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# Influence of Temperature and Acid on Time of Set of Silicic Acid Gels

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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.

Angelo J. Marotta

Approved by Charles B. Hurd

June 1937



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INTRODUCTION

The chief purpose of this research was to study the time of set of silicic acid gels produced by the reaction of phosphoric acid and sodium silicate solutions. The secondary purpose was to determine the heat of activation by means of the data procured through the main purpose.

The times of set of these gels were measured at four different temperatures. The pH of each gel was measured also. The pH of the above mentioned gels ranged from a pH of 3 to a pH of 10.



## HISTORICAL

Silicic acid gels have been a topic of research for many years. The earliest work done on these gels dates as far back as the Nineteenth Century. Since that time, many interesting and useful facts have been discovered concerning such gel formations.

It has been shown by previous workers that the setting of silicic acid is dependent on the following factors:

1. Composition of the solution
  - a. Concentration of the acid
  - b. Silica content
2. Brand of silicate used
3. Density of silicate used
4. Temperature
5. pH
6. Addition of soluble organic and inorganic materials
7. Purity
8. Degree of agitation

The temperature and pH vary inversely as the time of set, that is, the lower the temperature the greater the time of set. Likewise the lower the pH or the greater the acid volume in a fixed total volume, the greater is the time of set for acid gels. For basic gels it is reversed, that is, the higher the pH the greater is the time of set. The time of set is also a function of the brand of silicate used. It is dependent on the ratio  $\text{Na}_2\text{O};\text{SiO}_2$ . The more dense is the silicate solution, the less is the time required for the gel to set.

Prasad and Hattiangadi (1) showed that pyridene hastened the time of set and alcohol hastened the time of set of basic gels and delayed the time of set of acid gels. The addition of organic



substances was studied by Hurd and Carver (2). The fact that gelation is influenced by the presence of electrolytes and non-electrolytes was discovered by Prasad and Hattiangadi (3).

Hallstrom (4) continued this work at Union College and found that sodium di-hydrogen phosphate and di-sodium hydrogen phosphate caused large changes in pH.

The most important contribution to the study of the influence of higher temperatures on these gels and also the study of weak and strong acids on the time of set was accomplished by H.N. Holmes (7).

Hurd, Raymond and Miller (5) devoted their time to the study of the effect of pH concentration upon their time to the study of the effect of pH concentration upon the time of set using acetic acid

whereas Kerns and Coons (6) studied the time of set as a function of the hydrogen ion concentration. The effect of the temperature and the concentration of strong acids such as hydrochloric,

sulphuric, and nitric acids on the time of set was studied by Frederick (8). Priznar (9) found the same effect with the monochloro acetic acid and tri-chloroacetic acid. Fells and

Firth (10) observed that a slight alkalinity is the neighborhood of the neutralization point brought about immediate setting of the gel. These two gentlemen worked with hydrochloric acid. Fleming (11)

studied the time of set of silicic acid gels as a function of the concentration of water glass and acetic acid, and then with the aid of Holmes (12), the two studied the time of set as a function

of temperature. Sodium acetate was found to reduce the time of set whereas sodium chloride had no effect on the time of set by Hurd and Rothemich (13) in their study of the common ion effect.

A great deal of work has been accomplished in the study of the various properties of gels such as viscosity during setting,



syneresis, charge on gels, surface tension, etc. Prasad and Hattiagadi (14) found that the gels forming mixtures contain colloidal particles which are positive or negative according as to whether the mixtures are alkaline or acidic. Billiter (15) has similarly shown that the particles in a silicic acid solution are negatively charged in an alkaline solution and feebly charged in an acidic solution and positive at higher concentration of the mixture. The surface tension of the silicic acid mixtures was measured by Hurd and Letteron (16) and they found that the surface tension changed slowly at the beginning, progressed uniformly for some time and then reached a limiting value. Syneresis which was studied by Bonnel (17) is the gradual expulsion of water from a gel. The factors which accelerate the setting time of gels also increases the velocity of syneresis.

Hurd (18) found that the log time of set plotted against the reciprocal absolute temperature was represented by a linear function. Priznar (9) and Frederick (8) noticed that the log time of set plotted against the reciprocal absolute temperature was linear but as the temperatures increased the same runs at different temperatures were not parallel but that the slopes decreased.

The heat of activation have been calculated by Hurd and Letteron (16). By making the following assumptions:

1. Dealing with a process that follows the laws of an ordinary chemical reaction so far as the velocity is concerned.
2. That the Arrhenius equation may be applied.
3. That for a given run the time of set measures the time when a certain fixed proportion of the silica in whatever form, in solution was reacted.



they showed that

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

Q -- Arrhenius heat of reaction

Alkaline gels appear bluish in reflected light whereas acidic gels, a translucent gel, appears pinkish white. A solution which is practically neutral will give the quickest setting gel. Gels have a great affinity for absorbing vapors from gases and various colloidal materials from organic liquids.

During the many years in which silicic acid gels have been studied, various theories as to the structure of the gel have been proposed. The Micelle theory by Negeli (19) was the first theory published. This theory claims that the structure of the gel is due to the formation of small molecular aggregates formed from the colloidal matter of the solution, which interlocked among themselves. In a paper published by Mata Prasad (20), he believed that the gels are usually obtained by the slow coagulation of the colloidal solution provided there is a sufficient concentration of the colloid and the colloidal particles are hydrophelic in nature. The idea that gels are due to certain ions in solution which possess a dehydrating effect was proposed by Laskin (22). The fact that sodium ions in solution have a peptizing effect upon the silicic acid is the cause of the structure assumed by the gel according to Kroger (21). Hurd, Raymond, and Miller (5) believe that the peptizing action in an alkaline mixture containing silicic acid is due to the hydroxyl ion and it acts as a catalyst in acid solutions. Proctor and Robinson (23) proposed the fibrillar theory in which they claim that a gel is composed of long thread-like chains which spread out on polymerization. Zsigmondy (24) and W.A. Patrick (25) have established the gel as a system of

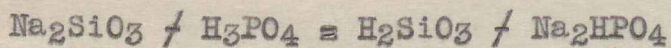


pores in a solid phase. The particles have coalesced until their size became sufficient to permit adjacent particles to touch and form one unified mass, will of necessity have composed great spaces between them filled with liquid phase from which the particles separated.

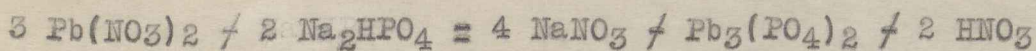


EXPERIMENTAL

The silicic acid gels which were studied in this research were prepared by the reaction of sodium silicate and phosphoric acid



The sodium silicate which was used, the E Brand silicate manufactured by the Philadelphia Quartz Company, was diluted to a normality of approximately 1.25. The resulting solution was standardized with a solution of sulphuric acid using methyl orange as the indicator. In this manner the normality of the silicate was found with respect to sodium hydroxide. The phosphoric acid was diluted until it had a normality of approximately 2.0. A solution of sodium hydroxide was used in order to standardize the phosphoric acid solution, in which methyl orange was used as an indicator in order to titrate the first hydrogen ion, phenolphthalein as the indicator to titrate the second hydrogen ion and finally to titrate the third hydrogen ion, it was necessary to add an excess of lead nitrate until a rose red solution was obtained which was then titrated with sodium hydroxide. The reaction taking place between the di-sodium hydrogen phosphate and the lead nitrate was



Distilled water which was previously boiled in order to expell the carbon dioxide was used to dilute the solutions of sodium silicate and phosphoric acid. The reason for boiling the distilled water was due to the fact that carbon dioxide has an *time of set, that is, the carbon dioxide has a coagulating effect on the* effect on the silicate solution.

