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# The Relation between the Concentration of Silica and Time of Set at Constant pH

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THE RELATION BETWEEN THE CONCENTRATION OF SILICA

AND TIME OF SET AT CONSTANT pH

*Edward Sheffer*

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THE RELATION BETWEEN THE CONCENTRATION OF SILICA  
AND TIME OF SET AT CONSTANT pH

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 Howard Sheffer

Approved by Charles B Hurd

May 1939



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### INTRODUCTION

Silicic acid gels result from practically any sol of hydrated silica, merely with the lapse of time. The gel must, however, contain a large enough concentration of silica to give sufficient strength or rigidity for the gel to set. A sol which contains less than .5 percent  $\text{SiO}_2$  will give a very weak gel, or no gel at all. Sols which are strongly alkaline will not set at all.

Certain conditions, such as concentration of silica, temperature, hydrogen-ion concentration, and concentration of other substances, are found to govern the time of set; but any sol containing over 2 percent  $\text{SiO}_2$  will set eventually to a gel, unless strongly alkaline.

### HISTORICAL

The study of silicic acid gels is carried on with the purpose of determining the structure of the gel, and explaining the mechanism in the setting of gels of hydrated silica. Some of the first work done was by Berzelius one hundred years ago. Walden and Nageli<sup>1</sup> were the first to propose a theory.

A study has been made by Hard, Fiedler, Raymond<sup>11</sup> to determine the effect, if any, of the soda silica ratio of the original sodium silicate upon the time of set of silicic acid gels. The gel mixtures were made by mixing solutions of sodium silicate and acetic acid. The soda silica ratio varied from 1:2.00 to 1:3.25. All variable factors except the original soda-silica ratio were carefully controlled. No measurable effect of the soda-silica ratio of the original silicate upon the time of set could be found.



The effect of added solution on the time of set of gel mixtures was studied by Hurd and Carver<sup>12</sup>. Acetic acid and sodium silicate solutions were used. The specific effects as different from the effects of the compounds themselves were separated. Ammonium hydroxide, methyl, dimethyl, and trimethyl-amine, pyridine, and aniline up to .04 M decreased the time of set mainly by increasing the pH of the mixture. There is, however, a specific effect apparent, greatest in the case of trimethylamine. A typical ester, ethyl acetate, apparently increases the time of set chiefly because of acetic acid set free during acid hydrolysis of the ester. Cane sugar and glycerin have little or no effect. Ethyl alcohol, acetaldehyde, and acetone show practically no effect on the pH, but show considerable specific effects on increasing the time of set.

Harman<sup>13</sup> has offered two suggestions as to what the anion is in a solution of sodium silicate. From transport number investigation it has been found that in order to explain the high values of the transport numbers for solutions of sodium silicate of different soda-silicate ratios, the following assumptions must be made:

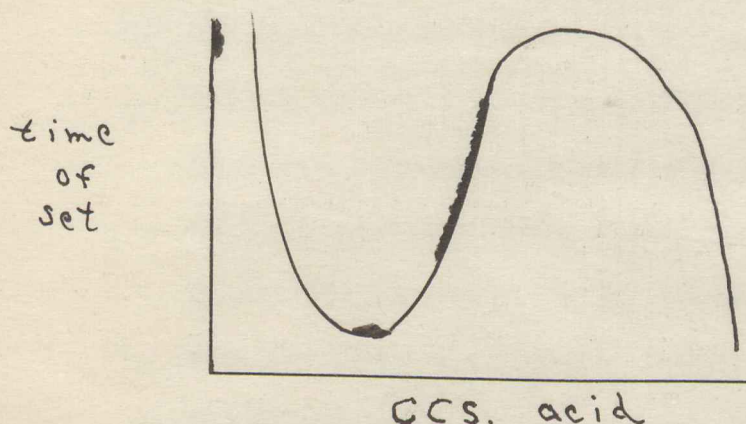
1. The anion may be a solvated aggregate of simple  $\text{SiO}_3$  ions, carrying a charge equal to the sum of the total charges on the separate ions, or a solvated aggregate containing more than one mol  $\text{SiO}_2$  per divalent charge, these aggregates splitting up on dilution; or,
2. The anion may be definite ions more complex than the simple  $\text{SiO}_3$  ion, i.e., definite salts of the formula given below may exist: -  $\text{Na}_2(\text{SiO}_3 \cdot \text{SiO}_2)$ ;  $\text{Na}_2(\text{SiO}_3 \cdot 2\text{SiO}_2)$ , etc., which ionize to give definite divalent silicate ions of the formula: -



$(\text{SiO}_2 \cdot \text{SiO}_2)$ ;  $(\text{SiO}_2 \cdot 2\text{SiO}_2)$ , etc.; also both conductivity and transport number experiments give evidence of silicate ions or complex ionic aggregates being present in solution as well as sodium ions and hydroxyl ions.

