

6-1945

# The Effect of Chlorides upon the Time of Set of Silicic Acid Gels

Leon F. Wardell

*Union College - Schenectady, NY*

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

 Part of the [Chemistry Commons](#)

---

## Recommended Citation

Wardell, Leon F., "The Effect of Chlorides upon the Time of Set of Silicic Acid Gels" (1945). *Honors Theses*. 2137.  
<https://digitalworks.union.edu/theses/2137>

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](mailto:digitalworks@union.edu).

THE EFFECT OF CHLORIDES  
UPON THE TIME OF SET OF SILICIC ACID GELS

\*\*\*\*\*

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 Leon F. Wardell

Approved by Charles B. Hurd.

June 1945.

UNION COLLEGE  
LIBRARY



UN<sup>2</sup>92  
W265e  
1945  
c.2

I. Introduction

II. Experimental

A. Preparation of Solutions

B. Mixing of Solutions

C. Determination of the Time of Set

D. Determination of the pH

III. Results

IV. Discussion of Results

V. Summary

VI. Bibliography

133251 F

September 12, 1947

## INTRODUCTION

The time of set of silicic acid gel mixtures has been found to depend fundamentally upon the concentration of silica in the mixture, upon the temperature, upon the hydrogen-ion concentration, upon the silicate and acid used, and upon the presence and concentration of additional soluble materials. Some work has been done in determining the effect of electrolytes upon the time required for gelation; but this work, except for that done by Hurd, Raymond and Miller (6) and that done by Hallstrom (8), did not stipulate whether or not the hydrogen-ion concentration remained constant with the varying quantities of electrolyte added. It is a well known fact (11) that any change in the hydrogen-ion concentration will have a pronounced effect upon the time of set of silicic acid gels. Therefore the specific effect of an electrolyte (5) is practically impossible to ascertain when a pH change accompanies the addition. The purpose of this research was to undertake the investigation of the effect of extra quantities of electrolytes, particularly those of divalent cations, upon the time of set of silicic acid gels, keeping in mind any effect the added electrolyte might have upon the solution's pH. The silicic acid gels studied were prepared by the method suggested by Hurd(9), consisting of a mixture of a solution of sodium silicate and a solution of acetic acid.



## EXPERIMENTAL

### Preparation of Solutions:

Approximately 1200 ml. of "E" brand, Philadelphia Quartz Co., silicate was diluted with distilled water to a total volume of about 3840 ml., giving a solution equivalent to approximately 1.25 normal sodium hydroxide. Its normality with respect to sodium hydroxide was determined by titration with 0.986 N sulfuric acid, using methyl orange. From this sodium hydroxide equivalent and the soda-silica ratio, i.e.  $\text{Na}_2\text{O}:\text{SiO}_2 = 1:3.29$ , the number of gram moles of silica per liter was calculated. Sodium hydroxide standardized with oxalic acid, was used to determine the normality of the sulfuric acid, again using methyl orange as indicator.

Approximately 471 ml. of 99.8 % acetic acid from the General Chemical Co. was diluted with distilled water to a total volume of about 4000 ml., giving approximately a two-normal solution. By titration with the same sodium hydroxide solution as previously mentioned, its normality was determined, using phenolphthalein as indicator.

All electrolytes added to the gel-mixture were prepared from reagent chemicals as one molar solutions in 250 ml. quantities. The following solutions of chlorides were prepared: magnesium chloride, calcium chloride, barium chloride, zinc chloride, cadmium chloride, ferric chloride, cobaltous chloride, nickelous chloride, cupric chloride and aluminum chloride.



### Mixing of Solutions:

Varied amounts of the electrolyte were added, but the total volume of silicic acid gel remained at 80 ml. for all mixtures investigated.

25 ml. of the silicate solution was placed in a 100 ml. beaker; and 25 ml. of the acid solution, along with 30 ml. made up of the electrolyte plus distilled water, was placed in another 100 ml. beaker. All the volume measurements, except those of distilled water, were made with pipettes; an automatic burette being used for the water measurements. These 100 ml. beakers were placed in a water-bath thermostat which was regulated at  $25.0 \pm 0.2^\circ\text{C}$ . When at this constant temperature, the solutions were mixed, always adding the silicate solution to the acid solution, by pouring from one beaker to the other and back again four times. The mixture was then placed back into the thermostat.

