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# Time of Set of Silicic Acid Gels

Michael Priznar

*Union College - Schenectady, NY*

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TIME OF SET OF SILICIC ACID GELS

AS A FUNCTION OF THE TEMPERATURE

Michael Priznar UC 1936

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TIME OF SET OF SILICIC ACID GELS  
AS A FUNCTION OF THE TEMPERATURE

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

Michael Priznar

Approved by Charles B Hurd

May, 1936

## INTRODUCTION

The purpose of this work is to study the time of set of silicic acid gels as a function of the temperature. All data are confined entirely to acid gels made by mixing sodium silicate and an acid.

Previous work has been done on these gels, where investigators sought to determine the structure of the gels by investigating the effect of certain factors: temperature, concentration, viscosity, conductivity changes during setting, and hydrogen ion concentration on time of set.

They have shown the setting of a silicic acid gel is governed by a relation similar to Arrhenius' equation for a homogeneous chemical reaction.

In this investigation one brand of silicate was used. The following acids were used: monochloro acetic, trichloro acetic, and phosphoric. The time of set and pH were measured for the following gels, and log time against pH was plotted. From these graphs, log time versus reciprocal absolute temperature was plotted, and by means of a derived equation heat of activation was found for the different acids at different pH's.

## HISTORICAL

The first investigation of silicic acid gels goes back to the middle of the nineteenth century. Since then, investigators have worked on these gels in order to find what the structure of these gels was. Several theories have been proposed, and one of the earliest was proposed by Negeli<sup>1</sup>. This theory, called the Micelle theory, proposed the solid colloidal matter of the solution formed small molecular aggregates which locked together to form the so-called silicic acid gel. In 1914, Proctor and Robinson<sup>2</sup> proposed the fibrillar theory which pictures the gel as being composed of long thread-like chains which spread out on polymerization, forming a structure similar to a cobweb. This theory has been corroborated by men such as Zsigmondy<sup>3</sup>, Von Wiemarn<sup>4</sup>, Bogue<sup>5</sup>, and Bailey<sup>6</sup>.

Much work has been done on properties of gels and factors affecting gel reactions. Fleming and Holmes<sup>7</sup> were the first to study the time of set as a function of the temperature. Hurd and Letteron<sup>8</sup> followed up this work and showed that for acetic acid, log of time was a linear function of reciprocal absolute temperature:

$$\frac{d \ln t}{d(1/T)} = -\frac{Q}{R} \quad \text{where } Q \text{ is Arrhenius' heat of reaction}$$

This came out to be about 16,940 calories/gram molecule. Hurd and Miller<sup>9</sup> worked further, using six different silicates, and found mean value of heat of activation to be about 16,500 calories/gram molecule. Haynes<sup>10</sup> found it to be about 17,292 calories.

Other properties of these gels have been studied: viscosity during setting and the effects of salts on the time of set. The common ion effect was studied by Hurd and Rothemich<sup>11</sup>, who found that sodium acetate reduced time of setting, while sodium chloride gave no effect.

Syneresis, the gradual exclusion of water from a gel when allowed to stand for some time, has been studied recently by Bonnel<sup>12</sup>. He stated that the

hydrogen ion concentration had a marked effect on the velocity of syneresis, that for a pH range from eleven to eight the velocity increases, below eight the velocity decreases. He also concluded that the vapor pressure of the water is taken up by the gel in an uncombined form.

There have been several recent theories on gels. Prakash<sup>13</sup> proposed that the gel results from metathetical reactions by formation of a colloidal phase of sufficient concentration stabilized by ions of one charge, and subsequent coagulation by absorption of ions of opposite charge. If at the same time the particles become hydrated, the precipitate is gelatinous. If hydration predominates, we have opaque gels. If the gel is transparent, agglomeration is negligible in comparison with hydration. Holmes states that acid molecules have a dehydrating effect upon silicic acid. Laskin<sup>14</sup> believes that certain ions in solution possess a dehydrating effect. Kroger<sup>15</sup> reported that sodium ions in solution have a peptizing effect upon silicic acid.

From their studies on these gels Hurd, Raymond and Miller<sup>16</sup> concluded that peptizing action in alkaline mixtures containing silicic acid is due to hydroxyl ion, and that this same hydroxyl ion acts as a catalyst in the acid mixtures.

## EXPERIMENTAL

The silicic acid gels were made by the reaction between a water solution of commercial sodium silicate and an acid. The sodium silicate used was the "E" brand made by the Philadelphia Quartz Company. The  $\text{Na}_2\text{O}/\text{SiO}_2$  ratio by weight was 1/3.19 with a specific gravity of 1.394. The distilled water used was always boiled for several minutes to insure a minimum carbon dioxide content, because the carbon dioxide has a coagulating effect on silicate solutions. All the chemicals used were chemically pure substances. The sodium silicate was diluted approximately to a certain normality and then standardized against standard sulfuric acid using methyl orange as the indicator. The other acids used were titrated with standard sodium hydroxide using phenolphthalein as the indicator.

