

6-1936

Effect of salts on the setting time of silicic acid gels

Gustav F. Hallstrom

Union College - Schenectady, NY

Follow this and additional works at: <https://digitalworks.union.edu/theses>

 Part of the [Chemistry Commons](#)

Recommended Citation

Hallstrom, Gustav F., "Effect of salts on the setting time of silicic acid gels" (1936). *Honors Theses*. 1837.
<https://digitalworks.union.edu/theses/1837>

This Open Access is brought to you for free and open access by the Student Work at Union | Digital Works. It has been accepted for inclusion in Honors Theses by an authorized administrator of Union | Digital Works. For more information, please contact digitalworks@union.edu.

A thesis, presented to the Department of
Chemistry of Union College, in partial ful-
fillment of the requirements for the Degree
of Bachelor of Science in Chemistry, by

Gustav F. Hallstrom

Approved by

Charles B. Hurd

May 22, 1936.

THE EFFECT OF SALTS ON THE SETTING TIME
OF SILICIC ACID GELS

UNION COLLEGE
LIBRARY

INTRODUCTION

It has been stated by Prasad and Hattiangadi (1) that the process of setting of mixtures of solutions of sodium silicate and acetic acid consists of three stages:

- (a) The formation of silicic acid by the interaction of the acid with sodium silicate.
- (b) The formation of the colloidal solution of silicic acid.
- (c) The coagulation of the colloidal solution by the electrolytes liberated in the first reaction.

The present investigation was undertaken with a view to examine the effect produced on the time of setting of the silicic acid gels by the addition of extra quantities of electrolytes to the gel-forming mixtures. As the pH of the gel-forming mixture has a marked effect on the time of setting any change in pH of the mixture due to the addition of the electrolyte was carefully noted.

HISTORICAL

The time of setting of silicic acid gels has been found to be affected by various factors. The fundamental factors are:

- (1) The concentration of silica
- (2) The concentration of acid
- (3) Agitation
- (4) Temperature
- (5) The pH of the mixture
- (6) The presence of additional soluble materials

Holmes (2) noted the effect of the acid and gives directions for the preparation of gels setting in any desired time. Holmes also found that the time of set was different for equal concentrations of different acids. Studies of the effect of the acid has also been made by Fleming (3) and Hurd and Letteron (4). The later also found that the logarithm of the time of set could be represented as a linear function of the reciprocal of the absolute temperature. Fells and Firth (5) observed that a slight alkalinity in the neighborhood of the neutralization point brought about immediate setting of the gel. Ray and Ganguli (6) in studying the effect of the pH on the setting of silicic acid gels found that for each concentration of alkali silicate there is a limiting range of pH in which gel-formation takes place. Hurd, Raymond and Miller (7) have investigated the effect of the hydrogen-ion concentration upon the time of set. Numerous investigators have studied the effect of adding soluble material to the gel mixture. Krozer (8) noted that sodium tungstate lowered the time of setting for silicic acid gels prepared from hydrochloric acid and sodium silicate. Hurd and Carver (9) studied the effect of various organic compounds upon the time of set. The effect of salts upon the time of set has been investigated by Werner (10), Pappada (11) and Prasad and Hattiangadi (12). The investigation carried out in this paper is somewhat similar to that of Prasad and Hattiangadi.

EXPERIMENTAL

Preparation of solutions:

The sodium silicate used in all investigations was the "E" brand silicate produced by the Philadelphia Quartz Company. Its $\text{Na}_2\text{O}/\text{SiO}_2$ ratio by weight was 1/3.19. The silicate was diluted with freshly boiled water. By titrations with standard sulfuric acid its normality with respect to sodium hydroxide was found to be 1.254 N. Methyl orange was used as the indicator.

The acetic acid used in all investigations was prepared from 99.5% glacial acetic acid by dilution with distilled water. Its strength was determined by titration with standard sodium hydroxide, using phenolphthalein as the indicator and found to be 2.004 N.

All salts added to the gel mixture were prepared by weighing out samples of the salt and diluting with freshly boiled distilled water to the desired normality.