For the 24.8°C, 35.1°C, and the 49.7°C runs the gel mixtures



were made up to total volume of 80cc., 25cc. being sodium silicate and the remaining 55cc. being composed of phosphoric acid and distilled water (which was previously boiled in order to expell all the carbon dioxide possible). The volumes were measured by means of burettes and pipettes. However, since the gels were not reproducible, double mixtures were made up for every gel, the silicate and acid solutions were placed in separate beakers and they were then thermostated. After remaining in the thermostat for about fifteen minutes they were mixed quickly by pouring the silicate into the acid and mixing the solutions thoroughly by pouring them back and forth several times. After the solutions were mixed well, one-half was placed in a one-hundred cubic centimeter (K) beaker to be used in obtaining the time of set while the remaining half was placed in another beaker of the same size to be used in measuring the pH of the solution. The beakers were also allowed to remain in the thermostat for approximately fifteen minutes before the gel was placed in them. However for the 0°C run it was found best to measure out one hundred and sixty cubic centimeters, of which 50cc. was sodium silicate and the remaining 110cc. was water and phosphoric acid. These solutions were placed in 200cc. erlenmeyer flasks which were stoppered with paraffined corks and covered with 50cc. beakers in order to prevent the snow from getting into the gel. The recording of the time of set and the measurement of the pH was accomplished by following the same procedure as in the other runs. In all the runs the recording of the time of set was started as the silicate solution was poured into the acid and not after the mixture had been mixed thoroughly.

The method which was used in order to determine when the gel was set was the tilted rod method. For all the runs except the



0°C run the gel was considered set if it could support a glass rod 10cm. long and 3mm. in diameter at an angle of about 15 to 20° to the vertical. For the 0°C run, rods of length 14cm. and 3mm. in diameter were used.

The thermostats which were used in the 24.8°C, 35.1°C, and the 49.7°C runs were water thermostats which were electrically heated, and which were stirred mechanically. The temperature was regulated by means of a mercury regulator and a telephone relay. In the case of the 0°C run, well insulated metal cans filled with wet snow were used. The snow was packed well around each erlenmeyer flask in order to insure a uniform temperature.

The pH of each gel whose pH varied from 3-7 was measured by the quinhydrone method which was found by Hurd and Carver (2) after careful study to be the most applicable for measuring the pH of acid gels. The apparatus consisted of a Leeds and Northrup potentiometer which was balanced by means of a dry cell, a calomel cell which contained mercury which was ground with mercurous chloride or calomel and a platinum wire electrode. The pH was read from the potentiometer in millivolts and was then converted into pH units by means of a graph. All pH measurements were taken at 25°C. The pH could be calculated by means of the equation

$$\text{pH at 25 C} = \frac{.4532 - E}{.0591}$$

where E is the measured potential

The arm of the calomel cell and the platinum wire electrode were placed in the solution of sodium silicate, distilled water, and phosphoric acid to which a pinch of quinhydrone had been added. These two electrodes were in turn connected to the potentiometer from which the potential was read in millivolts. The platinum



wire was cleaned by washing it in boiling sodium hydroxide, and then rinsing it first in a solution of hydrochloric acid and then in distilled water, and finally flashed in a hot flame.

The pH of the basic gels were measured with the Beckman pH meter that is for gels whose pH ranged from 7-10.5. The Beckman pH meter is essentially the same as the quinhydrone except that a glass electrode containing a .1N solution of HCL with a pinch of quinhydrone is substituted for the platinum wire electrode used in the other method. The glass electrode and the calomel cell were cleaned off with cotton and Kleenex tissues. Before using the pH meter the solutions of each electrode were changed, and the meter was adjusted by means of a buffer solution. The pH meter proved a very expensive method of measuring pH's because the glass electrode became coated with silicate which clogged up the porous membrane of the glass electrode and made the electrode useless.

Due to lack of time, the basic gels were run only at two temperatures, namely, 24.8°C and 35.1°C. The pH measurements of these gels may not be very accurate because the electrode became coated with silicate and at what point the coating occurred could not be found. However, adjustments were made for each gel. Before the pH of the gel was measured, the meter was adjusted with a buffer solution, and after the pH of the gel was measured it was again adjusted and the necessary correction for the pH of the gel was made. However, it can be said that the pH's if they are incorrect should be higher rather than lower than what they are. The pH drift was also noticed in these gels, but not as great as with the acid gels.

As I have already stated, the quinhydrone apparatus was used



to measure the pH of the acid gels. However, Dr. Hurd and myself did considerable work in comparing the results obtained by measuring the pH with the Glass Electrode and the quinhydrone apparatus. It was found that the quinhydrone apparatus checked with the Glass Electrode with all acid gels, but there was no agreement whatsoever for gels whose pH was over 7.5, and to be safe the quinhydrone method should not be used for gels whose pH is greater than 7.0. The Glass Electrode or the more commonly known Beckman pH meter did not register a pH drift as great as did the other apparatus, which was due to the fact that it takes considerable time for the electrode to measure pH's which are quite wide apart. It was found that with the Glass Electrode that if the pH's of the different solutions did not differ by very much the reading would become constant in a short time, however, if the pH's differed by 2 or 3 pH then it would take at least  $\frac{1}{2}$  hour for the reading to become constant. In order to determine whether or not the apparatus showed a pH drift it was necessary to run two samples of the same solution. The first sample was used to bring the reading of the pH meter to the pH of the gel and the second sample was used in order to determine whether or not the gel solution still registered a pH drift.

At higher temperatures evaporation was great enough to cause a marked effect in the time of set, therefore, the watch glass which covered the gel mixtures was removed for as short a time as possible when testing the gel to see whether or not it had set. Also at higher temperatures, the temperature of the gel was taken and not the temperature of the bath because these temperatures differed by several tenths of a degree.

Measurement of the time of set was found for the various



temperatures namely: 0°C, 24.8°C, 35.1°C, and 49.7°C for the acid gels and 24.8°C and 35.1°C for the basic gels. The pH was measured for all gels at 25°C because it has been noticed by previous workers that the temperature has very little effect on the pH of the solution.

A very perplexing problem which was confronted during the work on the acid gels was what is known as a pH drift. Frederick(8) who did work on the acid gels of the strong acids also noticed this effect. It was found in all cases that the pH started at a minimum and then gradually increased to a point at which it became constant. The constant reading was taken as the pH of the gel. With gels whose pH ranged from 4.68 to 3.80, the pH drift was very much smaller than those whose pH ranged from 4.68 to higher values. In some of the latter gels the pH became constant at a certain point and then dropped suddenly when they were about to set. The constant reading was taken in these cases in order to conform with the pH's of the other gels.

With the basic gels the pH tended to drift from a high pH to a low pH that is all gels tend to drift towards the neutral pH. Due to lack of time, this could not be studied further. ~~It~~

It was noticed also in this work that a white precipitate was formed in gels whose pH was less than 4.75. The amount of precipitate increased up to a pH of about 3.80 and then gradually decreased for gels whose pH was less than 3.80. It was also noted that as the temperature of the gel was increased the amount of precipitate also decreased. The precipitate did not start to become evident until a pH of about 4.50 was reached.