Hurd and Rothenich<sup>14</sup> studied the effect of sodium acetate and sodium chloride on the time of set. As the gels used were formed by the reaction of sodium silicate and acetic acid, then sodium acetate gave a strong common ion effect repressing hydrogen and silicate ions and hastening gelation. Sodium chloride gave no observable effect.

The plot of time of set against pH or c.c. of acid for constant concentration of silicate and temperature has the shape of the following curve:



The minimum point, "n", that is, the point for which the time of set reaches a minimum, was studied by Kern<sup>15</sup>. He found that the minimum time of set increases with increasing silicate concentration, but not linearly. The pH's at the minimum points for the gels studied were all on the alkaline side. The pH's of the minimum point were higher (more alkaline) with increasing concentration of silica.

Batchelor<sup>16</sup> summarized the conclusion from the study of silica sols as:



1. Increasing concentration of sols reduces gelation time;
2. Log of gelation time is a lineal fraction of initial pH value for pH of 4.2 to 5.5;
3. General opinion is that gelation of acid silica sols is attended by little or no change in pH, but in neutral and alkaline sols there is increase in pH;
4. Increasing temperature reduces gelation time.

Batchelor made a study of the gelation time and shift in pH value of silica gels as functions of concentration, initial pH, and temperature. He also studied gelation time as function of pH, concentration, and temperature. He represented his data in three dimensional figures. Most of his work lead to a revision of conclusion (3) above. The revised conclusion 3 is:

- (3)<sup>1</sup> The pH values of silica gels having neutral and alkaline initial pH values shift toward the alkaline side; the pH of silica gels slightly acid remain stable; the pH of more strongly acid gels shift toward more acid side; the shifts in pH were greater at higher temperature; for the extremely acid and extremely alkaline initial pH values the shifts during reaction were less marked than for moderately acid or alkaline reactions; the shifts in pH were largely independent of variation in concentration.

Itona and Arakawa<sup>17</sup> concluded in 1930 that the Quinhydrone Electrode was more accurate than the Hydroquinone. Coons<sup>18</sup> and Cooney<sup>19</sup> suggested the platinum electrode rather than the gold as suggested by Leeds and Northrup. A boiling solution of NaOH has been recommended by Hurd to clean the platinum electrode.



Several investigators, Holmes<sup>4</sup>, Batchelor<sup>16</sup>, Frederick<sup>10</sup>, have worked at various concentrations of silica, but their interest has been centered on the relation between time of set and some variable, other than concentration, such as pH, temperature, or heat of activation. It would be interesting to know how time of set varied with silica concentration for constant temperature and constant hydrogen ion concentration. That is, to see whether the plot of concentration against time of set, other variables constant, is linear.

#### PROPERTIES OF THE SOL OF HYDRATED SILICA

When first formed, considerable silicic acid passes easily with the electrolytes through the membranes used for dialysis. With the lapse of time, all silicic acid becomes unable to pass through the membrane. This fact, as well as the change in molecular weight, points unmistakably to the belief that silicic acid, when first formed, consists of small molecules, but that with the lapse of time these condense, polymerize, or coalesce to form large groups.

The electrical charge on the particles of the sol has been shown by Losenbeck to be negative in alkaline, neutral, or weakly acid solution. In more strongly acid solution the particles become positively charged. The idea has been held that this change is entirely due to preferential adsorption, but it has been shown by Hurd that it is probably due to the ionization of the silicic acid, which, owing to the amphoteric character of the molecule, occurs in two ways, leaving the silica in either a negative or positive ion.

The sol of hydrated silica, as it is setting, suddenly shows the development of elasticity. Langmuir has observed that gels exhibit stretch up to a certain limit. As the gel sets, the limit of this stretch



becomes smaller. The phenomenon of thixotropy is shown by the gel mixture in the early stages of setting; that is, the gel will knit itself together after being stirred or separated.