When pH measurements were taken, each constituent of the gel-mixture was doubled and 250 ml. beakers were used in place of the 100 ml. beakers. After the mixing, half the solution was poured into one 100 ml. beaker and replaced in the thermostat where the time of set was determined. The other half of the solution was placed in another 100 ml. beaker, adding with vigorous stirring sufficient quinhydrone to produce a saturated solution, and used for the pH determination.

Each beaker was covered with a watch glass in order to minimize evaporation, and lead weights were placed upon the watch glasses to prevent overturning of the beakers into the water-bath.



#### Determination of the Time of Set:

The exact time required for gelation can not be determined since there is no means of deciding when the process of setting is absolutely completed. When first prepared, the gel-mixture is transparent; but, as it stands, a faint opalescence appears which increases until after the gel has set. When the opalescence becomes quite marked, the viscosity of the mixture increases rapidly and elasticity develops. From these observations, Hurd and Letteron (4) obtained a means of determining a relative time of set known as the "tilted rod" method. This method consists of inserting a dull-pointed glass rod, 3 mm. in diameter and 10 cm. long, into the gel-mixture at an angle of  $20^{\circ}$  to the vertical. If the rod is supported in this position, the gel is considered set. Earlier applications of this method have been found to give results which are accurate to within two percent. The time of set was taken as the interval between the mixing of the silicate and acid solutions and the setting of the gel-mixture as determined by the above method.

#### Determination of the pH:

The quinhydrone electrode was used for these determinations, since a careful study of the applicability of this method made by Hurd and Griffeth (7) found it to be reliable for measurements of pH of silicic acid gels.

A saturated calomel electrode and a gold electrode were used, and the pH was calculated from the following expression:

$$\text{pH} = \frac{0.4570 - E}{0.591} \quad T = 25.0^{\circ}\text{C.}$$

Since the pH is a linear function of E, a graph was plotted to



facilitate the obtaining of these pH values.

Readings of the potential, i.e. E, were taken after the gel had set. Because the gold electrode, when exposed to the air, easily became coated with an oxide or a film of oxygen, thus requiring a longer interval of time for the equilibrium to be reached, it was kept in a buffer solution of sodium acetate and acetic acid.

### RESULTS

The effect of magnesium, calcium and barium salts of hydrochloric acid upon the gel-forming mixture was studied and all three were found to decrease the time required for gelation. Tables I and Figure #I show that this effect is not very large, but the range of electrolyte concentration was limited due to the formation of the corresponding insoluble silicate of the metal. It was found that when the concentration of magnesium chloride was much greater than 0.125 gm.-ions per liter a flocculent white precipitate was formed and the time required for setting was greatly increased. In the case of calcium chloride, the maximum concentration was between 0.075 and 0.125 gm.-ions per liter. Barium chloride with a concentration of 0.075 gave a flocculent white precipitate; but for any concentration of this electrolyte, the solution became cloudy upon mixing. There was a marked pH increase noted in the case of magnesium chloride.

Table II and Figure #I show the effect of the zinc and cadmium salts of hydrochloric acid upon the gel-forming mixture.



Both of these were found to cause an increase in the time required for gelation and an increase in the pH of the mixture. Again high concentrations of zinc chloride were impossible because of the insoluble precepiate formed. The quantity of precepiate formed was much less in the case of zinc than in the case of magnesium, calcium and barium.

The effect of iron (ic), cobalt (ous) and nickel (ous) salts of hydrochloric acid upon silicic acid gels is shown in Figure #2 and Table III. Ferric chloride was found to increase the time of set and to decrease the pH considerably, while both cobaltous and nickelous chloride decreased the time of set and increased the pH. Cupric chloride was found to have an effect similar to that of ferric chloride, i.e. to increase the time of set and to decrease the pH.

Aluminum chloride, Table IV was found to have an irregular effect upon silicic acid gels. (See Figure 3) Over a very small range of chloride concentration the time required for setting was greatly increased and then abruptly decreased. Also there was a considerable decrease in the pH of the gel-mixture. These silicic acid gels were found to exhibit the following peculiarities: (1) with higher concentration of the chloride they did not vibrate, i.e. they showed very low elasticity, and (2) with higher concentration of the chloride they were found to be white, opaque gels.