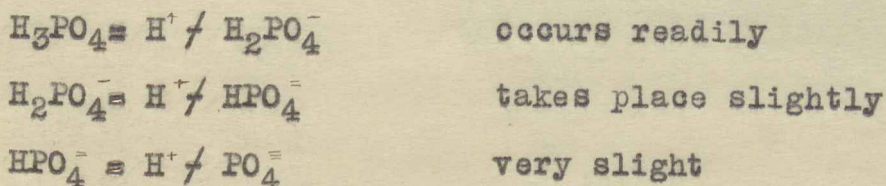
I have come to the conclusion that the precipitate which occurred in these gels must be di-sodium hydrogen phosphate. The



possible precipitates which could be formed are: tri-sodium phosphate, di-sodium hydrogen phosphate, mono-sodium phosphate, calcium phosphate, and magnesium phosphate. The calcium and magnesium arise from the impurities in the sodium silicate used. However, these two substances forming precipitates is very improbable inasmuch as the amount of the metallic substance present as impurities is very small so that the salts thus formed are not enough to exceed their respective solubility products. Also since Frederick (8) who worked with sulphuric acid reported no precipitate in his gels excludes definitely the calcium sulphate since this salt is very insoluble. The fact the magnesium phosphate is rather soluble in aqueous solutions, and since very little magnesium is present, the possibility of this salt being precipitated is very small. Therefore, the remaining possibilities which remain are the three sodium salts of phosphoric acid. I believe the precipitate which was formed is the di-sodium hydrogen phosphate due to the following reasoning:

(1) According to the solubility tables di-sodium hydrogen phosphate is the least soluble of the three phosphates of sodium. This salt increases in solubility with the increase of temperature. In the case of the gels, the amount of precipitate present decreased with increase in temperature, that is, at the same concentration of phosphoric acid the precipitate formed was greater at 25°C than at either 35.4°C or 50°C.

(2) According to the ionization of phosphoric acid,



Therefore, it has been concluded from the above that at a pH of



approximately 4.75 and less, the concentration of the  $\text{HPO}_4^{2-}$  ion is great enough so that the salts mentioned before are formed in large enough quantity so that its solubility product is exceeded, thereby, causing a precipitate to appear.

(3) I performed the following experiment and obtained the following results:

5 grams of  $\text{NaH}_2\text{PO}_4$  in 25cc. of water-----all dissolves

5 grams of  $\text{Na}_2\text{HPO}_4$  in 25cc. of water-----very little dissolves

5 grams of  $\text{Na}_2\text{HPO}_4$  in 25cc. of water-----more dissolved than  
plus 10cc. of 2N  $\text{H}_3\text{PO}_4$ ----- with no acid

This explains the fact that after a certain concentration, the precipitate formed in the gel decreases which was due to the fact that the solution has a large excess of acid and tends to dissolve some of the di-sodium hydrogen phosphate formed since it is soluble in an acid solution.

(4) I found that with the occurrence of the precipitate the pH of the gels showed a considerable jump and this is accounted for by Hallstrom (4) who worked with the addition of salts to silicic acid gels. He found that when di-sodium hydrogen phosphate was added to the gels, a considerable jump in pH occurred.

As yet it seems very difficult to explain the pH drift in the gels. However, it may be due to the splitting out of water from the mono-ortho silicic acid to form the more complex acids. I have found that the drift was much greater for the gels whose pH was greater than 5, that is, for the gels whose time of set was small. The reason that the pH drift was less for the gels whose pH was less than 4.75 may be due to the formation of the phosphates of sodium and therefore a buffering effect of these salts may cause the drift to become less. That is, the greater



the greater the amount of the salts present the less is the pH drift. This was found to be the reason for no pH drift in the gels which were prepared with acetic acid and sodium silicate, namely, due to the buffering effect of the sodium acetate formed. In the gels just referred to, the buffering effect must be very pronounced inasmuch as no trace of a pH drift was found.



## RESULTS

The results consist chiefly of the data which concerns the times of set of the silicic acid gels which were prepared by mixing solutions of phosphoric acid and sodium silicate at several different temperatures. The times of set with the corresponding pH's have been tabulated in tables I and II. The pH's which were measured with the quinhydrone apparatus are tabulated in table I whereas those measured with the glass electrode are in table II. For each groups of gels the logs of the time of set were plotted against the corresponding pH's as shown in graphs I, II, and III.

Also from the data in table III, which consists of interpolated values of the logs of time of set for the various pH's, a graph was plotted for the log time of set against the reciprocal absolute temperature. This is shown in graphs IV and V.

The values of the heats of activation ( $Q$ ) were calculated for the phosphoric acid at each tabulated pH by multiplying the slopes of the curves in graph IV and V by 2.303 R. The values obtained are tabulated in table IV. As is shown in graph VII the values of  $Q$  obtained above were plotted against the corresponding pH's.

In order to show the pH drift for the various acid gels using the quinhydrone apparatus, the pH was plotted against the time since the gel was mixed. The data for this work is contained in table V and the plot is designated as graph VI.



TABLE I

Phosphoric Acid Gels

All pH's measured with the quinhydrone apparatus.

A. Temperature -- 0°C

<u>Time to Set (Minutes)</u>	<u>Log Time of Set</u>	<u>Emf. (Millivolts)</u>	<u>pH</u>
9.75	.98	-128	5.5
17.	1.23	-135	5.4
27.5	1.44	-142	5.28
43.25	1.63	-147	5.18
62.5	1.80	-152	5.10
73.	1.86	-154	5.08
86.	1.93	-155	5.06
91.	1.95	-156	5.04
98.	1.99	-158	5.00
117.	2.06	-159	4.98
132.5	2.12	-162	4.93
154.	2.19	-164	4.91
179.	2.25	-165	4.90
188.	2.27	-167	4.85
233.5	2.37	-170	4.81
302.	2.48	-176	4.74
419.	2.62	-179	4.68
530.	2.73	-182	4.60
652.	2.81	-184	4.56
811.	2.86	-185	4.55
1145.	3.07	-191	4.46
1925.	3.28	-200	4.30
1607.	3.21	-198	4.34



<u>Time to Set (Minutes)</u>	<u>Log Time of Set</u>	<u>Emf. (Millivolts)</u>	<u>pH</u>
1607.	3.21	-198	4.34
3025.	3.48	-206	4.20
4461.	3.65	-212	4.15
6360.	3.80	-220	4.00

B. Temperature -- 24.8°C

4.12	.615	-146	5.22
5.55	.744	-148	5.18
6.80	.832	-152	5.12
8.40	.924	-155	5.07
13.20	1.120	-158	5.00
21.85	1.339	-168	4.85
27.5	1.439	-173	4.75
40.65	1.609	-177	4.70
49.30	1.693	-179	4.64
61.6	1.789	-183	4.60
105.5	2.023	-190	4.45
115.	2.061	-192	4.40
164.	2.215	-196	4.38
212.	2.326	-204	4.26
302.	2.481	-208	4.18
422.	2.625	-213	4.04
965.	2.980	-222	3.90
1293.	3.111	-230	3.80

C. Temperature -- 35.1°C

3.0	.47	-152	5.10
4.5	.65	-160	4.98



<u>Time to Set</u> <u>(Minutes)</u>	<u>Log Time</u> <u>of Set</u>	<u>Emf.</u> <u>(Millivolts)</u>	<u>pH</u>
7.0	.84	-168	4.84
14.0	1.14	-179	4.64
16.0	1.20	-182	4.58
20.5	1.30	-189	4.52
23.0	1.36	-190	4.50
34.	1.53	-195	4.40
47.	1.67	-202	4.28
81.	1.91	-210	4.13
111.	2.05	-216	4.05
182.	2.26	-223	3.92
141.	2.14	-220	3.98
304.	2.48	-232	3.76
257.	2.41	-230	3.80
444.	2.62	-240	3.64
369.	2.57	-238	3.67
422.	2.63	-240	3.64
481.	2.68	-242	3.60
527.	2.72	-244	3.58
628.	2.80	-247	3.50
737.	2.87	-250	3.46
858.	2.93	-252	3.43
910.	2.96	-253	3.42
968.	2.99	-254	3.40
1078.	3.03	-255	3.38
1199.	3.08	-257	3.33
1360.	3.13	-260	3.30
1527.	3.20	-261	3.28
2005.	3.30	-265	3.20



