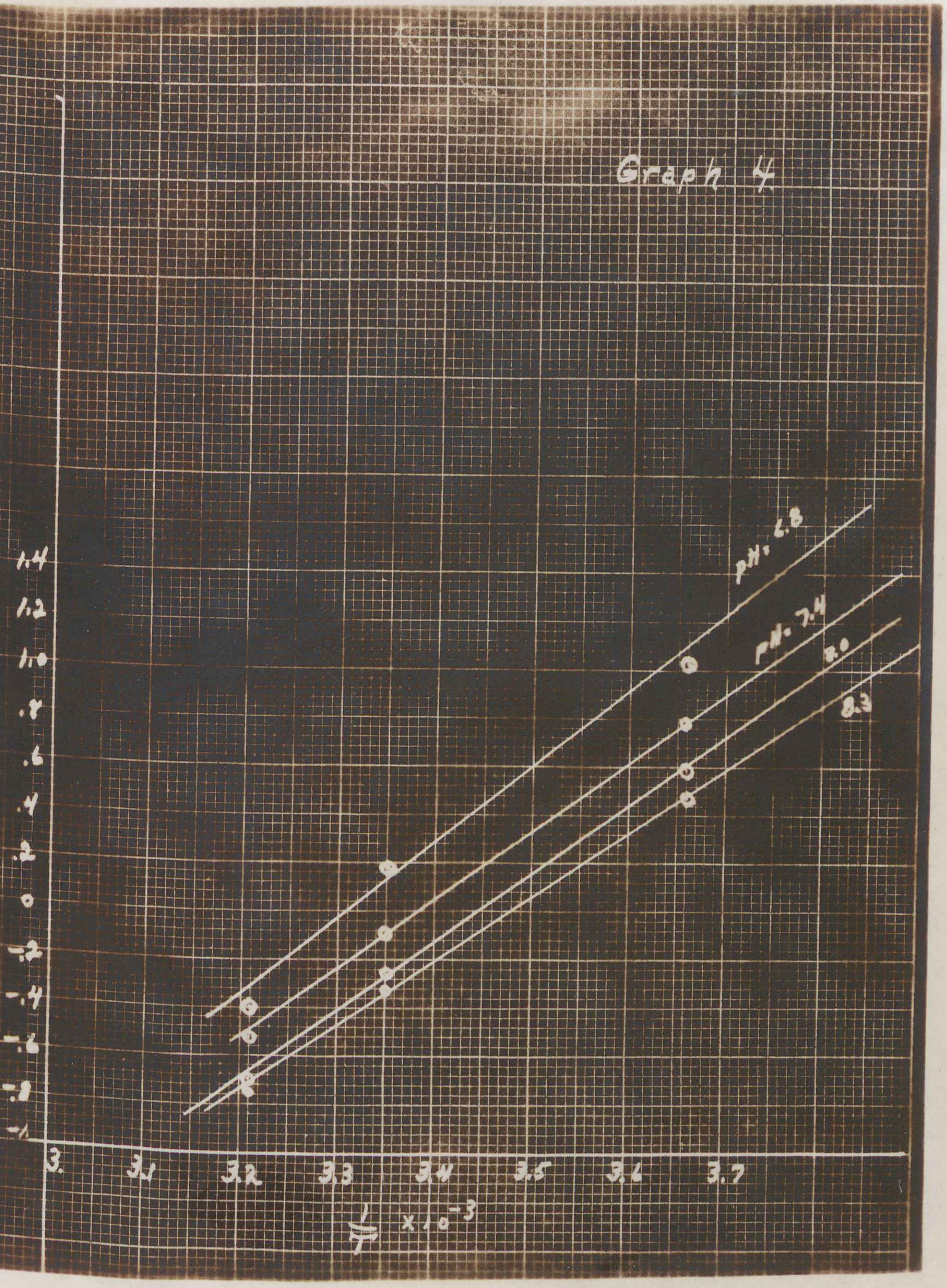
TABLE III. (for Graph 3)