TABLE I

The effect of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  upon the Time of Set and upon the pH of Silicic Acid Gels.

<u>Conc. of <math>\text{MgCl}_2</math> (gm.-ions/liter)</u>	<u>pH</u>	<u>Time of Set (Minutes)</u>
0.000	4.61	89.4
0.0125	-	88.4
0.050	-	85.6
0.075	4.81	83.1
0.125	4.86	81.1

The effect of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  upon the Time of Set of Silicic Acid Gels.

<u>Conc. of <math>\text{CaCl}_2</math> (gm.-ions/liter)</u>	<u>Time of Set (Minutes)</u>
0.000	89.4
0.0125	89.6
0.050	85.8
0.075	84.0
0.125	84.6*

The effect of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  upon the Time of Set of Silicic Acid Gels.

<u>Conc. of <math>\text{BaCl}_2</math> (gm.-ions/liter)</u>	<u>Time of Set (Minutes)</u>
0.000	89.4
0.0125	88.8
0.050	83.9
0.075	80.3
0.125	80.5*

Temperature 25.0-0.2°C.

Solutions contained:

25 ml. of Sodium Silicate -- 1.26 N with respect to sodium hydroxide

25 ml. of acetic acid -- 2.05 N

30 ml. of chloride plus water

Chloride varied: 0-1-4-6-10 ml. of 1.M

Concentration of  $\text{SiO}_2$  = 2.07 gm.-mole/liter.

\* Flocculent white ppt. settled out upon mixing.

TABLE I (CONT'D)

The effect of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  upon the Time of Set and upon the pH of Silicic Acid Gels.

<u>Conc. of <math>\text{BaCl}_2</math> (gm.-ions/liter)</u>	<u>pH</u>	<u>Time of Set (Minutes)</u>
0.000	4.56	94.9
0.0125	4.56	92.0
0.025	4.56	90.3
0.050	-	89.6
0.0625	-	85.0
0.125	-	86.5*

Temperature 25.0-0.2°C.

Solutions contained:

25 ml. of sodium silicate -- 1.27 N with respect to sodium hydroxide

25 ml. of acetic acid -- 2.10 N

30 ml. of chloride plus water

Chloride varied: 0-1-2-4-5-10 ml. of 1.M.

Concentration of  $\text{SiO}_2$  = 2.08 gm.-mole/liter

\* Flecculent white ppt. settled out upon mixing.



TABLE II

The effect of  $\text{ZnCl}_2$  upon the Time of Set and upon the pH of Silicic Acid Gels.

<u>Conc. of <math>\text{ZnCl}_2</math> (gm.-ions/liter)</u>	<u>pH</u>	<u>Time of Set (Minutes)</u>
0.000	4.61	89.4
0.0125	-	89.6
0.050	-	90.9
0.075	4.79	94.1
0.125	4.84	96.5
0.250	-	131.2*

The effect of  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$  upon the Time of Set and upon the pH of Silicic Acid Gels.

<u>Conc. of <math>\text{CdCl}_2</math> (gm.-ions/liter)</u>	<u>pH</u>	<u>Time of Set (Minutes)</u>
0.000	4.45	89.4
0.025	-	91.3
0.050	-	94.7
0.075	4.69	94.8
0.100	4.69	96.5

Temperature 25.0-0.2°C.

Solutions contained:

25 ml. of sodium silicate -- 1.26 N with respect to sodium hydroxide

25 ml. of acetic acid -- 2.05 N

30 ml. of chloride plus water

Chloride varied: 0-1-4-6-10-20 ml. of 1.0 N

Concentration of  $\text{SiO}_2$  = 2.07 gm.-moles per liter

\* Flocculent white ppt. settled out upon mixing.