Silicic acid gel is affected little by strong acid, but dissolves in sodium hydroxide quickly.

### THEORIES OF GEL STRUCTURE

The earliest theory proposed was that of Nageli<sup>1</sup>, who proposed the Micellae Theory. This theory proposed that the solid colloidal particles were combined in small molecular aggregates. A honeycomb theory was proposed by Butschli<sup>2</sup> as a result of his work on foams, emulsions, and gels of gelatin and silicic acid. This theory assumed that solid films, which included the liquid phase, were built up. Proctor and Robinson<sup>3</sup> proposed a fibrillar theory in 1914 which is the most popular today. The gels are believed to consist of long thread-like chains, formed by polymerization. The total gel structure then exists as an interlocking mass of chains spread out like a cobweb.

Holmes<sup>4</sup> and Prakash<sup>5</sup> have presented some recent theories. Prakash proposed that gels resulted from the 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 colloidal particles whose charge is being neutralized by electrolytes agglomerate, precipitation occurs. If agglomeration is negligible in comparison with hydration, the gel is transparent. Kroger believes that sodium ions in solution have a peptizing effect upon silicic acid. Hurd, Raymond, and Miller<sup>6</sup> concluded from their results that the peptizing action in alkaline mixtures containing silicic acid is due to the hydroxyl ion and that this same hydroxyl ion acts as a catalyst in the acid mixtures.

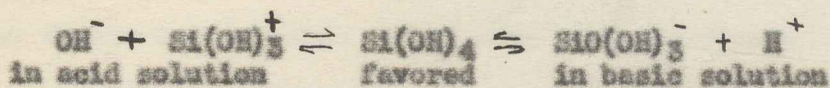


### MECHANISM OF CONDENSATION

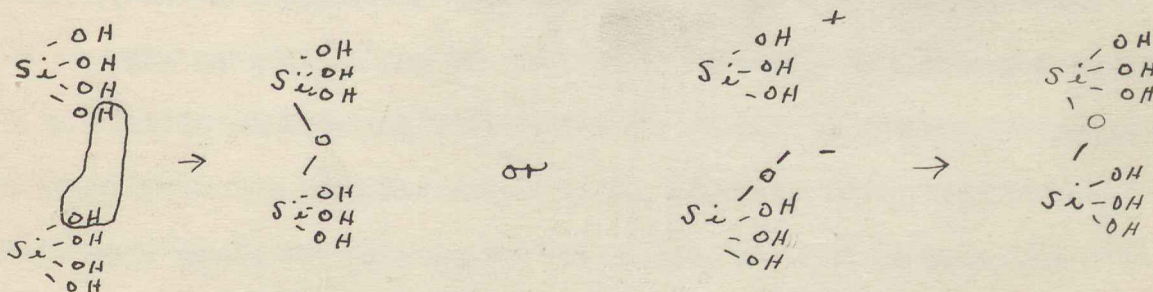
A theory has been proposed by Kurd<sup>8</sup> to explain the condensation of silic acid to form a polysilicic acid structure. Assumptions:

1. That a monosilicic acid is formed in the first stage of the process, or perhaps more correctly, silicon dioxide;
2. That this acid is amphoteric, giving either hydrogen or hydroxyl ions;
3. That condensation occurs when the positive and negative ions containing the silicon come into contact;
4. That water remains combined or adsorbed in the structure.

It is well established that the particles in a sol of hydrated silica are positive in strongly acid solution, but that they become negative in weakly acid, neutral, and basic solution. The process is shown for silicon hydroxides:



Condensation may occur by splitting out water from two molecules containing OH groups:



The fact that the minimum time of set occurs at a pH around 8 for various concentrations of silica, substantiates the second of the above two possibilities which would be likely to occur if the two substances were present in the same relative amounts.



The shift of hydrogen ion concentration during time of set is toward the neutral point, indicating that the  $\text{Si}(\text{OH})_4$  dissociates to the favored ions (in basic solution to  $\text{H}$  and  $\text{SiO}(\text{OH})_3^-$ ), which immediately makes the solution more neutral than it was before.