Mixing of the solutions:

In making the gels 50 cc silicate solution was placed in one beaker and the other constituents namely; 50cc acetic acid solution and 60 cc salt solution plus boiled distilled water were placed in another beaker. The amount of salt solution was varied but the total volume of salt solution plus water was always 60 cc. All volume measurements were made with pipettes. These beakers were placed in a water bath at 23.5°C. In mixing the silicate solution was always poured into the acid

solution. Equal volumes of the mixture were poured into two 100 cc beakers. One of these was placed in a water bath at 25.0 C where the time of set was determined. The other was placed in a water bath at 25.0 C where the pH was determined. In order to prevent excess evaporation watch glasses were placed over the mixtures.

Determination of the time of set:

It was impossible to determine the exact time of set as there were no means of determining when the three stages of the process of setting were absolutely completed. However a relative time of set was obtained by the tilted rod method described by Hurd and Letteron (4). The method consists of inserting a small stirring rod into the gel at an angle of about 20° to the vertical until the gel is stiff enough to hold the rod in the tilted position. The glass rod is about 3 m.m. in diameter, about 8 cm. long and drawn to a point. It has been found that this method gives results in time accurate to two percent.

Determinations of the pH

The quinhydrone method of determining the pH was used. Hurd and Griffeth (13) made a careful study of the applicability reliability of this method and they found that it gave reliable results. Laskin (14) found close agreements between measurements of pH of silicic acid sols by means of a Pt, H₂ electrode and the quinhydrone method. In some cases in this investigation the pH changed slightly during the setting of the gel, for such cases the final constant reading was taken. The Pt electrode used in the quinhydrone determination of pH was fre-

quently cleaned with a solution of sodium hydroxide in order to loosen any coating of silica which might have collected on the Pt.

RESULTS

The effect of sodium, potassium and lithium salts of hydrochloric acid on the gel-forming mixture has been studied and as shown in Tables 1, 7, 8 and in Figure 1 each of these salts caused a marked decrease in the time of set. Each of the salts caused an appreciable decrease in the pH which should cause an increase in the time of set estimated at about nine minutes in the case of the highest concentration of the salts.

The effect of the potassium and sodium salts of sulfuric and nitric acids is shown in Tables 2, 3, 9, 10 and in Figures 2 and 3. Here again a decided decrease in the time of set is noticed. The decrease in pH was the same as for the chloride salts with the exception of potassium sulfate which showed no change in pH.

Mono-sodium phosphate in small concentrations decreased the time of set as shown in Table 4 and in Figure 2, but in larger concentrations the time of set was increased. The pH varied considerably in these mixtures at first increasing and then as the concentration of the salt became larger the pH decreased. The pH no doubt played the important part in the variation of the time of set.

Di-sodium phosphate decreased the time of set more than

any other salt studied. However the pH of the mixture was increased considerably and consequently most of the decrease in time of set was due to the increase in pH.

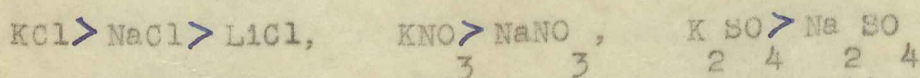
Sodium oxalate decreased the time of set, but as the concentration of the salt was increased a minimum point was reached as shown in Figure 4.

The effect of bivalent and trivalent basic radicals could not be studied as most of these react to give insoluble silicates.

DISCUSSION OF RESULTS

It will be seen in Figures 1, 2, 3, and 4 that the addition of salts with the exception of mono-sodium phosphate accelerates the gel-formation in acid mixtures. The increase in time of set in the presence of mono-sodium phosphate can be accounted for by the decrease in pH.

Not considering the phosphate and the oxalate salts the order in coagulating power of the salts studied is as follows:



This is a confirmation with the observation of Prasad and Hattiangadi (12) who found the same order for the coagulating power to be true in both acid and basic gel mixtures. The coagulating power seems to be intimately connected with the position of the metals in the periodic system being of the order: $\text{K} > \text{Na} > \text{Li}$. Pappada found the order to be $\text{Cs} > \text{K} > \text{Na} > \text{Li}$.