FIGURE No. 1

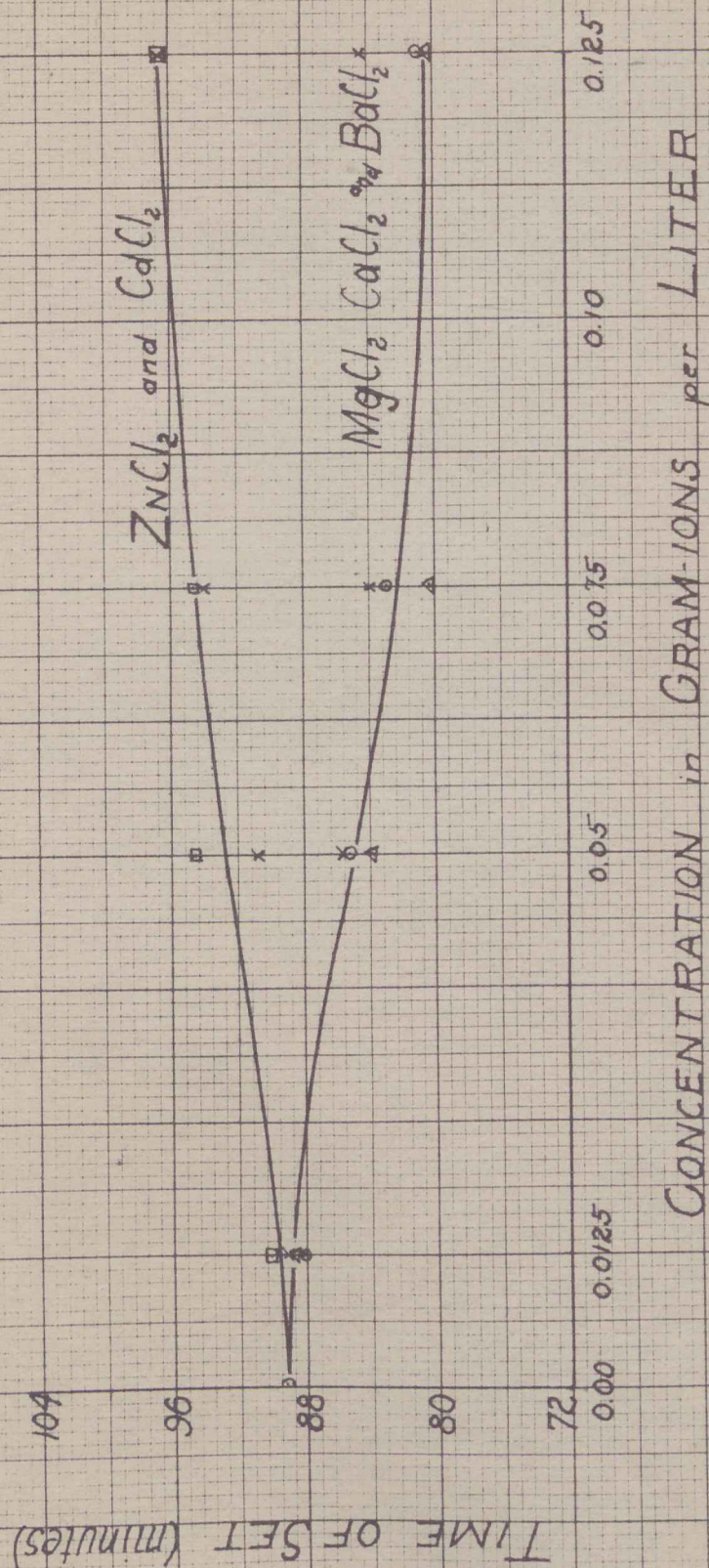




TABLE III

The effect of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  upon the Time of Set and upon the pH of Silicic Acid Gels.

<u>Conc. of <math>\text{FeCl}_3</math> (gm.-ions/liter)</u>	<u>pH</u>	<u>Time of Set (Minutes)</u>
0.000	4.45	83.8
0.025	4.12	91.5
0.050	3.68	107.3

The effect of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  upon the Time of Set and upon the pH of Silicic Acid Gels.

<u>Conc. of <math>\text{CoCl}_2</math> (gm.-ions/liter)</u>	<u>pH</u>	<u>Time of Set (Minutes)</u>
0.000	4.45	83.8
0.025	4.52	81.7
0.050	4.52	81.4

The effect of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  upon the Time of Set and upon the pH of Silicic Acid Gels.

<u>Conc. of <math>\text{NiCl}_2</math> (gm.-ions/liter)</u>	<u>pH</u>	<u>Time of Set (Minutes)</u>
0.000	4.45	83.8
0.025	4.49	81.8
0.050	4.46	81.8
0.075	-	80.8
0.100	-	80.7

The effect of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  upon the Time of Set and upon the pH of Silicic Acid Gels.