The gel mixtures made up to a volume of 160 cc., 50 cc. being silicate solution measured out with the same 50 cc. pipette throughout, and the remaining 110 cc. being acid and water, the respective volumes of each being measured out with burettes. The silicate and water and acid solutions were placed in 250 cc. beakers, and these beakers covered by watch glasses were placed in a water bath  $1.5^\circ\text{C}$ . below the working temperature. At the same time, two 100 cc. K beakers were placed in a water bath at the working temperature. After letting beakers and solutions remain in the bath for forty minutes, the silicate and water and acid solutions were mixed by pouring the silicate into the water and acid solution, and the result mixed thoroughly by pouring back and forth several times. Then it was divided into two 80 cc. portions, one portion being poured into a 100 cc. beaker and placed in the water bath at the working temperature, where the time of set was determined by the tilted rod method; the other portion being placed in a water bath at  $25^\circ\text{C}$ ., where the pH was determined by the quinhydrone method, using a platinum wire electrode and solid quinhydrone.

The reason for heating the solution to 1.5° C. below working temperature is that when the silicate and acid are mixed, there is a rise in temperature due to the neutralization of the sodium hydroxide by the acid. The tilted rod method is the method of determining when the gel set. The glass rod was 10 cm. long and 3 cm. thick, and tapered at one end so that the gel would not be too ruptured during testing. The gel was considered set when the rod was supported at an angle of 20° to the vertical. The quinhydrone method consists merely of taking the potential of the gel by a Quinhydrone Potentiometer Calomel Cell platinum wire set-up. The potential was converted into pH by the use of a derived equation:

$$\text{pH } 25^{\circ} \text{ C. } = \frac{.4532 - E}{.0591} \quad \text{where } E \text{ is the measured potential.}$$

Owing to the difficulty in getting the potential of the setting gel, the platinum wire had to be cleaned often. This was done by washing the platinum wire in boiling sodium hydroxide and rinsing in hydrochloric acid and water, and then flashing in flame. This cleaned the electrode satisfactorily.

The work was carried out at different temperatures for the different acids: monochloro-acetic, 0°, 25.3°, 35.2°, and 50.1° C.; trichloro-acetic, 0°, 25.3°, 35.1°, and 50.1° C.; and phosphoric at 25.0° and 35.1° C. The procedure was somewhat different in the 0° runs. The total volume was 240 cc., of which 75 cc. was silicate and the rest acid and water. These mixtures were placed in 250 cc. Erlenmeyer flasks and cooled down by placing them in a snow bath. After bringing the mixtures down to 0° C., they were mixed and divided into two portions, one portion of 160 cc. placed in a 200 cc. Erlenmeyer flask which had been cooled also, where the time of set was recorded by the tilted rod method; the other portion of 80 cc. placed in a 100 cc. beaker, where the potential was recorded with the Quinhydrone Potentiometer set-up mentioned above.

In the case of the 50.1° C. runs, the temperature of the gel was recorded, and not the water bath itself. The gel did not reach the temperature of the bath because of radiation. In the taking of the time of set by the tilted rod method, the watch glass was removed only for a very short time while the gel was being tested, because evaporation has a marked effect upon the time of set.

## RESULTS

The time of set was taken along with the potential. The log of time of set was then plotted as ordinates against the pH as abscissae, where the potential was converted into pH.

Sodium silicate Normality - 1.2599

Monochloro-acetic acid Normality - 2.001

### At 0° C.

<u>Time of set (min.)</u>	<u>Log time</u>	<u>Millivolts</u>	<u>pH</u>
2158	3.334	180	4.63
3051	3.479	187	4.51
3983	3.602	194	4.38
4989	3.698	202	4.25
6373	3.804	208	4.15
7224	3.859	212	4.08

### At 25° C.

541	2.733	224	3.88
528	2.723	222	3.92
478	2.679	219	3.96
378	2.577	212	4.08
313	2.496	210	4.12
245	2.389	202	4.25
205	2.312	197	4.33
161	2.206	189	4.45

### At 35.2° C.

136	2.134	205	4.20
188	2.274	215	4.03
220	2.342	219	3.96
254	2.405	223	3.90
277	2.442	226	3.84
319	2.504	230	3.78