It is evident from Figures 2 and 3 that the coagulating power of the anion is in the order $Cl > NO_3 > SO_4$. The behaviour of the sulfate in being a poor assistant in the gel-formation is abnormal. The silicate sol particles are considered to be positive in acid mixtures and hence the sulfate ion should have a greater coagulating power than the monovalent anions. The coagulating power of the chloride and nitrate ions are nearly of the same order.

Due to the large pH change in the mixtures containing phosphate salts it is difficult to see what effect the phosphate ion had on the time of set. But I think that it can be safely said that its coagulating power is less than that of the sulfate ion.

Taking into account the pH change in the sodium oxalate mixtures the oxalate ion has about the same effect as the chloride ion.

It appears from the similarity of the results obtained in this investigation with those obtained by Werner (10), Graham (15), Pappada (11) and Prasad and Hattiangadi (12) that gel-formation is really a case of coagulation of the colloidal silicic acid by electrolytes. The sodium acetate formed by the reaction of the acetic acid and the sodium silicate also played an important part in the coagulation of the colloidal silicic acid.

It has been found that a pure hydrosol of silicic acid has a tendency toward coagulation and that this tendency is more pronounced in the more concentrated solutions. This

coagulation tendency is most likely due to the presence of some of the silicic acid in true solution which would act as an electrolyte and cause coagulation. Mylius and Groschuff (16) found considerable amount of silicic acid present in true solution when it had been freshly separated from silicate.

SUMMARY

The effect of added salts on the time of set of gel mixtures produced by mixing solutions of acetic acid and sodium silicate have been studied. In order to obtain specific effects of the salts themselves changes in pH of the gel mixtures upon the addition of the salt has been noted.

Sodium chloride, potassium chloride, lithium chloride, sodium nitrate, sodium sulfate, potassium nitrate and potassium sulfate all accelerate the gel-formation and cause only a slight change in the pH of the mixture.

Mono-sodium phosphate, di-sodium phosphate and sodium oxalate cause large changes in the pH of the mixtures.

Gel-formation in a mixture of sodium silicate and acetic acid seems to be merely a case of coagulation of the colloidal silicic acid by electrolytes.

REFERENCES

1. Prasad and Hattiangadi J. Indian Chem. Soc. 6, 893 (1929)
2. Holmes J. Phys. Chem. 22, 510 (1918)
3. Fleming Z. physik. chem. 41, 427 (1902)
4. Hurd and Letteron J. Phys. Chem. 36, 604(1932)
5. Fells and Firth J. Phys. Chem. 29, 241 (1925)
6. Ray and Ganguli J. Phys. Chem. 34, 352 (1930)
7. Hurd and Raymond and Miller J. Phys. Chem. 38, 663 (1934)
8. Krozer Kolloid Z 30, 18 (1922)
9. Hurd and Carver J. Phys. Chem. 37, 321 (1933)
10. Werner J. Am. Pharm. Assoc. 9, 501 (1920)
11. Pappada Gazz. chim. ital. 35, 78 (1905)
12. Prasad and Hattiangadi J. Indian Chem. Soc. 7, 341 (1930)
13. Hurd and Griffeth J. Phys. Chem. 39, 1155 (1935)
14. Laskin Kolloid Z 45, 129 (1928)
15. Graham J. Chem. Soc. 17, 321 (1864)
16. Mylius and Groschuff Ber. d. deutch. chem. Ges. 39, 116 (1906)

Table 1.

The effect of sodium chloride on the time of set of silicic acid and on the Ph of the mixture.

Concentrations in gram moles per liter:

Sodium Silicate	Acetic Acid	Sodium Chloride	Ph	Time in Minutes
.3917 Na ₂ O	.6261	.000	4.81	96.0
"	"	.033	4.81	90.0
"	"	.067	4.80	86.6
"	"	.167	4.80	77.5
"	"	.333	4.79	67.5
"	"	.500	4.79	59.0
"	"	.667	4.76	53.9
"	"	.833	4.76	47.9
"	"	1.00	4.74	45.0

Temperature 25.0°C

Solutions before mixing were:

50 cc Sodium Silicate - 1.254 M

50 cc Acetic Acid - 2.004 M

60 cc Sodium Chloride plus water

Sodium Chloride varied:

0-2-4-10-20-30-40-50-60- cc of 2.667 M

Table 2.