<u>Conc. of <math>\text{CuCl}_2</math> (gm.-ions/liter)</u>	<u>pH</u>	<u>Time of Set (Minutes)</u>
0.000	4.45	83.8
0.025	4.06	86.5
0.050	3.58	90.2

Temperature 25.0-0.2°C.

Solutions contained:

25 ml. of sodium silicate -- 1.27 N with respect to NaOH

25 ml. of acetic acid -- 2.06 N

30 ml. of chloride plus water

Chloride varied: 0-2-4 ml. of 1.M in all cases except

$\text{NiCl}_2$  which varied 0-2-4-6-8 ml. of 1.M

Concentration of  $\text{SiO}_2$  = 2.08 gm.-moles per liter



FIGURE No. 2

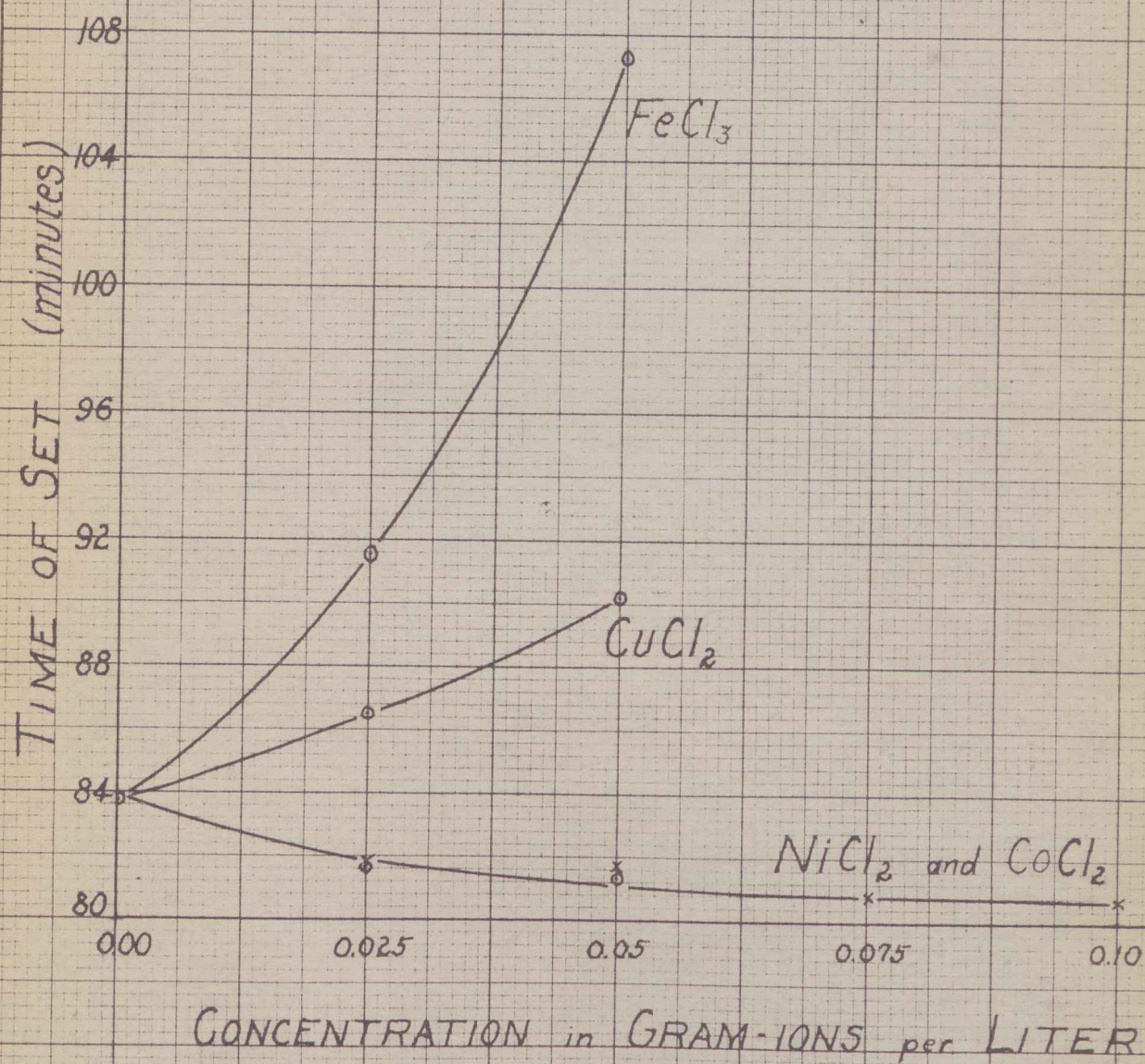




TABLE IV

The effect of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  upon the Time of Set and upon the pH of Silicic Acid Gels.