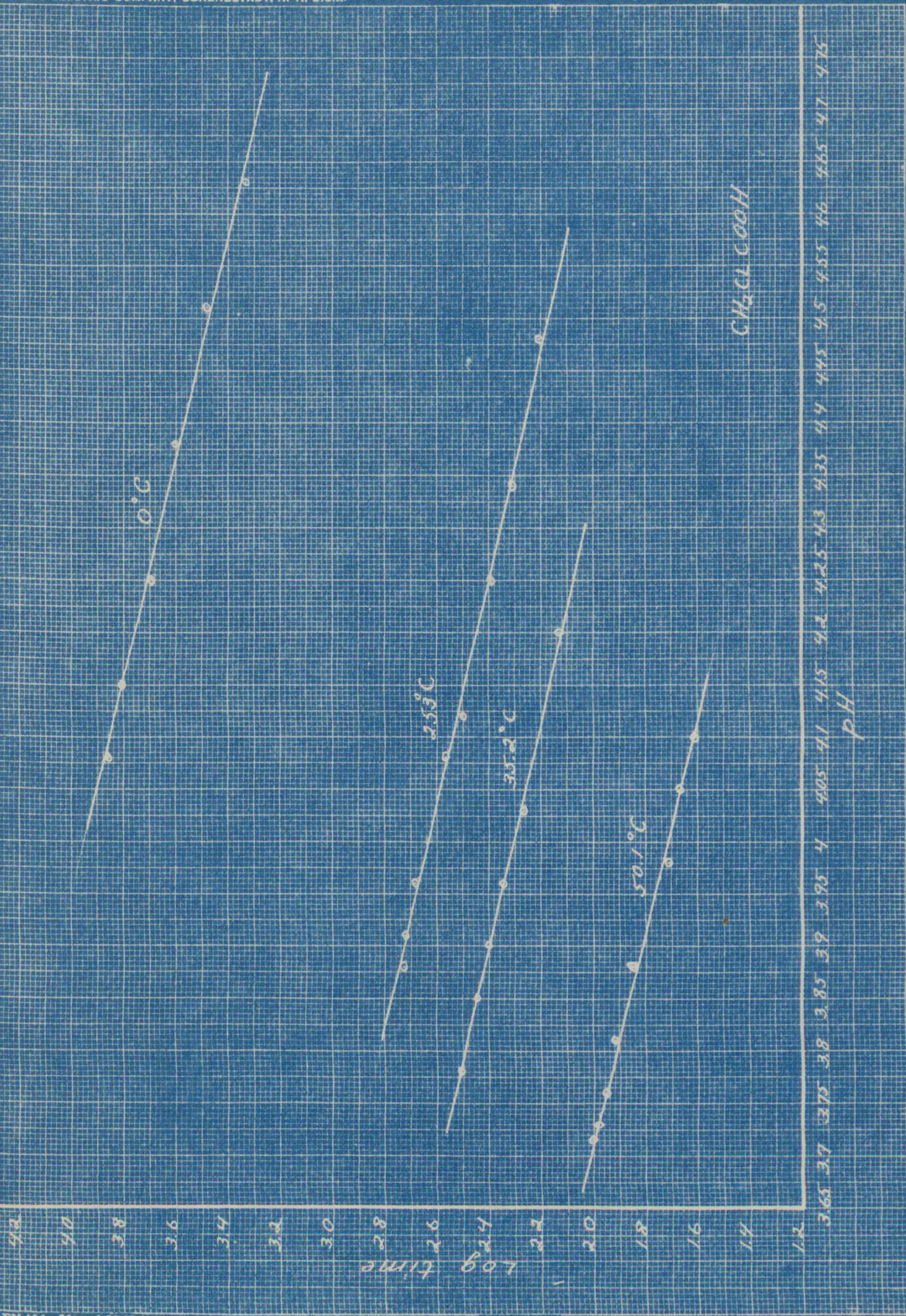
### At 50.1° C.

41	1.613	211	4.10
46	1.663	214	4.05
51	1.708	218	3.98
70	1.845	224	3.88
82	1.914	228	3.86
89	1.949	231	3.81
95	1.978	233	3.75
102	2.009	234	3.72

These data when plotted were linear and practically parallel to one another. Similar work on weak acids was done by Haynes. While monochloroacetic acid is a stronger acid than acetic, nevertheless it is a weak acid, and one would conclude that these curves should be similar to the ones done by Haynes. This is shown to be the case on the following graph.

The amounts of acid were varied in each case. These amounts were varied about .2 cc. in each case, starting as close to the neutralization point as possible, which was about 16 cc., to a maximum of 18 cc. to 25 cc. of silicate, and according to the temperature used. As was shown by previous workers, the greater the amount of acid, the longer the time of set; and the higher the temperature, the shorter the time of set. This likewise was noticed in working with all three acids.

It was noticed that when the potential was being obtained, there was a peculiar drifting effect - that is, the potential was not constant, but kept going downward. This drifting effect continued even after the gel had set. However, the potential of the gel was not taken until the potential of the gel was constant for quite a long period. Nevertheless, even still, the gel would drift, though very slowly.



Trichloro-acetic acid Normality - 1.9932

At 0° C.

<u>Time of set (min.)</u>	<u>Log time</u>	<u>Millivolts</u>	<u>pH</u>
45	1.653	111	5.8
82	1.914	123	5.6
135	2.130	132	5.45
1734	2.391	146	5.21
1889	2.762	164	4.90
2178	3.381	191	4.44
5240	3.720	208	4.14
5960	3.755	210	4.11

At 25.3° C.