D. Temperature -- 49.7°C

<u>Time to Set (Minutes)</u>	<u>Log Time of Set</u>	<u>Emf. (Millivolts)</u>	<u>pH</u>
4.25	.63	-170	4.74
6.25	.80	-180	4.64
15.	1.18	-200	4.31
30.	1.47	-215	4.06
61.	1.79	-230	3.80
102.	2.00	-240	3.62
146.	2.16	-248	3.49
184.	2.26	-254	3.38
230.	2.36	-259	3.32
272.	2.44	-263	3.24
309.	2.49	-267.5	3.18
380.	2.58	-270	3.12
444.	2.65	-272.5	3.07
540.	2.73	-276	3.01
954.	2.98	-288	2.80
1205.	3.08	-292	2.73
1459.	3.16	-298	2.65



### Phosphoric Acid Gels (HClid)

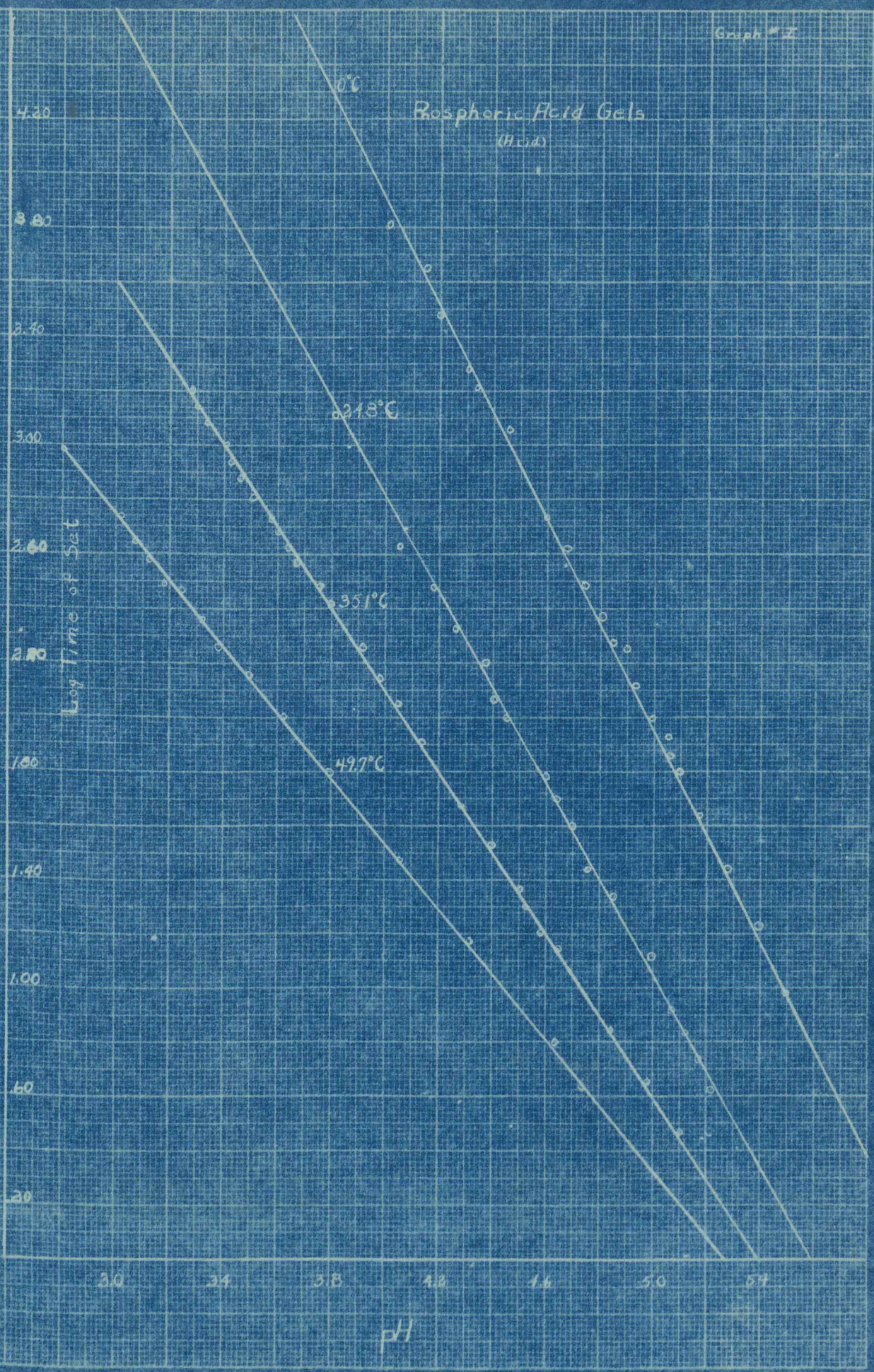




TABLE II

All pH's measured by means of the glass electrode.

## A. Temperature -- 24.8°C

<u>Time to Set (Minutes)</u>	<u>Log Time of Set</u>	<u>pH</u>
5.1	.71	5.40
2.9	.46	5.72
1.66	.20	6.20
1.25	.10	6.77
1.25	.10	7.16
1.25	.10	7.26
1.33	.13	7.80
2.76	.44	8.40
3.80	.58	8.62
13.0	1.12	8.96
20.	1.30	9.10
32.	1.51	9.21
58.	1.76	9.36
141.	2.14	9.60
240.	2.38	9.74
632.	2.80	9.99
2510.	3.40	10.41

## B. Temperature -- 35.1°C

1.25	.10	5.64
.866	-.06	6.12
.833	-.08	6.69
.833	-.08	7.80
.833	-.08	8.37
1.833	.26	8.82



<u>Time to Set</u> <u>(Minutes)</u>	<u>Log Time</u> <u>of Set</u>	<u>pH</u>
11.	1.04	9.40
31.	1.49	9.59
122.	2.09	9.98
322.	2.51	10.25
900.	2.95	10.46