<u>Conc. of <math>\text{AlCl}_3</math> (gm.-ions /liter)</u>	<u>pH</u>	<u>Time of Set (Minutes)</u>
0.000	4.45	83.8
0.025	-	144.5
0.050	-	143.3
0.075	3.83	1.0
0.100	3.55	0.5

Temperature  $25.0 \pm 0.2^\circ\text{C}$ .

Solutions contained:

25 ml. of sodium silicate -- 1.27 N with respect to sodium hydroxide

25 ml. of acetic acid -- 2.06 N

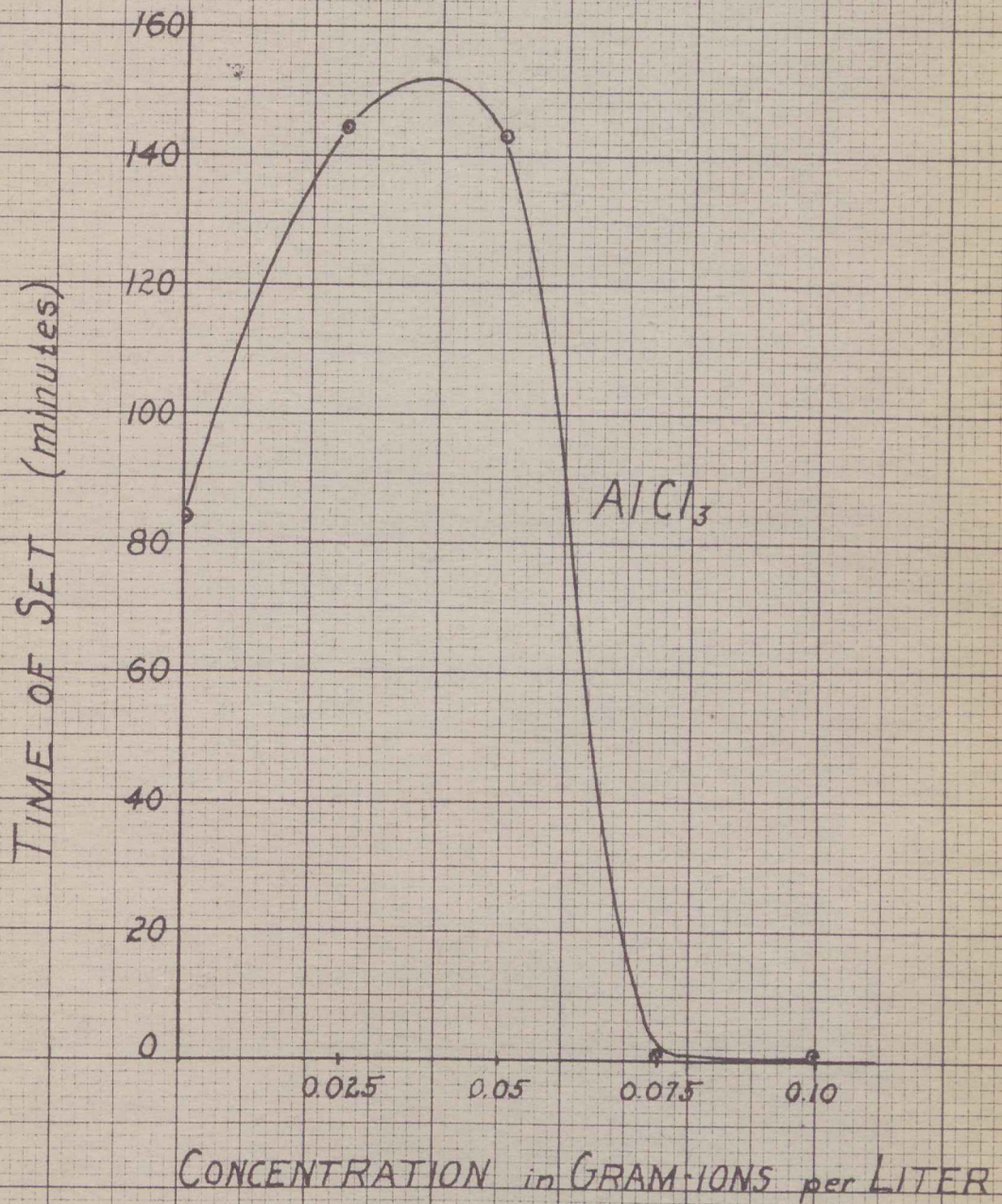
30 ml. of aluminum chloride plus water

Aluminum chloride varied: 0-2-4-6-8 ml. of 1.M

Concentration of  $\text{SiO}_2$  = 2.08 gm.-moles per liter



FIGURE No. 3





## DISCUSSION OF RESULTS

Prasad and Hattiangadi (3) stated that the addition of extra quantities of electrolytes to the gel-forming mixture corresponds to the case of coagulation of a colloidal solution by mixtures of electrolytes.

According to Hurd (10), the structure of a silicic acid gel is produced by condensation, water being split out between simple silicic acid molecules. The polysilicic acid structure is probably very heavily hydrated; and therefore, if extra quantities of electrolytes which take up water are added, they will hasten the process of condensation. Also such a condensation process should be affected very little by the presence of the ions of ordinary salts.

The results of the present investigation on the influence of other electrolytes in the presence of sodium acetate upon the gel-forming mixture of the silicic acid sol indicate the order of accelerating power in an acid medium as follows; although the overall effect was the same in each case as shown by Figures #1 and 2:



Werner (2), working with a pure silicic acid gel prepared with hydrochloric acid, found the order to be  $\text{CaCl}_2 > \text{BaCl}_2 > \text{MgCl}_2$ . Pappadà and Sadowski (1) stated that the time of set was increased with increasing atomic weight of the cation. This could explain why cobaltous and nickelous chlorides had an equal effect since their atomic weights are about equal. Also barium is the heaviest cation of those mentioned, although magnesium is the lightest cation and calcium is slightly lighter than nickel.