3	.477	100	5.98
7	.845	118	5.68
12.5	1.097	130	5.48
23	1.361	148	5.18
49	1.690	161	4.96
75	1.875	175	4.71
99	1.995	180	4.63
190	2.278	195	4.38

At 35.1° C.

19	1.279	156	5.05
40	1.602	173	4.74
58	1.763	183	4.58
108	2.033	198	4.33
184	2.265	214	4.05
342	2.534	229	3.80
473	2.675	238	3.65

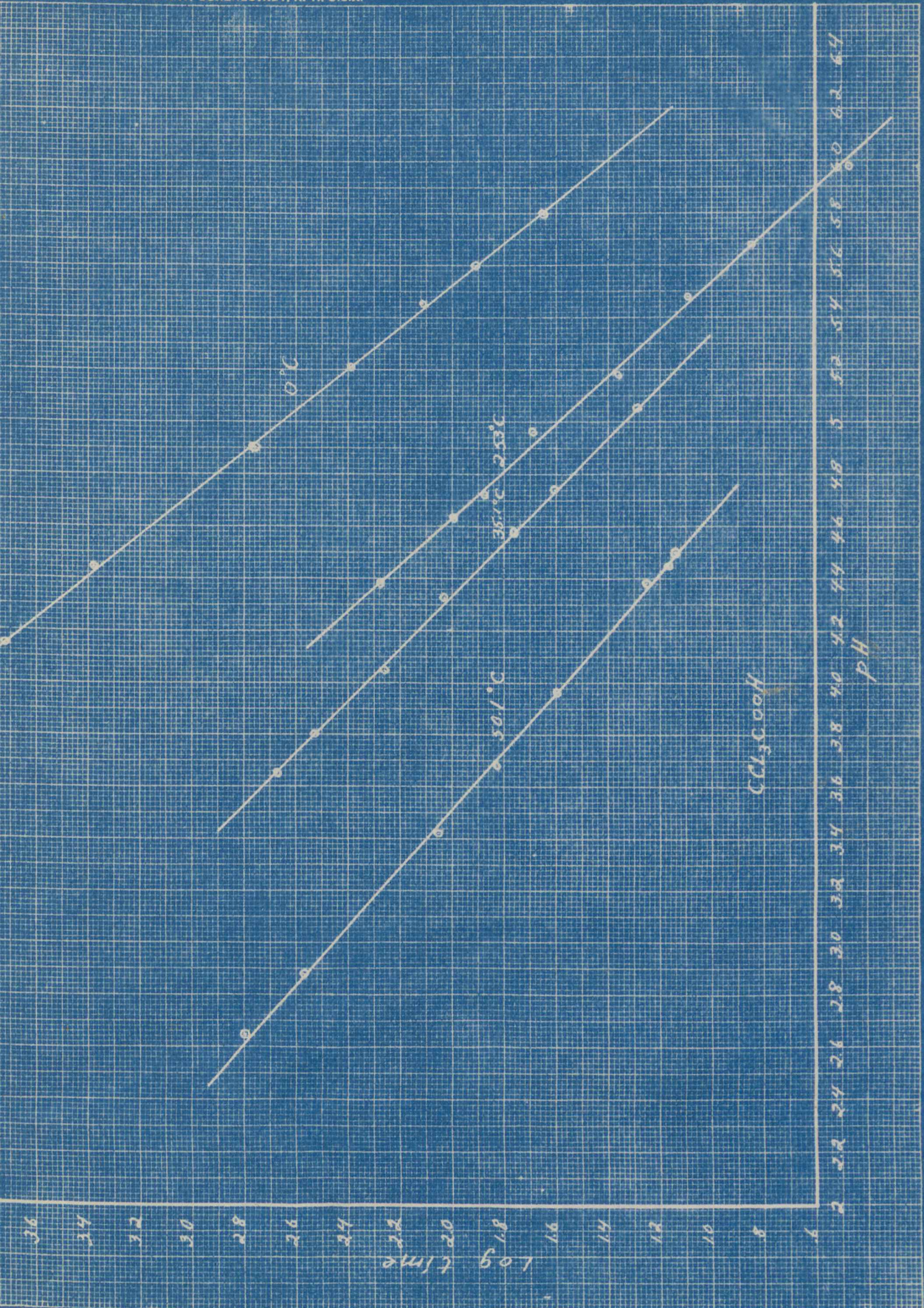
At 50.1° C.

14	1.146	188	4.49
15	1.176	191	4.45
18	1.255	195	4.38
40	1.602	219	3.96
67	1.826	236	3.68
115	2.061	251	3.42
379	2.579	283	2.88
620	2.793	297	2.65

The amounts of acids were varied similarly to the procedure of the monochloro-acetic acid, but since trichloro-acetic acid is a stronger acid, amounts were taken very close to the neutralization point.