### Rosaporia Acid Gels (Basic)

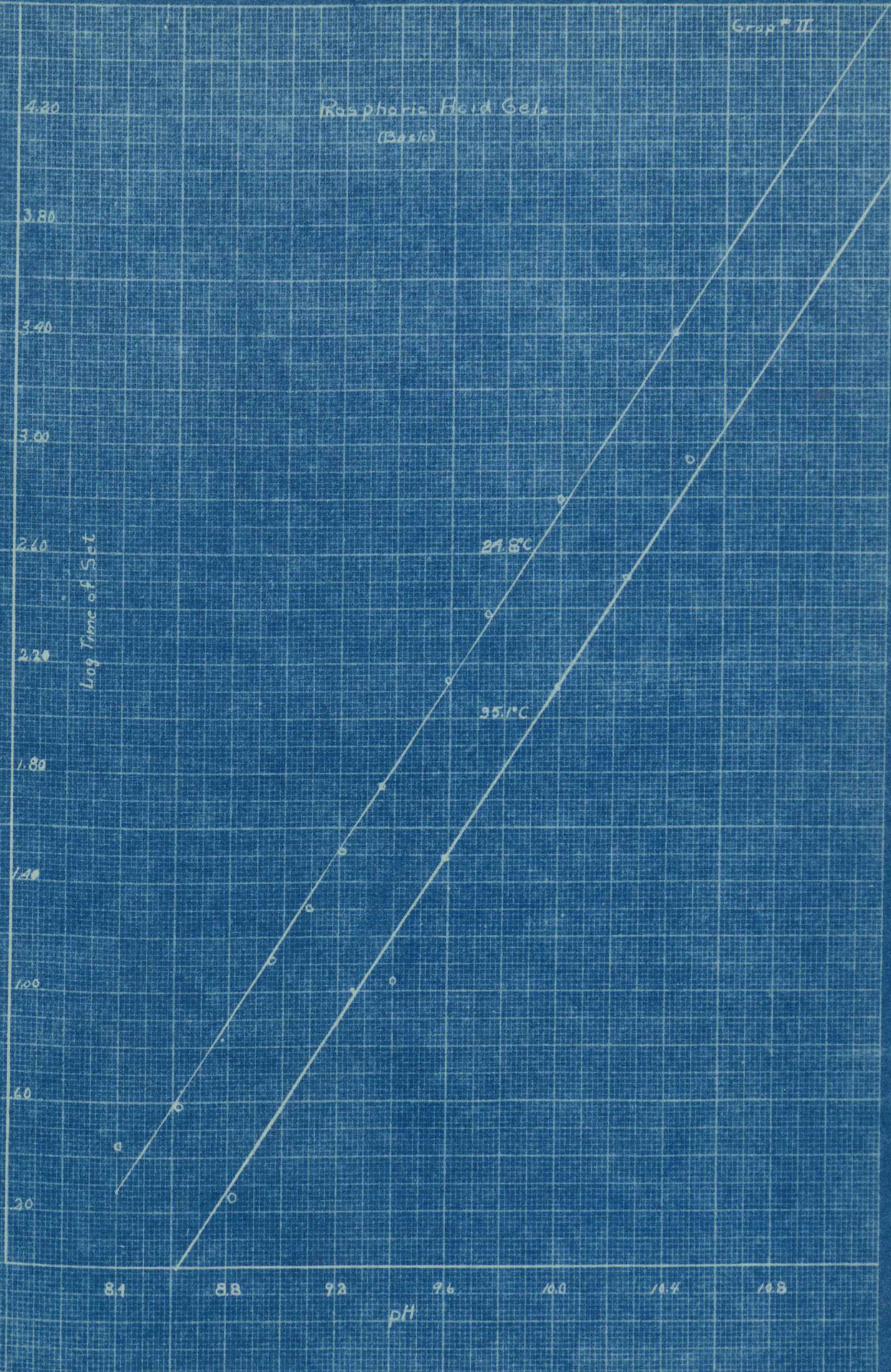
4.20  
3.80  
3.40  
3.00  
2.60  
2.20  
1.80  
1.20  
1.00  
0.60  
0.20

Log Time of Set

8.1 8.8 9.2 9.6 10.0 10.4 10.8

pH

24.8°C  
35.1°C



8.1

8.8

9.2

9.6

10.0

10.4

10.8



Phosphoric Acid Gels

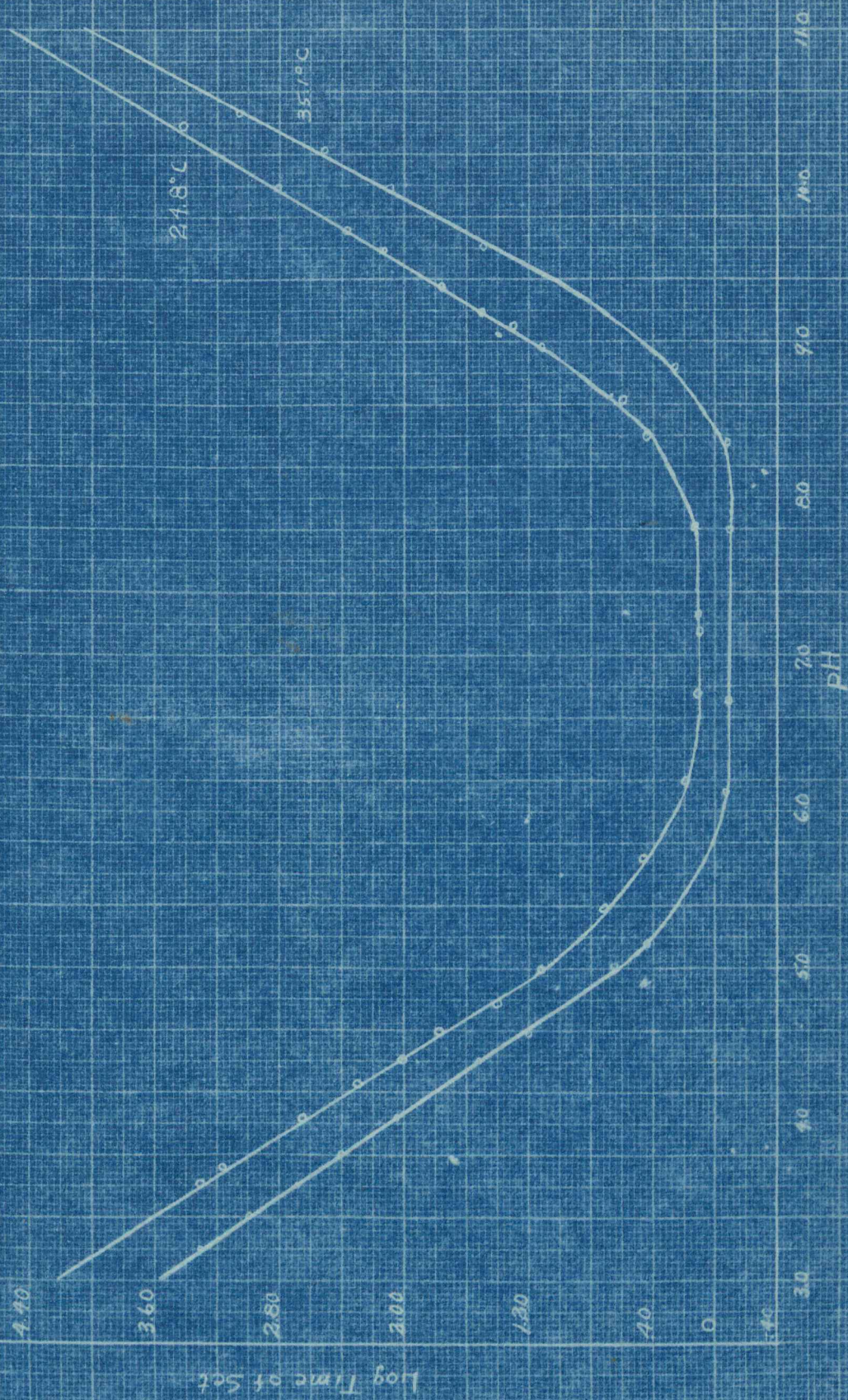




TABLE III

Interpolated values of log time of set.

A. Acidic gels

pH	Log Time of Set			
	<u>0°C</u>	<u>24.8°C</u>	<u>35.1°C</u>	<u>49.7°C</u>
5.0	2.00	1.06	.64	.32
4.5	2.88	1.93	1.36	.92
4.0	3.80	2.80	2.08	1.52
3.5	4.68	3.64	2.80	2.20
3.0	5.56	4.50	3.60	2.76

B. Basic gels

9.0	1.12	.50
9.5	1.96	1.32
10.0	2.80	2.16
10.5	3.60	3.00

TABLE IV

Calculated heats of Activation.