#### FACTORS AFFECTING GEL REACTIONS

Most of the recent work has been on the factors affecting gel reactions. The first to study the time of set as a function of temperature was Holmes<sup>4</sup>. Hurd and Letteron<sup>9</sup> pointed out that for acetic acid, sodium silicate gels the logarithm of the time was a linear function of reciprocal temperatures:

$$\frac{d \ln \text{Time}}{d / \text{temp}} = \frac{Q}{R}$$

where  $Q$  is the Arrhenius' heat of activation which came out to be 16,940 calories per gram mol, or nearly in the center of heats of activation for ordinary chemical reactions. Hurd, Frederick and Haynes<sup>10</sup>, working with nitric, hydrochloric, sulfuric acid, obtained by plotting log time of set against  $1/T$  values for " $Q$ " respectively of 16,370, 17,700 and 21,580. These values, given for  $Q$  represent the average of values found for different pH's.

The explanation for the fact that  $Q$  is found to differ for various pH's is found by considering that during the process of setting the gel mixtures have shown a measurable change in pH. Since as Hurd, Raymond and Miller<sup>6</sup> have shown, the velocity of the setting reaction is inversely proportional to the hydrogen ion concentration, these gels are undergoing a reaction whose velocity varies. As velocity of reaction varies, so does  $T$  and consequently  $Q$ .



### APPARATUS

The temperature was kept constant at 25° C. by means of a thermostat run by a vacuum tube arrangement using a relay. The thermoregulator consisted of an adjustable mercury contact. The thermostat consisted of an insulated water bath maintained at the correct temperature by an electric heater. Circulation was maintained by stirring vanes run by a small motor.

Temperature was kept constant for measuring pH by using another thermostat kept at 25° C. by a thyatron tube arrangement with an adjustable mercury contact.

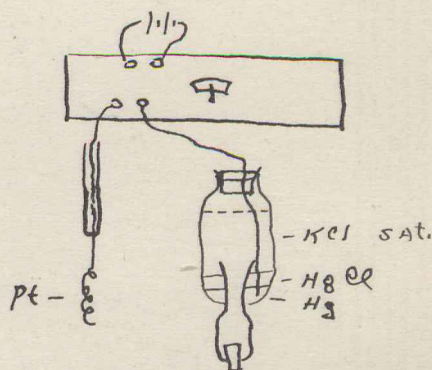
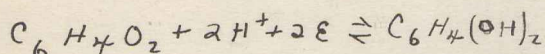
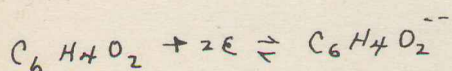
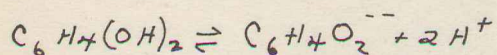
Another thermostat was kept at 23.5° C. to bring the solutions, one of sodium silicate and the other of water and acetic acid, to the correct temperature before mixing. There is a slight heat of solution which raises the temperature of the gel approximately 1.5° in the range of 25° C.

A thermostat of wet snow was used for zero degree runs. Bottles with paraffined corks were used to hold solution and tilt rod method for time of set as before. It was noticed that the gels stood about the same height in the bottles when a total volume of 50 c.c. was used. The tilt rod method still proved accurate if care was taken not to allow the rod to brace itself on the ridge at the bottom.

A third temperature of 40° C. was obtained by using a water bath with heater, stirrer, glass thermoregulator, and thyatron tube control for temperature. The thyatron control proved to hold the temperature much more constant than the vacuum tube arrangements in spite of the fact that in place of the adjustable mercury contact made with metal casing, a glass tube with toluene and mercury was substituted to do away with shocks obtained when a metal casing is used with the thyatron circuit. A glass tube thermoregulator is subject to more change than a metal casing, and is more difficult to adjust initially.



Hydrogen ion concentration was measured by means of a quinhydrone electrode which has been found to work well in the range studied - pH of 3 to pH of 8. The electrode was a platinum wire of sufficient length to give accurate measurements (4 cm.). A saturated calomel cell was used as the reference electrode. The potential was measured by means of the Leeds and Northrup potentiometer No. 7354.



A platinum wire No. 28 placed in this solution acquires a potential depending on the ratio of the oxidized to the reduced form which is a measure of the pH.