Over the range of concentrations studied, zinc and cadmium chlorides were found to have an equal effect in increasing the time of set. Applying Pappadè and Sadowski's principle, cadmium chloride due to its high atomic weight, should cause an effect comparing with that of barium chloride.

The main factor not noted by either Werner (2) or Pappadè and Sadowski (1) was the marked pH change accompanying the addition of these electrolytes. Each of the pH changes in the gel-mixtures containing magnesium, zinc and cadmium chlorides should have caused an increase in the time of set estimated (5) at about thirty minutes in the case of the highest concentration of the chlorides.

Cupric chloride and ferric chloride were found to increase the time of set and to decrease the pH of the gel-mixture. This pH decrease should have caused an increase in the time of set estimated at approximately 110 minutes in the case of copper and 100 minutes in the case of iron. Werner (2) stated that the irregular behavior of cupric chloride and ferric chloride was undoubtedly due to hydrolysis of these salts.

The peculiar effect of aluminium chloride might possibly have been due to some chemical combination between this chloride and the silicic acid. Also a considerable pH decrease was noted which should have caused an increase in the time of set estimated at 115 minutes.

Even though only low concentrations of electrolytes were investigated, it appears from the results obtained here, excluding



aluminum chloride, that the small effect upon the time of set caused by the presence of added quantities of electrolytes supports the theory that the gel-formation is a process of condensation of silicic acid molecules, because these low concentrations would have had a much greater effect upon the time of set were the addition of extra quantities of electrolytes merely a case of coagulation. The presence of these electrolytes may have caused either an increase or a decrease in the ionization of the silicic acid molecules (10), thus accounting for obtaining only small effects.

#### SUMMARY

The effects of various chlorides in the presence of sodium acetate upon the time required for gelation of silicic acid gels have been studied. Changes in pH of the gel-mixtures have been noted in order to ascertain the specific effects of the chlorides.