A. Acidic gels

<u>pH</u>	<u>Q</u>
5.0	18,320
4.5	21,343
4.0	24,724
3.5	27,022
3.0	30,503
Average value -- 24,382	

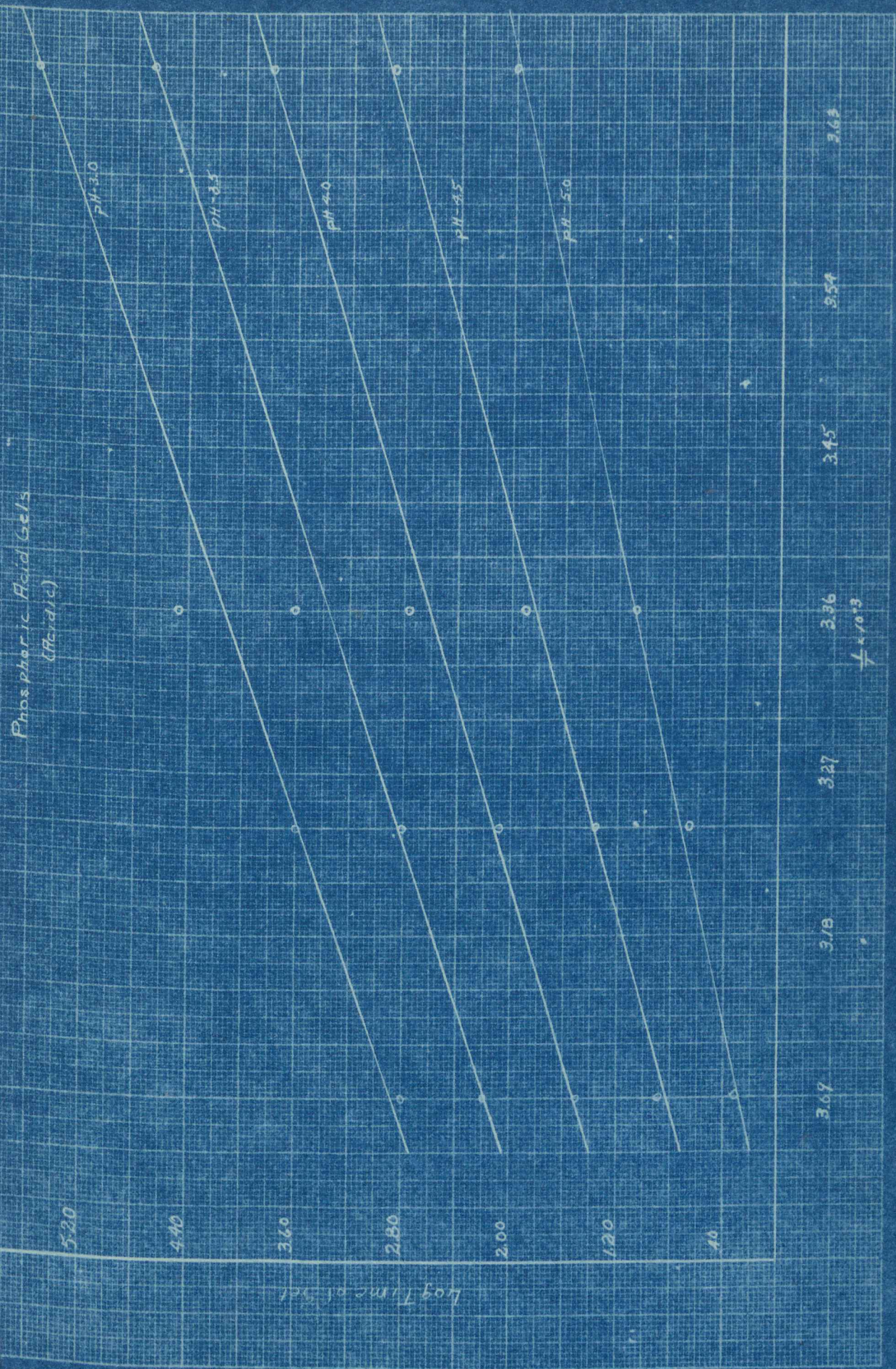
Basic gels

9.0	23,862
9.5	24,594
10.0	24,780
10.5	24,869
Average value -- 24,526	

Average value of basic and acid gels -- 24,454 calories



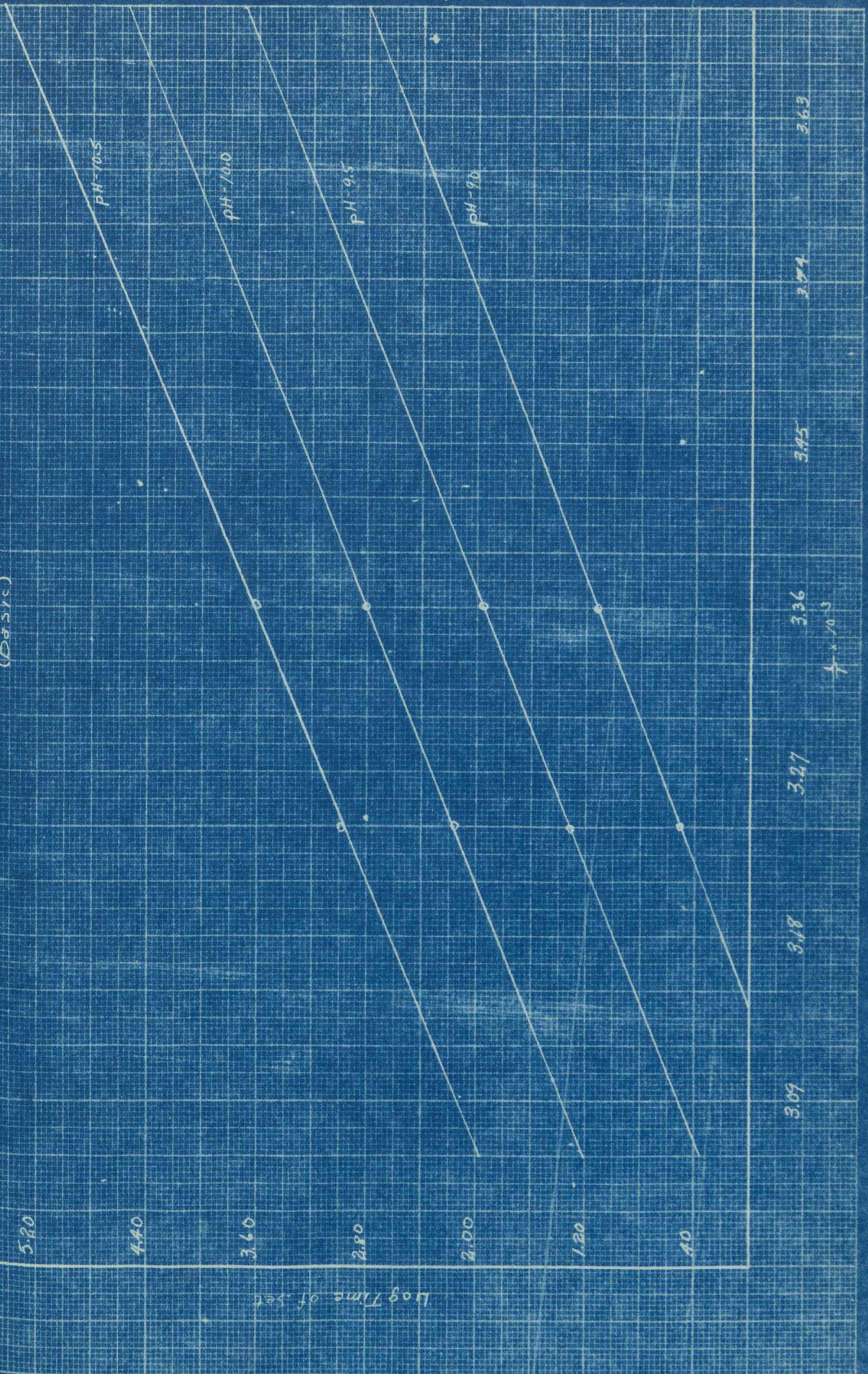
Phosphoric Acid Gels  
(Hardic)