Quinone and hydroquinone form an equimolecular compound  $C_6H_4O_2 \cdot C_6H_4(OH)_2$  called quinhydrone, which maintains constant and equal concentration of quinone and hydroquinone:

$$E = E^0 - \frac{.059}{2} \log \frac{a_{\text{hydroquinone}}}{a_{H^+}^2 \cdot a_{\text{quinone}}}$$

$$E = E^0 + .059 \log a_{H^+} \quad ; \quad \text{since} \quad \frac{a_{\text{hydroquinone}}}{a_{\text{quinone}}} = 1$$

This electrode cannot be used in alkaline solutions above a pH of 8.5 on account of the chemical reaction and oxidation of the hydroquinone, and because the "salting out" effect on the hydroquinone and quinone may not be



exactly the same. 21, 22, 25, 20

Temperatures were taken with the same 100° C. thermometer. 100 c.c. K beakers were used for time of set at 25° C. and 80 c.c. bottles were used for time of set at 0° C. and 40° C.

The platinum electrode must be cared for to obtain accurate results. It is cleansed by immersion in a strong, hot solution of sodium hydroxide and rinsed in distilled water.



### EXPERIMENTAL

The "E" brand silicate manufactured by the Philadelphia Quartz Company was diluted with distilled water until 1.21 N sodium silicate solution was obtained. The soda silicate ratio is 1:3.25 by weight for the "E" brand. The silicate solution was made by diluting 5 liters of "E" brand to 16  $\frac{2}{3}$  liters of solution. The acetic acid 2.04 N was made by diluting 1.1 liters of concentrated acetic acid to 10 liters of solution. The distilled water was boiled and stoppered in large flasks and used when needed to insure CO<sub>2</sub> free water, because CO<sub>2</sub> has a coagulating effect on the silicate solution. The sodium silicate was standardized against HCl using methyl orange indicator, the acetic acid against NaOH using phenolphthalein.

All gel mixtures at 25° C. were made up to a total volume of 100 c.c., half of which was used to measure time of set, the other half to measure pH. The volume of silicate was held constant and the volume of acetic acid and water varied to give a curve log time of set against pH. However, six different constant volumes of silicate solution were used. A curve is obtained for log time of set against silicate concentration by taking the log time of sets for the same pH from the six different curves, and plotting these log times, changed to times, against silicate concentration.

The solutions were first thermostated at 23.5° C., and the time of mixture taken. The silicate in a 100 c.c. K beaker was poured into the acetic acid and water in a 250 c.c. beaker, and then poured back and forth three times. Half was left in the 100 c.c. K beaker and the other half poured into another 100 c.c. beaker for pH measurements. The pH and time of set were taken.

The time of set was determined by the tilt rod method as described by Rurd and Miller<sup>6</sup>. The criterion devised by Rurd and Rothenich (1930) was used. A gel is considered set when a pointed rod 9 cm. long and 3 mm. in



diameter is supported by the gel structure at an angle of about  $15^{\circ}$  to the vertical. In the short period gels the disturbing of the gel structure by continual insertion of the rod seemed to have little effect compared to the effect that it had in long period gels. Good checks were difficult in slow setting gels. With these slow setting gels the time would be figured approximately by extrapolation so that only a few testings would be taken. In this way the error caused by rupturing the gel structure was minimized. As soon as the rod could be supported anywhere the time of set was taken.

It was surprising how well the tilt rod method worked. I had to get the time of set for gels with a very low concentration of silica (.48%  $\text{SiO}_2$  was the lowest that set). Although I did not get a perfect curve, the tilt rod proved just as reliable as a substitute method that I thought it might be necessary to use. This substitute method was that of considering a gel set when it no longer runs when placed in a test tube, allowed to set, and then inverted.

Watch glasses were used to cover the beakers containing long setting gels to prevent evaporation from causing an error in time of set by increasing the fraction of the silica content. Evaporation is the greatest error in the experiment, and probably explains the slight variation of the points from the curves.

Agitation has an appreciable effect on time of set, and may even mislead one to believe that a gel never will set. This is especially true of low concentration silica gels. Since I was interested in the lowest concentration that would set, I was careful that the gels received no agitation and only tested two or three times and then estimated the time of set.

The pH was varied for each concentration of silica by varying the amount of acetic acid used and making up to the same total volume with water.



All pH's were taken with a Leeds and Northrup potentiometer which is supposed to be good up to a pH of 9.

All gels were made with pH's lower than 8 so that the Quinhydrone method could be used.

The pH is determined by adding to the solution in a 100 c.c. beaker a pinch of Quinhydrone and stirring. The platinum wire and arm of the calomel cell are placed in the solution. Readings of the galvanometer are taken until the pH reaches a constant value. This takes place for short time of set after the gel has set. The calomel was flushed out and washed off. The platinum wire was dipped in concentrated NaOH and then rinsed with distilled water. The pH drift was toward the neutral point from both sides of the pH of 7.