Temperature 38.5° C.   1/T = .00321

25 c.c. sodium silicate

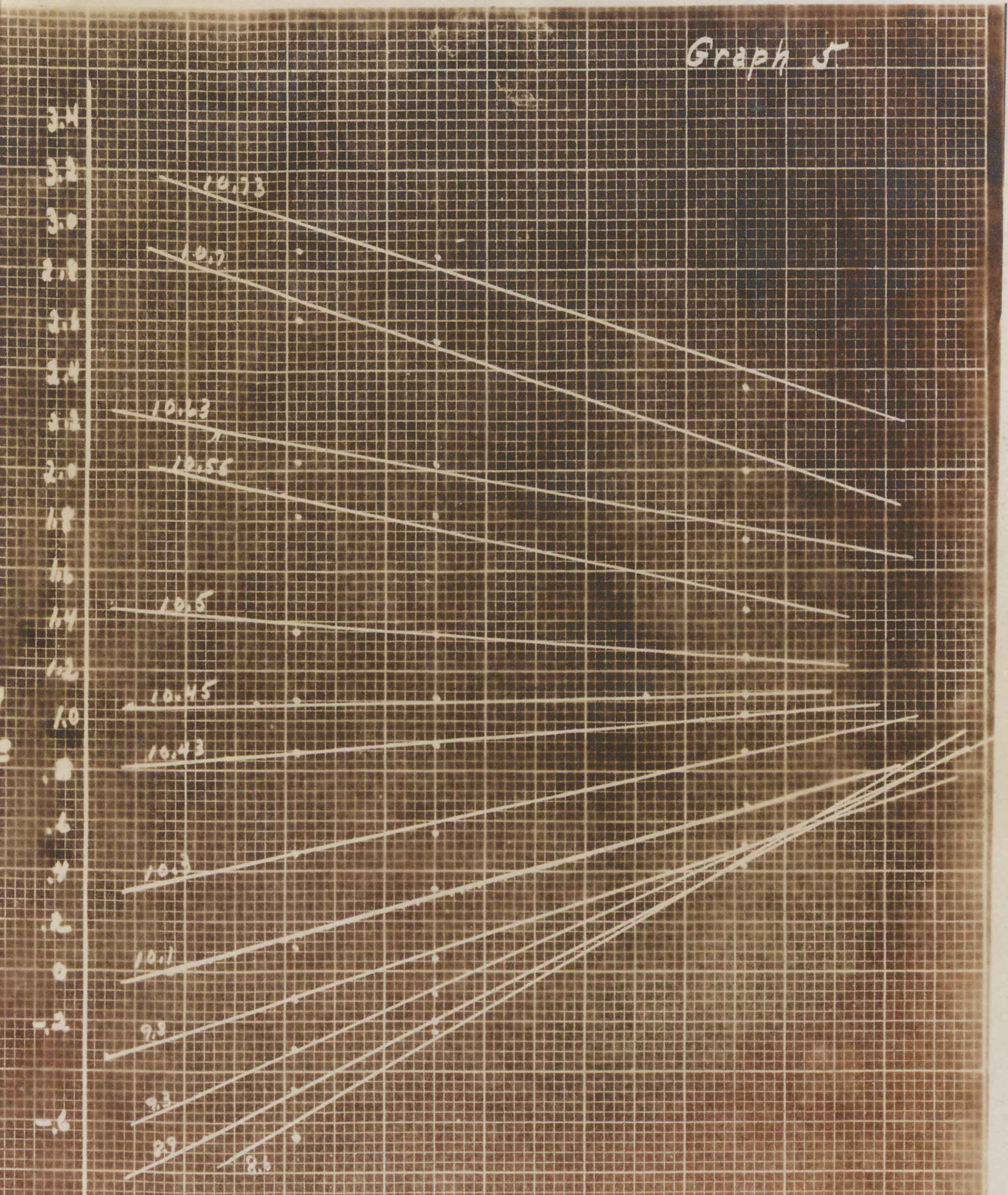
c.c. HAc	c.c. H_2O	Time (min.)	Log Time	pH
30	25	.40	-.398	6.8
29	26	.30	-.523	7.4
28	27	.20	-.699	8.0
27	28	.183	-.737	8.3
26	29	.216	-.665	8.6
25	30	.333	-.477	8.9
24	31	.484	-.315	9.3
23	32	.759	-.119	9.8
22	33	1.225	.088	10.1
21	34	2.96	.471	10.3
20	35	7.542	.877	10.43
19.5	35.5	12.0	1.079	10.45
19	36	22.67	1.355	10.5
18	37	65.	1.813	10.55
17	38	154.	2.187	10.63
16	39	390.	2.591	10.7
15	40	746.	2.873	10.73


Graph 3
38.5°C
pH.
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
-1.0
-.5
0
.5
1.0
1.5
2.0
2.5
Log Time Set.