$\frac{1}{\times 10^3}$



Phosphoric Acid Gels  
(Basic)



5.20  
4.40  
3.60  
2.80  
2.00  
1.20  
1.00

Log Time of Set

9.0 9.5 10.0

3.09 3.18 3.27 3.36 3.45 3.54 3.63

x 10<sup>3</sup>



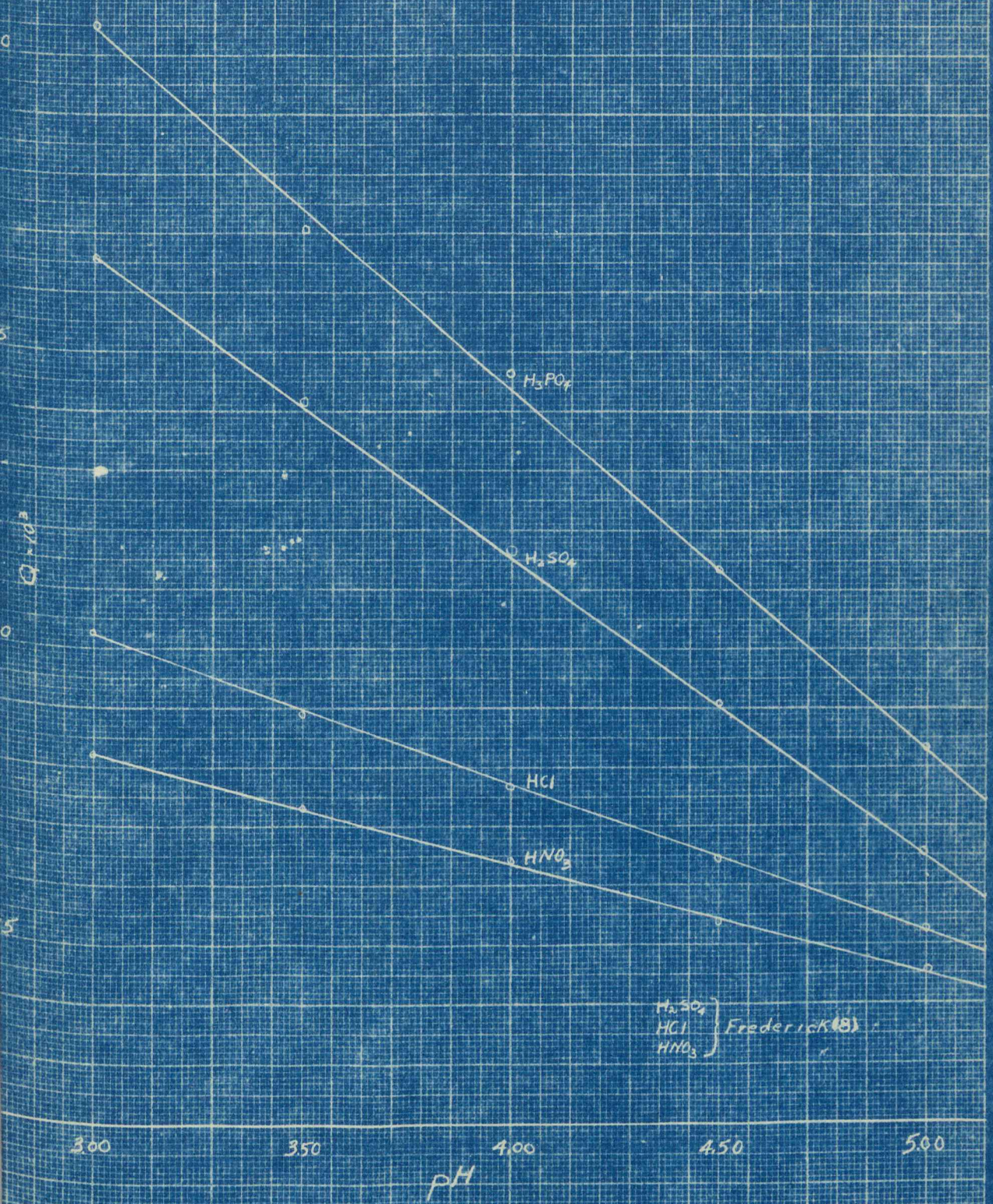




TABLE V

pH Drift

A. 35cc of phosphoric acid -- 2.043N

25cc of sodium silicate -- 1.25N

20cc of distilled water

Temperature -- 25°C

<u>Time Since Mixing (Minutes)</u>	<u>Log Time of Set</u>	<u>Emf. (Millivolts)</u>	<u>pH</u>
1.0	.0	-192.5	4.42
2.0	.30	-183	4.60
3.0	.48	-178.5	4.67
5.0	.70	-173.5	4.75
7.0	.85	-170.	4.80
9.0	.95	-168	4.85
14.0 set	1.15	-167.5	4.86
22.0	1.34	-167.5	4.86

B. 38cc of phosphoric acid -- 2.043N

25cc of sodium silicate -- 1.25N

17cc of distilled water

Temperature -- 25°C

1.0	.0	-218	4.01
2.5	.40	-206	4.20
3.5	.54	-203	4.26
5.5	.74	-198	4.33
7.0	.85	-194	4.40
8.5	.93	-192	4.44
11.5	1.06	-187.5	4.51
14.5	1.16	-183	4.58
17.5	1.24	-180	4.64



<u>Time Since Mixing</u> <u>(Minutes)</u>	<u>Log Time</u> <u>of Set</u>	<u>Emf.</u> <u>(Millivolts)</u>	<u>pH</u>
21.5	1.33	-178	4.68
26.5	1.42	-176	4.70
29.5	1.47	-176	4.70
56.5	1.	-176	4.70

39cc. of phosphoric acid -- 2.043N

25cc. of sodium silicate -- 1.25N

16cc. of distilled water

Temperature -- 25°C

1.0	.00	-240	3.62
2.0	.30	-225	3.89
4.0	.60	-216	4.05
6.0	.78	-211	4.13
8.0	.90	-208	4.16
12.0	1.08	-204	4.22
17.0	1.23	-194	4.40
22.0	1.34	-185	4.50
29.0 set	1.46	-184	4.57
32.0	1.50	-180	4.63
42.0	1.62	-180	4.63

40cc. of phosphoric acid -- 2.0431N

25cc. of sodium silicate -- 1.25N

15cc. of distilled water

Temperature -- 25°C

3.5	.54	-280	2.94
4.5	.65	-276	3.00
6.0	.78	-270	3.10



<u>Time Since Mixing (Minutes)</u>	<u>Log Time of Set</u>	<u>Emf. (Millivolts)</u>	<u>pH</u>
9.0	.95	-261	3.27
12.0	1.08	-258	3.31
18.0	1.26	-256	3.34
37.0	1.57	-254	3.41
60.0	1.78	-252	3.42
120.0	2.08	-251	3.43
180.0	2.26	-251	3.42
240.0	2.38	-251	3.42