### RESULTS

The acid gels on the high silicate curves showed extreme rigidity and were opaque. Those on the lower silicate curves were clearer. The very low silicate gels were very weak. The neutral and slightly alkaline gels were white and opalescent. The lower silica concentrations were the clearer.

At a pH of 5.5, points could be obtained for three temperatures for the time of sets for three different concentrations of silica. By making certain simple assumptions that in these mixtures with a constant concentration of silica the time of set represents the time required for a certain definite fraction of the complete reaction, and also that we may apply the methods of treatment used for ordinary chemical reactions, we may obtain an energy quantity analogous to the "energy of activation." This is obtained by multiplying the slope of the curve ( $\ln$  Time against  $1/T$ ) by 2.3 R. 7, 8, 23, 24

<u>Concentration</u>	<u>Energy of Activation</u>
10*	14,520
20	15,750
30	16,590
40	16,800

\*Two points used

Letteron and Hard<sup>3</sup> attempted to calculate "n", the order of reaction, or the number of molecules of the substance which react. One of the assumptions which they made, that in each of their runs the time measured by the time of set represents the same fraction of the original concentration, "a", converted during the reaction, was unjustified because of the large effect on the time of set of the relative amount of acid and sodium silicate, i.e., of the pH of the solution. However, since in my experiment I have taken time of set against



silicate concentration at constant pH, the effect of the pH is taken care of.

**Assumptions:**

1. That we are dealing with a process which follows the laws of an ordinary chemical reaction so far as its velocity is concerned;
2. That the Arrhenius equation may be applied to our results;
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, has reacted.

Concerning this last assumption, it might be pointed out that the ionic reaction between sodium silicate and acetic acid is almost certainly a very rapid reaction. The idea that the slow stage of the gelation reaction represents an agglomeration of silicic acid or hydrated silica molecules analogous to a polymerisation, may not be so readily accepted. From surface tension results it appears that we are probably measuring the time of set of a slow reaction followed by a very rapid process<sup>3</sup>.

The ordinary expression for the velocity of a chemical reaction:

$$(1) \quad \frac{dx}{dt} = k(a - x)^n$$

$x$  = amount changed in time  $t$

$a$  = original concentration

$n$  = order of reaction

$$\int_0^x \frac{dx}{(a-x)^n} = \int_0^t k dt$$

$$\frac{1}{n-1} \left[ \frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right] = kt$$



In applying expression (1) which is usually used to indicate the result of interaction of " $n$ " molecules of the substance " $A$ ", we are indicating our belief that we are dealing with an interaction between like molecules of the same substance (or as in theory of formation of  $\text{SiO}(\text{OH})_3$  and  $\text{Si}(\text{OH})_3$ , the interaction between ions) to form the condensed silicate structure. This process would be slow as indicated by work on purified hydrosols of silica. Our " $a$ " represents the concentration of silica, in whatever form, which results from the ionic reaction of sodium silicate and acetic acid:

For any fractional change of  $a$ , the time  $t'$

$$t' = \frac{c'}{ka^{n-1}} \quad c' = \text{constant depending on } \frac{x}{a} \text{ and } n$$

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

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

$$c = \ln t' + (n-1) \ln a$$

$$c = \ln t_1' + (n-1) \ln a_1$$

$$c = \ln t_2' + (n-1) \ln a_2$$

$$\ln t_2' + (n-1) \ln a_2 = \ln t_1' + (n-1) \ln a_1$$

$$n-1 = \frac{\ln t_1' - \ln t_2'}{\ln a_2 - \ln a_1}$$

$$n-1 = \frac{\ln t_1'/t_2'}{\ln a_2/a_1} = \frac{\log t_1'/t_2'}{\log a_2/a_1}$$

$n$  at given pH

	<u>5.0</u>	<u>5.5</u>	<u>6.0</u>
20-30	2.79	2.98	2.97
20-40	2.85	3.18	2.83
20-10	<u>3.08</u>	<u>3.16</u>	<u>3.25</u>
	2.91	3.10	3.02

$$\text{Average } n = 3.01$$



A fourth assumption has been used in calculating n:

- (4) That in each run the time measured by time of set represents the same fraction of the original concentration,  $a$ , converted during the reaction.