The pH was plotted against the log time for the different temperatures, and the curves were all straight lines. However, the slopes were not parallel - that is, as the temperature went up, the slope decreased. This is illustrated on the following graph. A co-worker has reported a similar effect, working upon hydrochloric and sulfuric acids.

The peculiar drifting effect which occurred in the monochloro-acetic acid was again noticed in the trichloro-acetic acid, but very much more prominently. It was noticed that the drifting of the potential occurred over a greater length of time than the monochloro-acetic acid. It seems, therefore, that the stronger the acid, the greater and longer the drift, for it was reported that no drift occurred in the acetic acid gels, and the drift in the monochloro-acetic acid is much less than that of the trichloro-acetic acid. It is hoped that future work will confirm this result.



Phosphoric acid Normality - 2.004

At 25° C.

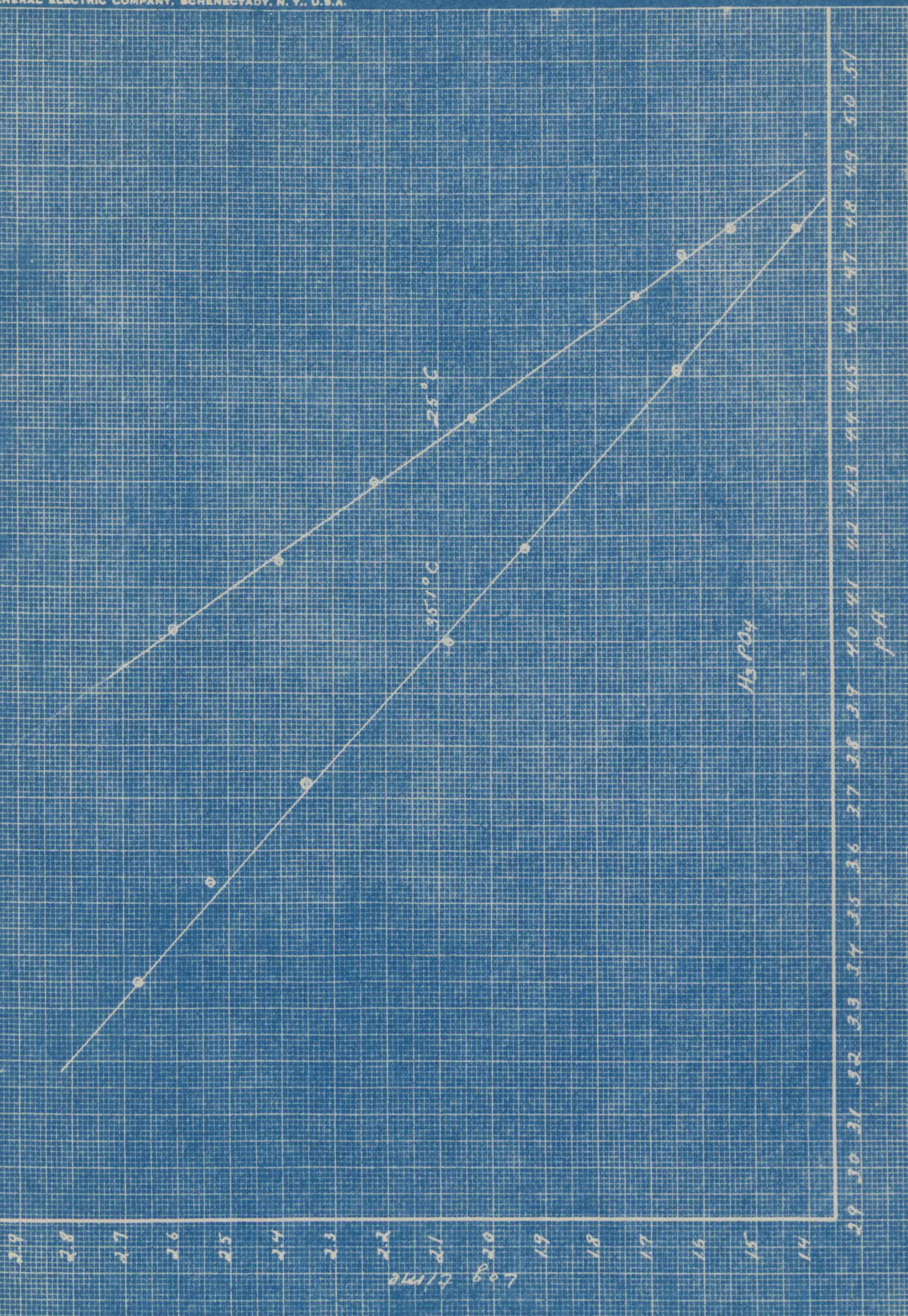
<u>Time of set (min.)</u>	<u>Log time</u>	<u>Millivolts</u>	<u>pH</u>
39	1.591	171	4.78
43	1.635	174	4.73
53	1.724	179	4.65
109	2.037	195	4.42
167	2.220	199	4.30
260	2.415	208	4.15
405	2.607	216	4.02

At 35.1° C.