E. 50cc. of phosphoric acid -- 2.043N

25cc. of sodium silicate -- 1.25N

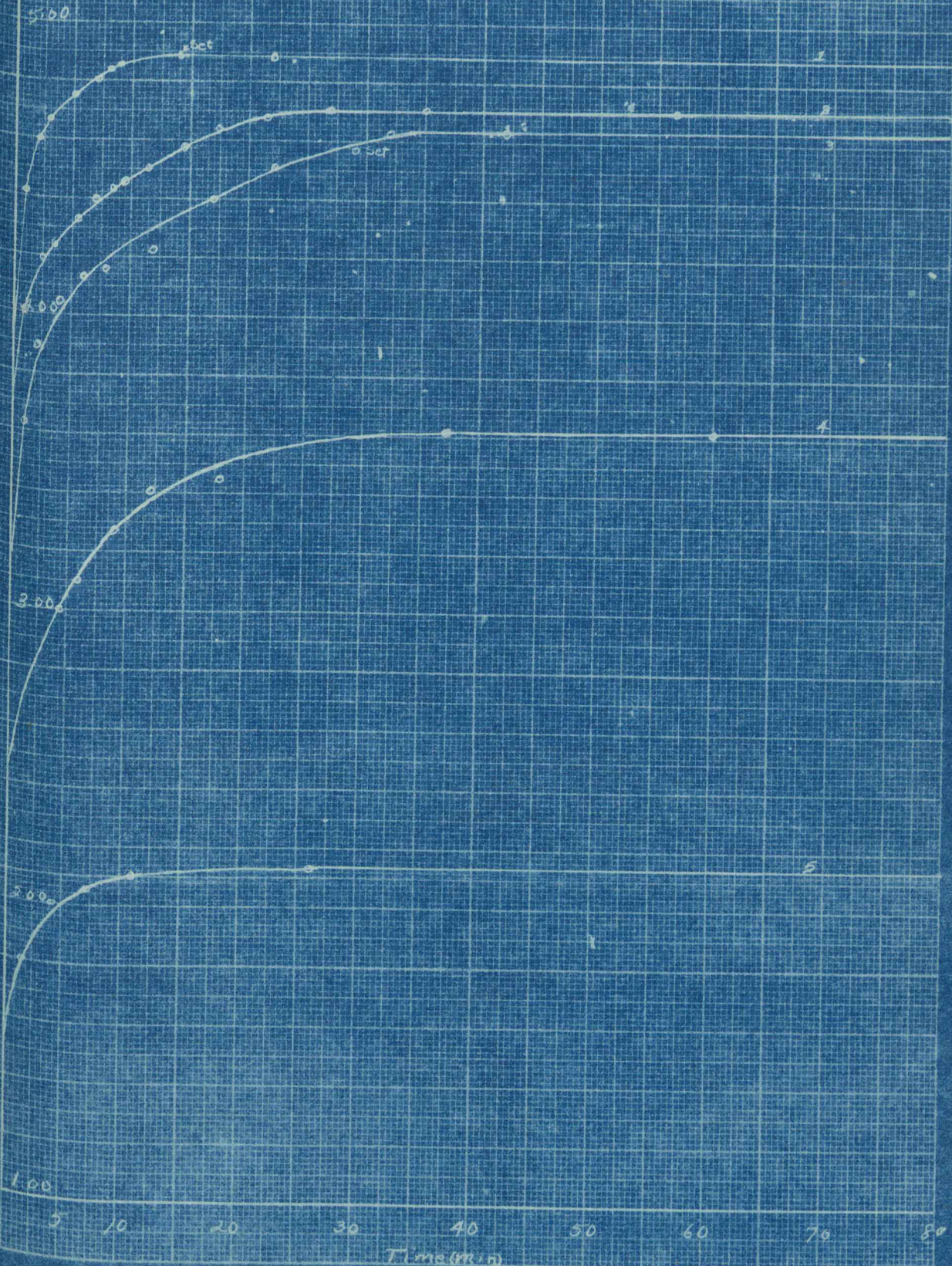
5cc. of distilled water

Temperature -- 25 °C

1.5	.18	-347.5	1.80
4.0	.60	-337	2.00
7.0	.85	-332.5	2.06
11.0	1.04	-330	2.10
26.0	1.42	-328	2.14
131.0	2.12	-327	2.15
431.0	2.63	-326	2.17
4560.0	3.66	-325	2.18
6060.0	3.78	-325	2.18



Phosphoric Acid Gels





## DISCUSSION OF RESULTS

It is rather difficult to give a detailed discussion of the pH drift because the exact cause of this phenomena is not known. However, this factor can be attributed to the splitting out of water from the mono-ortho silicic acid to form the more complex acids of silicic acid whose degree of ionization is lower. The pH tends to drift from a low pH to a higher pH for the acidic gels which can be explained by the above in that when two molecules of mono-ortho silicic acid combine and split out water, the stronger hydrogen ion and likewise the hydroxyl ion combine to form water thereby decreasing the hydrogen ion concentration and increasing the pH. As the molecules combine to form the more complex silicic acids, the stronger hydrogen ions and the hydroxyl ions seem to split out until the maximum complex molecules are formed, and at this point the pH remains constant. This is true for the acid gels only. As for the basic gels, time did not permit me to investigate the direction of the pH drift.

A short time was spent on determining the change of pH with the time after mixing. It was found that the greater part of the reaction occurs much before one-half of the time of set has passed. That is, the greater part of the pH drift occurs much before one-half of the time of set has passed. This also indicates that the formation of the more complex silicic acids from the mono-ortho silicic acid takes place during the previously mentioned time limit. With gels whose final pH was between 4.25-5.20, the pH drift occurred until approximately one-half the time of set had passed, whereas with the gels whose pH was below 4.25, the drifting stopped before one-tenth or less of the time of set had elapsed. This seems to indicate that the



time of set which was determined by the tilted rod method measures practically the complete reaction. The drift in pH for gels is practically negligible at the time of set for most gels.

It has been assumed that a linear function exists between the log time and reciprocal absolute temperature for the calculation of the heats of activation for these gels. This does not seem to be the case for the phosphoric acid gels as was also shown for gels prepared from the action of sulphuric acid and sodium silicate solutions as was shown by Frederick (8).

As was shown from the calculated values of the heat of activation for the acid gels, the heat of activation increases with decreasing pH. However, with the basic gels the heat of activation tends to be constant. This can be attributed to the fact that the basic gels were run only at two temperatures, therefore, the curves which were plotted were drawn through two points only. Under these conditions the curves for the various pH's could be drawn parallel. In order to get the true values for the heat of activation the gels should be run at at least two more temperatures.

Since the values for the heats of activation on both the basic and acid gels are practically equal indicates that the mechanism of the reaction is the same for both types of gels. However, the times of set are just the opposite to one another, that is, the time of set for the acid gels increased with a decrease in pH whereas for the basic gels the time of set increased with an increase of pH.

Frederick (8), who worked with the strong acids, found that the heat of activation for the gels prepared with sulphuric acid



was greater than those prepared with hydrochloric acid, and it was found in this research that the heat of activation for the gels prepared with phosphoric acid are greater than either those prepared with sulphuric and hydrochloric acids, indicates that the heat of activation is dependent on the number of hydrogen ions contained in each molecule of the acid. This is true for the stronger acids only.



SUMMARY

The effect of temperature upon the time of set of silicic acid gels, both basic and acidic, by mixing solutions of phosphoric acid and sodium silicate have been studied.

Values of the heat of activation for gels of phosphoric acid have been calculated. Average value of  $Q$  for the range of pH 3-5 was found to be 24,382 calories and for the range 9-10.5 was found to be 24,526 calories.

The pH of the gels were measured and it was found that for acid gels the pH increased with time of set, whereas for basic gels it increased with time.

The change of pH with time of the acid gels has been studied. The pH of these gels increased with time.



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