This assumption seems justified if the pH is kept constant.

The values of  $n$  would be expected to increase as the pH increased until the neutral point is reached and then decrease as the neutral point is passed with approach of higher pH, if the  $H$  ion was an important factor in the reaction, because as the concentration of  $H$  increases (lower pH) one of the factors in the reaction would become increasingly large and approach the role played by water in many chemical reactions (that is, the role of a constant factor).

However the data is limited. I have values of  $n$  for three pH's (5, 5.5, 8). They are, respectively, 2.91, 3.10, 3.02. These values increase to a maximum for  $n$  at pH of 5.5. Sufficient data is lacking to draw too many conclusions. This seems to indicate that the effect of some reactant reaches a maximum value at pH of 5.5. It might be the  $H$  ion, but it is not too conclusive evidence.

When I plotted the time of set against  $1/s^2$ , where  $a$  original concentration of silicate, a straight line was obtained for concentrations from 1.55% to 6.2%. The point for concentration of .95% did not fall on the curve, but this time of set is for such a weak structure gel that it is extremely inaccurate. This seems to verify the fact that the reaction is a third order reaction.<sup>23, 24</sup>

I attempted to find the time of set of low concentration gels at both 25° C. and 38.5° C.



Gels at 25° C. of a concentration of .93% silica set in about 60 hours. One gel of concentration of .78% silica set also in about the same time. Gels of concentration of .62% silica seemed set, but structure was too weak to support a rod.

Gels at 38.5° C. of a concentration of .62% silica set in about 35 hours. One gel of concentration of .47% silica set in 120 hours. Gels of concentration of .31% silica had a cloudy fibrillar structure after one month. Gels of concentration of .15% silica were clear after one month.

The curves for a given pH for concentration of silicate against time of set seem to approach infinite time asymptotically with different concentrations for 25° C. than for 38.5° C. or for 0° C. This would seem to indicate that it would be possible to obtain a gel with a very low concentration of silicate at high temperatures.



DATA FOR CURVE I - TEMPERATURE 0° C.

Corresponds to concentration of 40 for total volume of 80 c.c.

<u>Silicate</u>	<u>NaCl</u>	<u>H<sub>2</sub>O</u>	<u>Time in Sec.</u>	<u>Galv.</u>	<u>pH</u>
25	16.0	7.0	6500	-138	5.36
25	17.5	7.5	5850	-132	5.45
25	17.0	8.0	2750	-127	5.55
25	16.5	8.5	1784	-121	5.55
25	16.0	9.0	696	-106	5.95
25	15.5	9.5	250	-85	6.25

Corresponds to concentration of 27.2 for total volume of 80 c.c.

17.5	13.5	19.0	10800	-135	5.45
17.5	13.0	19.5	5890	-121	5.65
17.5	12.5	20.0	5310	-118	5.71
17.5	12.25	20.25	900	-95	6.10

Corresponds to concentration of 20.0 for total volume of 80 c.c.

12.5	9.5	28.0	15100	-121	5.85
12.5	9.0	28.5	7560	-112	5.82
12.5	8.5	29.0	3900	-98	6.05
12.5	8.25	29.25	642	-80	6.68
12.5	8.0	29.5	225	-30	7.20



DATA FOR CURVE II - TEMPERATURE 25° C.

<u>Silicate</u>	<u>H<sub>2</sub>SiO<sub>3</sub></u>	<u>H<sub>2</sub>O</u>	<u>Time</u>	<u>Calv.</u>	<u>pH</u>
55	25.0	0.0	immed.		
50	30.0	0.0	immed.		
45	35.0	0.0	960	-152	5.13
45	33.0	2.0	745	-142	5.29
45	30.0	5.0	595	-122	5.64
35	45.0	0.0	4200	-175	4.75
35	41.0	4.0	3560	-168	4.86
35	38.0	7.0	3150	-163	4.94
35	35.0	10.0	2520	-157	5.05
35	32.0	13.0	1780	-148	5.20
35	30.0	15.0	1380	-141	5.32
35	27.0	18.0	1140	-136	5.40
35	25.0	20.0	780	-126	5.57
35	20.0	25.0	immed.		
25	25.0	30.0	5920	-169	4.85
25	24.0	31.0	5720	-163	4.84
25	23.0	32.0	5530	-167	4.86
25	22.0	33.0	4725	-163	4.93
25	21.0	34.0	4540	-160	4.99
25	20.0	35.0	3790	-158	5.02
25	19.0	36.0	3080	-154	5.10
25	18.0	37.0	2540	-149	5.18
25	17.0	38.0	1805	-142	5.30
25	15.75	38.25	1696	-131	5.41
25	15.50	38.50	1205	-120	5.67
25	15.25	38.75	924	-110	5.84
25	15.0	39.0	780	-116	5.75
25	15.0	39.0	712	-112	5.81
25	15.75	39.25	469	-69	6.18
25	15.25	39.75	150	-72	6.43
25	15.00	40.0	138	-62	6.64
25	14.75	40.25	75	-42	6.98
25	14.75	40.25	55	-28	7.20
25	14.50	40.5	20	36	8.30