The effect of sodium nitrate on the time of set of silicic acid gels and on the Ph of the mixture.

Concentrations in gram moles per liter:

Sodium Silicate	Acetic Acid	Sodium Nitrate	Ph	Time in Minutes
.3917 Na ₂ O	.6261	.000	4.81	96.0
"	"	.033	4.81	91.0
"	"	.067	4.80	86.0
"	"	.167	4.80	78.3
"	"	.333	4.76	67.0
"	"	.500	4.79	59.8
"	"	.667	4.79	54.3
"	"	.833	4.79	48.3
"	"	1.00	4.80	45.0

Temperature 25.0°C

Solutions before mixing were:

50 cc Sodium Silicate - 1.254M

50 cc Acetic Acid - 2.004 M

60 cc Sodium Nitrate plus water

Sodium Nitrate varied:

0-2-4-10-20-30-40-50-60- cc of 2.667 M

Table 3.

The effect of sodium sulfate on the time of set of silicic acid gels and on the Ph of the mixture.

Concentrations in gram moles per liter.

Sodium Silicate	Acetic Acid	Sodium Sulfate	Ph	Time in Minutes
.3917 Na ₂ O	.6261	.000	4.81	96.0
"	"	.033	4.80	93.2
"	"	.083	4.79	89.5
"	"	.167	4.79	85.0
"	"	.250	4.79	82.0
"	"	.333	4.76	79.0
"	"	.416	4.74	77.2
"	"	.500	4.74	77.0

Temperature 25.0°C

Solutions before mixing were:

50 cc Sodium Silicate - 1.254 M

50 cc Acetic Acid - 2.004 M

60 cc Sodium Sulfate plus water

Sodium Sulfate varied:

0-4-10-20-30-40-50-60-cc of 1.333 M

Table 4.

The effect of Mono-sodium Phosphate on the time of set of silicic acid gels and on the Ph of the mixture.

Concentrations in gram moles per liter:

Sodium Silicate	Acetic Acid	Mono-sodium Phosphate	Ph	Time in Minutes
.3917 Na ₂ O	.6261	.000	4.81	96.0
"	"	.033	4.95	95.0
"	"	.067	4.98	93.7
"	"	.167	5.39	92.0
"	"	.333	4.90	97.0
"	"	.500	4.90	97.0
"	"	.667	4.76	105.0
"	"	.833	4.76	109.0
"	"	1.00	4.63	110.0

Temperature 25.0° C

Solutions before mixing were:

50 cc Sodium Silicate - 1.254 M

50 cc Acetic Acid - 2.004 M

60 cc Mono-sodium Phosphate plus water

Mono-sodium Phosphate varied:

0-2-4-10-20-30-40-50-60- 2.667 M

Table 5.

The effect of Di-sodium Phosphate on the time of set of Silicic Acid gels and on the Ph of the mixture.

Concentrations in gram moles per liter:

Sodium Silicate	Acetic Acid	Di-sodium Phosphate	Ph	Time in Minutes
.3917 Na ₂ O	.6261	.000	4.81	96.0
"	"	.083	5.00	55.0
"	"	.125	5.28	38.0
"	"	.167	5.38	27.3
"	"	.208	5.66	19.0
"	"	.250	5.78	13.0

Temperature 25.0° C

Solutions before mixing were:

50 cc Sodium Silicate - 1.254 M

50 cc Acetic Acid - 2.004 M

60 cc Di-sodium Phosphate plus water

Di-sodium Phosphate varied:

0-20-30-40-50-60- .6667 M

Table 6.

The effect of Sodium Oxalate on the time of set of Silicic Acid gels and on the Ph of the mixture.