Graph 4.

pH=6.8
pH=7.4
8.0
8.3
1.4
1.2
1.0
.8
.6
.4
.2
0
-.2
-.4
-.6
-.8
-1
3.
3.1
3.2
3.3
3.4
3.5
3.6
3.7
$\frac{1}{T} \times 10^{-3}$

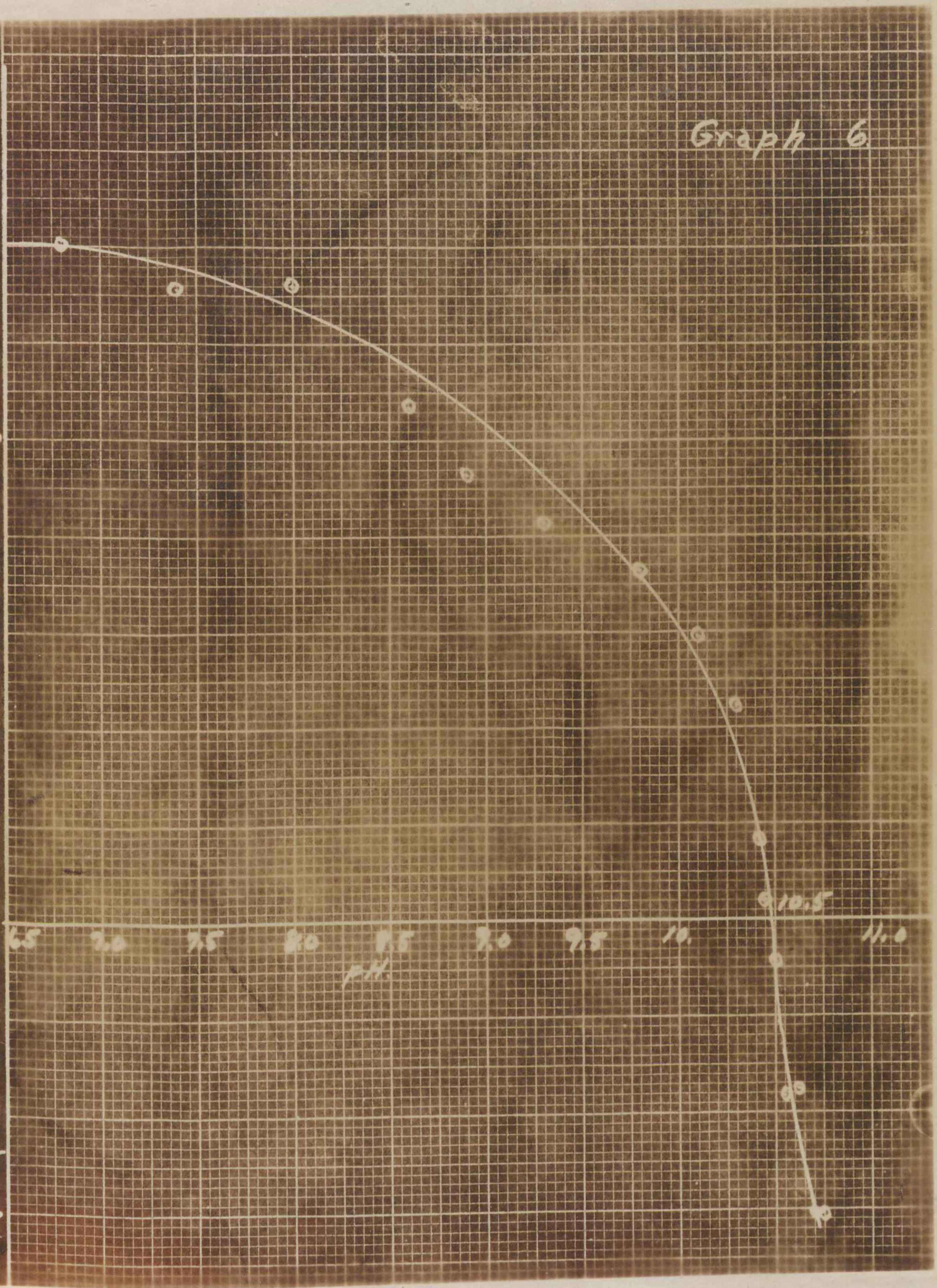


Graph 5.

10.73
10.7
10.63
10.56
10.5
10.45
10.43
10.3
10.1
9.9
9.3
8.9
8.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
-.2
-.6
-1
3.
3.1
3.2
3.3
3.4
3.5
3.6
3.7
$\frac{1}{T} \times 10^3$

TABLE VI. (for Graph 6)

pH	Slope of curves on Graphs 4 and 5 times 2.3 R
6.8	14,000
7.4	13,100
8.0	13,200
8.3	12,200
8.6	10,680
8.9	9,280
9.3	8,320
9.8	7,310
10.1	5,900
10.3	4,460
10.43	1,630
10.45	406
10.5	-915
10.55	-3,660
10.63	-3,560
10.7	-8,100
10.73	-6,100


Graph 6.

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