26	1.415	171	4.78
44	1.643	187	4.51
85	1.929	196	4.18
119	2.075	218	4.00
224	2.351	233	3.73
343	2.535	244	3.54
476	2.667	256	3.35

In working with phosphoric acid, several interesting results were obtained:

1. The amount of acid used was almost double the amount of monochloro-acetic acid which was used in the previous run. This was necessary to make it an acid gel. This amount was about 61 cc., whereas 32 cc. were used in the monochloro-acetic acid.
2. Phosphoric acid is a very strong acid, but there was no abrupt change of pH, as greater amounts of acid were used, while in the case of trichloro-acetic acid, there was an abrupt change in pH upon addition of only a few tenths of a cc. This abrupt change in pH was noticed in the work of a co-worker (Frederick), who was working on strong acid gels.
3. When about 67 cc. were used in a gel mixture, there was noticed a cloudy suspension. This settled down to the bottom of the beaker. Stirring this precipitate gave a different pH than when it was not stirred. However, no suspension was noticed when the amount was close to the neutralization point.



There were only two temperatures used because of lack of time. The pH was plotted against the log of time. It was noticed again that as the temperature increased, the slope decreased. This was mentioned in the case of the trichloro-acetic acid.

Hurd and Letteron made the following assumptions in interpreting their result on a similar type of work:

1. We are dealing with a process which follows the laws of ordinary chemical reactions as far as velocity is concerned.
2. We may apply Arrhenius' equation to our results.
3. The time of set measures the time when a certain portion of the silica, in whatever form, has reacted.

In developing our ordinary equations for the velocity of a chemical reaction, we have:

$x$  - amount changed in time  $t$

$a$  - original concentration

$n$  - order of the reaction.

We can obtain the following:

$$1. \quad dx/dt = k(a-x)^n$$

$$2. \quad dx/(a-x)^n = k dt$$

$$3. \quad \frac{1}{n-1} \left( \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right) = kt$$

It is easily shown that for any fractional changes of the concentration,  $a$ , the time,  $t'$ , is given by the reaction

$$4. \quad t' = c'/ka^{n-1}$$

where  $c'$  is a constant depending on  $x/a$  and on  $n$ .

We may now write Arrhenius' equation

$$5. \quad \frac{d \ln k}{dT} = \frac{Q_2}{RT} \quad \text{or} \quad \frac{d \ln k}{d(1/T)} = \frac{Q}{R}$$

If we now maintain  $a$  and  $x/a$  constant, we may obtain from 5 and 6,

which is

$$6. \ln t' = \ln c' - \ln k - (n-1) \ln a$$

the following equation:

$$7. \ln t' = Q/RT - (n-1) \ln a \quad c''$$

Differentiating, with a constant gives

$$8. \frac{d \ln t'}{d(1/t)} = \frac{Q}{R}$$

For the three acids used, the reciprocal absolute temperature as abscissae was plotted against log of time as ordinates, using certain values of pH.

Monochloro-acetic acid:

The four curves were plotted, and were found to be linear for different pH's.

Results:

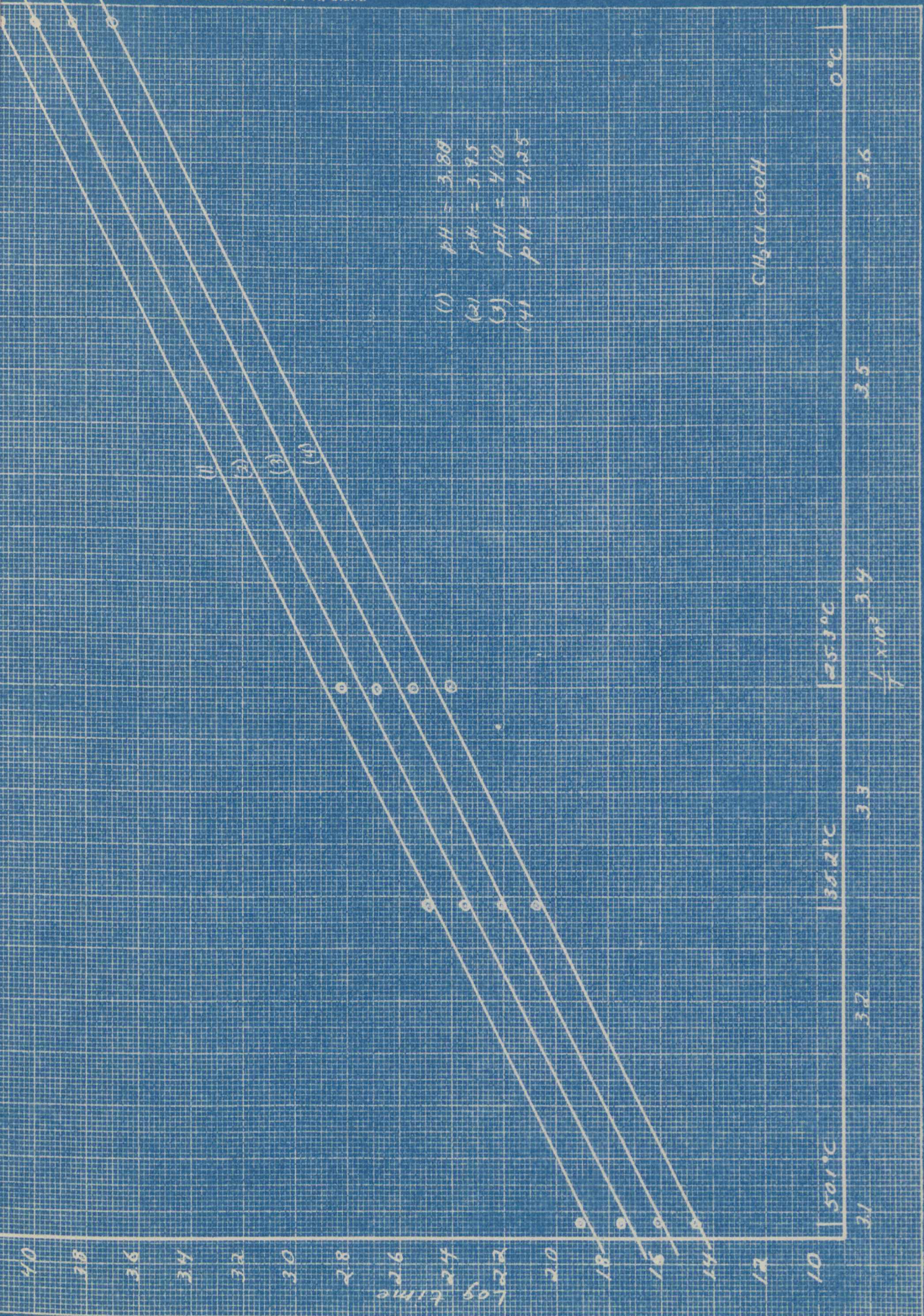
Value of slope of curve for log of time of set against reciprocal absolute temperature:

<u>pH</u>	<u>slope</u>	<u>value of heat of activation</u>
3.8	3959	18,115
3.95	3961	18,124
4.10	3960	18,120
4.25	3930	<u>17,985</u>

Average 18,086 calories per gram molecule

The value of the heat of activation was obtained by multiplying the slope by 2.703 R, where R is a constant.

The average value for the heat of activation of monochloro-acetic acid is 18,086 calories/gram molecule. This seems plausible, for this is stronger acid than acetic, and therefore would cause a greater heat in reacting.



## Trichloro-acetic acid:

Here again log time was plotted against reciprocal temperature. There was noticed that the curves are not straight lines, but seem to follow a straight line from zero to  $35.1^{\circ}\text{C.}$ , and then from  $35.1$  to  $50.1^{\circ}\text{C.}$  curves downward. Why this part of the curve curved downward is peculiar, for it did not happen in the cases of acetic and monochloro-acetic acids. The time of set at  $50.1^{\circ}\text{C.}$  was carefully measured, because evaporation caused a cooling effect, thereby producing a longer time of set. If the pH was made greater, the curvature would not have occurred, but the potential of these gels had a constant value when measured.

Upon looking at the curves (log of time of set against reciprocal absolute temperature), it is seen that the curves are not parallel, and that the greater the pH, the greater the slope.

In order to calculate the heat of activation, it is necessary to divide the whole line into two portions, the curve portion, and the straight line portion. We will find the ratio of one portion to another, and their slopes, thereby enabling us to get an average slope for the whole line.

Ratio of curve portion to straight line portion - 1 to 3.42

Example:

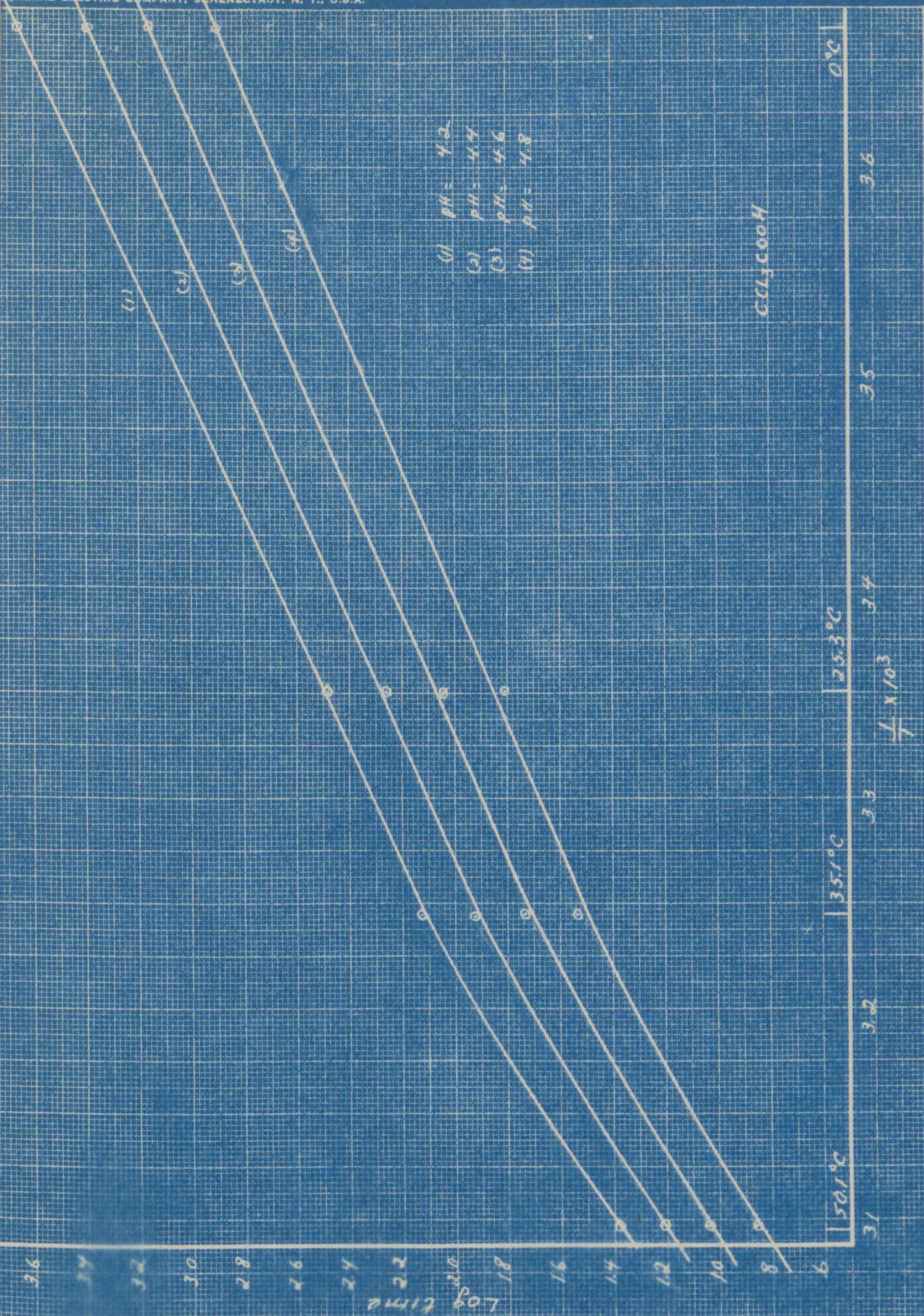
At pH equal to 4.2

slope of curve portion	5000
slope of straight line portion	3692
Multiply 5000 by 1	5000
Multiply 3692 by 3.42	<u>12626</u>
Totalling	17626, hence average slope is 3988 (divide total by 4.42)

Results:

<u>pH</u>	<u>Average slope</u>	<u>Heat of Activation</u>
4.2	3988	18,244
4.4	3866	17,686
4.6	3777	17,043
4.8	3649	<u>16,694</u>

Total average 17,416 calories per  
gram molecule



### Phosphoric Acid:

This acid, as has been said before, gave some interesting results.

As it was only used at two temperatures, 35.1 and 25° C., the heat of activation can be found, but these results are not quite complete.

#### Results:

<u>pH</u>	<u>Slope</u>	<u>Heat of activation</u>
3.8	5835	26,670
4.0	4785	21,380
4.2	3844	17,577
4.4	3000	13,728
4.6	2000	9,152
4.8	1219	5,577

These results are very varied. More work should be done on phosphoric acid, using all four temperatures: 0, 25, 35 and 50° C.

Due to the lack of time, the other two temperatures were neglected, but it is hoped that more work will be done on phosphoric acid.



### SUMMARY

The set time of silicic acid gels has been studied as a function of the temperature, using the following acids: monochloro-acetic, trichloro-acetic, and phosphoric; and the following temperatures: 0, 25, 35, and 50° C.

Monochloro-acetic acid behaved just like acetic acid. The mean value of the heat of activation for monochloro-acetic acid was about 18,000 calories/gram molecule, while Haynes found a value of 17,292 calories/gram molecule.

Trichloro-acetic acid did not follow the behavior of monochloro-acetic acid quite completely, as there was a dip in the curve. Using an average value for the slope of the curve, the mean value for the heat of activation for trichloro-acetic acid was found to be 17,416 calories/gram molecule.

Phosphoric acid was not studied completely. Results as were obtained have to be re-checked. Due to several interesting factors, and lack of time, the acid was only used at two temperatures.

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