Concentrations in gram moles per liter:

Sodium Silicate	Acetic Acid	Sodium Oxalate	Ph	Time in Minutes
.3917 Na ₂ O	.6261	.0000	4.81	96.0
"	"	.0033	4.81	94.0
"	"	.0067	4.83	92.0
"	"	.0167	4.83	87.7
"	"	.0333	4.85	83.7
"	"	.0500	4.85	79.7
"	"	.0667	4.90	79.7
"	"	.0833	4.92	81.4
"	"	.1000	4.92	80.5

Temperature 25.0° C

Solutions before mixing were:

50 cc Sodium Silicate - 1.254 M

50 cc Acetic Acid - 2.004 M

60 cc Sodium Oxalate plus water

Sodium Oxalate varied:

0-2-4-10-20-30-40-50-60- cc of 2.667 M

Table 7.

The effect of Lithium Chloride on the time of set of Silicic Acid gels and on the Ph of the mixture.

Concentrations in gram moles per liter:

Sodium Silicate	Acetic Acid	Lithium Chloride	Ph	Time in Minutes
.3917 Na ₂ O	.6261	.000	4.80	96.0
"	"	.033	4.80	91.3
"	"	.067	4.80	88.3
"	"	.167	4.79	83.2
"	"	.333	4.79	73.5
"	"	.500	4.76	67.6
"	"	.667	4.76	61.1
"	"	.833	4.74	55.7
"	"	1.00	4.72	51.0

Temperature 25.0°C

Solutions before mixing were:

50 cc Sodium Silicate - 1.254 M

50 cc Acetic Acid - 2.004 M

60 cc Lithium Chloride plus water

Lithium Chloride varied:

0-2-4-10-20-30-40-50-60- cc of 2.667 M

Table 8.

The effect of Potassium Chloride on the time of set of Silicic Acid gels and on the Ph of the mixture.

Concentrations in gram moles per liter:

Sodium Silicate	Acetic Acid	Potassium Chloride	Ph	Time in Minutes
.3917 Na ₂ O	.6261	.000	4.81	96.0
"	"	.033	4.80	86.0
"	"	.067	4.80	80.5
"	"	.167	4.80	68.3
"	"	.333	4.80	54.7
"	"	.500	4.77	45.0
"	"	.667	4.72	39.7
"	"	.833	4.74	35.7

Temperature 25.0°C

Solutions before mixing were:

50 cc Sodium Silicate - 1.254 M

50 cc Acetic Acid - 2.004 M

60 cc Potassium Chloride plus water

Potassium Chloride varied:

0-2-4-10-20-30-40-50-60- cc of 2.667 M

Table 9.

The effect of Potassium Nitrate on the time of set of Silicic Acid gels and on the Ph of the mixture.

Concentrations in gram moles per liter:

Sodium Silicate	Acetic Acid	Potassium Nitrate	Ph	Time in Minutes
.3917 Na ₂ O	.6261	.000	4.81	96.0
"	"	.033	4.81	88.0
"	"	.067	4.80	82.0
"	"	.167	4.80	70.5
"	"	.333	4.80	56.0
"	"	.500	4.79	46.8
"	"	.667	4.76	41.8
"	"	.833	4.76	37.5
"	"	1.00	4.74	34.1

Temperature 25.0° C

Solutions before mixing were:

50 cc Sodium Silicate - 1.254 M

50 cc Acetic Acid - 2.004 M

60 cc Potassium Nitrate plus water

Potassium Nitrate varied:

0-2-4-10-20-30-40-50-60- cc of 2.667 M

Table 10.

The effect of potassium sulfate on the time of set of silicic acid gels and on the Ph of the mixture.