Magnesium chloride, calcium chloride, barium chloride, cobaltous chloride and nickelous chloride accelerated the process of gelation while zinc chloride, cadmium chloride, cupric chloride and ferric chloride lengthened the process of gelation. Aluminum chloride was found first to increase and then to drastically decrease the time of set.

Magnesium, zinc, cadmium, cupric, ferric and aluminum chlorides all caused a marked change in the pH of the gel-mixture which, in itself, should have caused a much greater alteration in the time of set than was apparent in most cases.

The comparative insensitiveness of the silicic acid mixture to electrolytes seems to support the theory that the process of forming a silicic acid gel is one of condensation rather than one of coagulation.



QUINHYDRONE and SAT. CALOMEL ELECTRODE

AT  
25°C

5.9

5.5

5.1

4.7

4.3

3.9

3.5

pH

-120

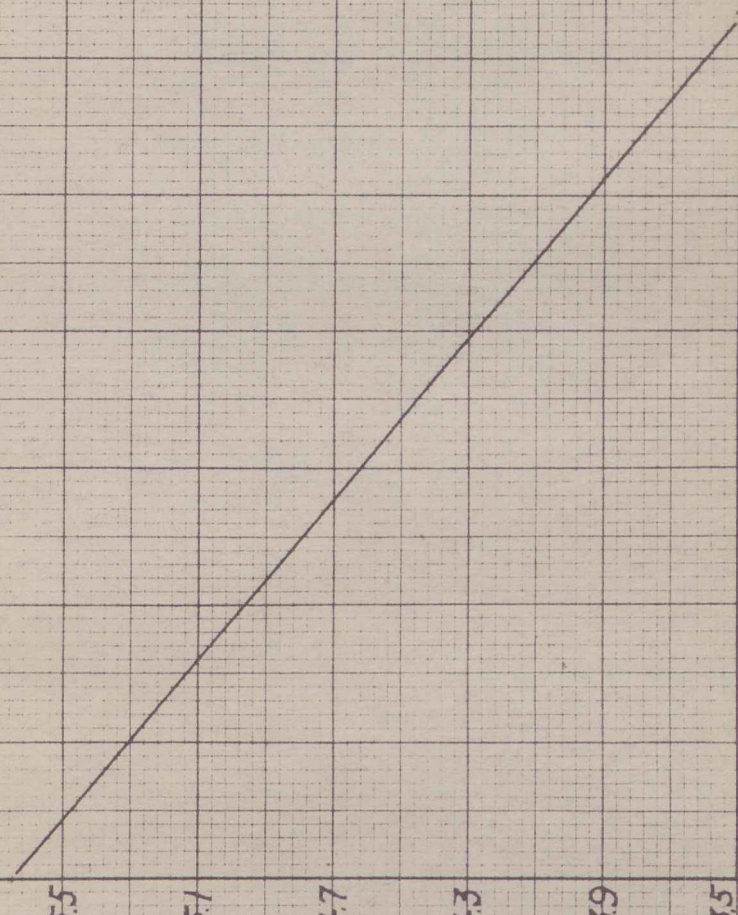
-160

-200

-240

-280

POTENTIOMETER READING  
(millivolts)





## BIBLIOGRAPHY

- (1) Pappada and Sadowski; Kolloid - Z. 6, 292 (1910)
- (2) Werner, L. : J. Am. Pharm. Assoc. 9, 501 (1920)
- (3) Prasad, M. and Hattiangadi, R.: J. Indian Chem. Soc. 7, 341 (1930)
- (4) Hurd, C. and Letteron: J. Phys. Chem. 36, 604 (1932)
- (5) Hurd, C. and Carver D.: J. of Phys. Chem., 37, 321 (1933)
- (6) Hurd, C., Raymond, C. and Miller, P.: J. of Phys. Chem. 38, 663 (1934)
- (7) Hurd, C. and Griffeth, R.: J. Phys. Chem., 39, 1155 (1935)
- (8) Hallstrom, G.: Thesis (B.S.) (1936)
- (9) Hurd, C.: J. of Chem. Education 14, No. 2 84 (1937)
- (10) Hurd, C.: Chemical Reviews 22, No. 3 (1938)
- (11) Hurd, C. and Paton, H.: J. Phys. Chem. 44, 57 (1940)