Concentrations in gram moles per liter:

Sodium Silicate	Acetic Acid	Potassium Sulfate	Ph	Time in Minutes
.3917 Na ₂ O	.6261	.000	4.81	96.0
"	"	.033	4.81	89.3
"	"	.083	4.81	81.0
"	"	.167	4.81	70.0
"	"	.250	4.81	64.3

Temperature 25.0°C

Solutions before mixing were:

50 cc Sodium Silicate - 1.254 M

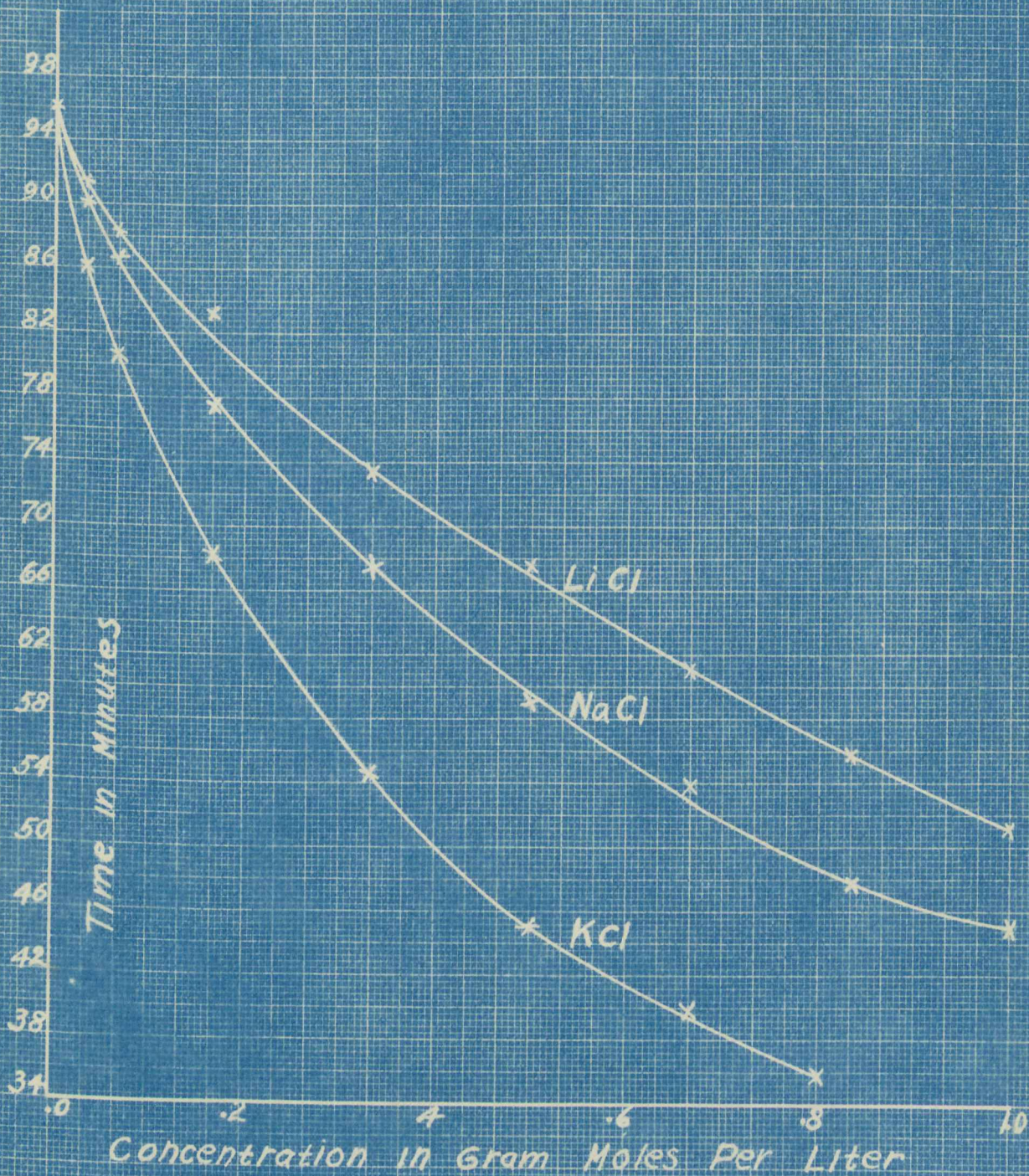
50 cc Acetic Acid - 2.004 M

60 cc Potassium Sulfate plus water

Potassium Sulfate varied:

0-8-20-40-60- cc of .6667 M

Figure 1



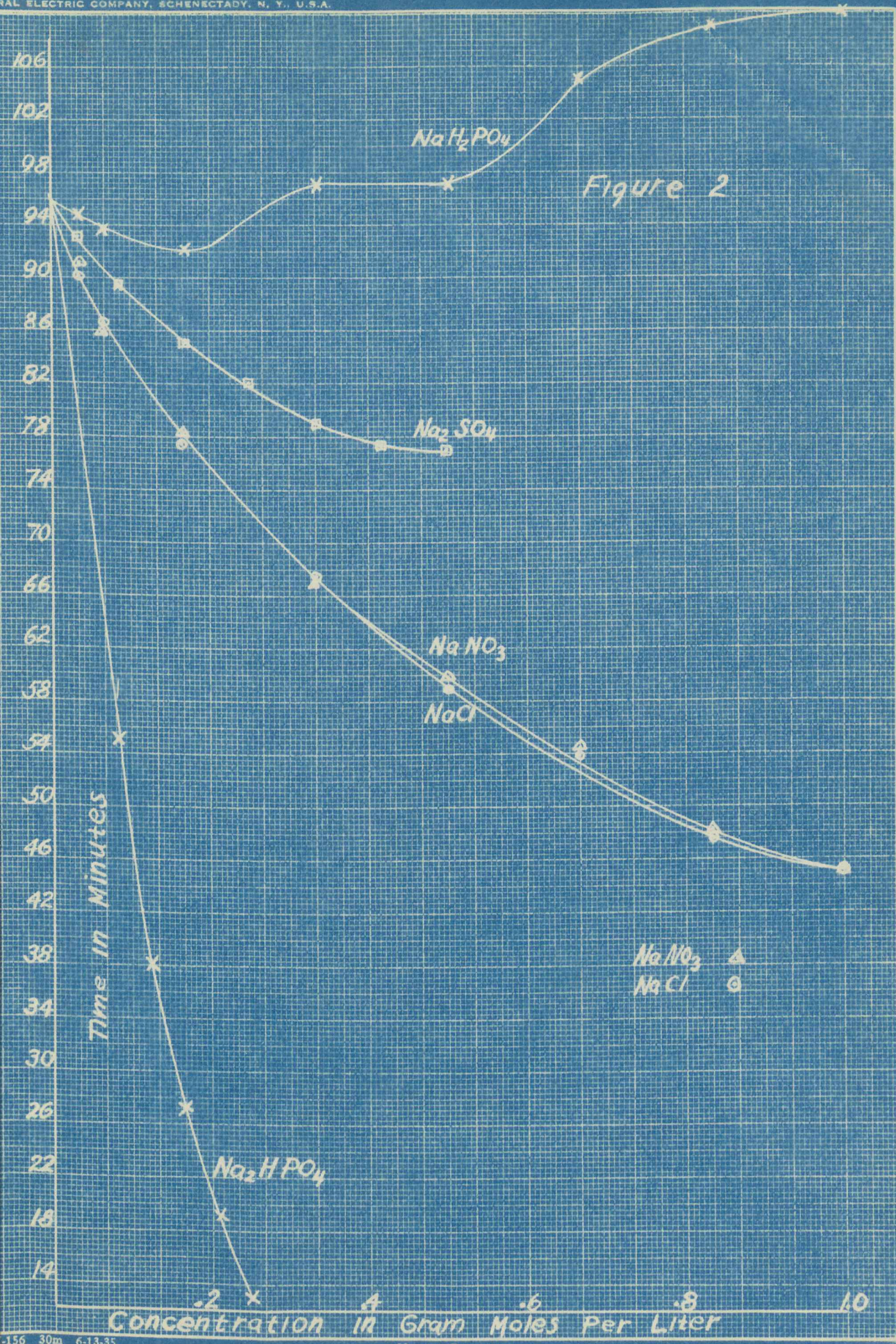


Figure 3