DATA FOR CURVE II - TEMPERATURE 25° C. (cont.)

<u>Silicate</u>	<u>HAc</u>	<u>H<sub>2</sub>O</u>	<u>Time</u>	<u>Galv.</u>	<u>pH</u>
20	22.0	58.0	11400	-171	4.81
20	21.0	59.0	10800	-169	4.84
20	20.0	40.0	9680	-165	4.90
20	19.0	41.0	9260	-163	4.95
20	18.0	42.0	8160	-158	5.02
20	17.5	42.5	4920	-145	5.20
20	17.0	43.0	4400	-141	5.32
20	16.5	43.5	3790	-138	5.37
20	16.25	43.75	3040	-134	5.42
20	16.0	44.0	2145	-127	5.55
20	15.75	44.25	1920	-124	5.59
20	15.5	44.5	1600	-120	5.66
20	15.0	45.0	1495	-116	5.73
20	14.0	46.0	1125	-105	5.94
20	13.75	46.25	1059	-104	5.95
20	13.5	46.5	578	- 89.5	6.18
20	13.25	46.75	516	- 72	6.46
20	13.0	47.0	125	- 48	6.87
15	16.0	49.0	12960	-163	4.94
15	15.5	49.5	12660	-162.5	4.94
15	15.0	50.0	11760	-160	4.99
15	15.0	50.0	11400	-160	4.99
15	14.5	50.5	10800	-154	5.08
15	13.5	51.5	10130	-156	5.08
15	12.5	52.5	7580	-146	5.24
15	12.0	53.0	7525	-146	5.24
15	11.5	53.5	6060	-141.5	5.30
15	10.5	54.5	4040	-134	5.43
15	10.25	54.75	3445	-132	5.47
15	10.0	55.0	2940	-123	5.62
15	9.75	55.25	2164	-110	5.84
15	9.5	55.5	2241	-124	5.60
15	9.25	55.75	1650	-113	5.76
15	9.25	55.75	1560	- 96	6.08
15	9.0	56.0	1059	- 85.5	6.25
15	8.75	56.25	984	- 76	6.40
15	8.75	56.25	934	- 71	6.48
15	8.50	56.5	745	- 62	6.50
15	8.25	56.75	540	- 50	6.55
15	8.25	56.75	390	- 54	6.77
15	8.00	57.0	215	- 39.5	6.95
15	8.00	57.0	140	31	9.20



DATA FOR CURVE II - TEMPERATURE 25° C. (cont.)

<u>Silicate</u>	<u>HAc</u>	<u>H<sub>2</sub>O</u>	<u>Time</u>	<u>Galv.</u>	<u>pH</u>
10	8.5	61.5	16800	-145	5.24
10	8.0	62.0	9120	-128	5.52
10	7.5	62.5	6400	-125	5.59
10	7.0	63.0	4260	-104	5.92
10	6.5	63.5	1845	-72	6.48
10	6.25	63.75	740	-20	7.35
10	6.0	64.0	1170	+30	8.20
6	7.0	67.0	604800	-188	4.50
6	7.0	67.0	584000	-180	4.65
6	6.5	67.5	604000	-189	4.84
6	6.5	67.5	518400	-184	4.91
6	6.0	68.0	100800	-160	5.00
6	6.0	68.0	259200	-153	5.10
6	5.5	68.5	240100	-147	5.25
6	5.0	69.0	288100	-145	5.24
6	4.5	69.5	219400	-157	5.38
5	5.0	70.0	550200	-145	5.22
4	5.0	71.0	29 days	-185	Seemed set, but structure was too weak to sup- port rod.
4	4.5	71.5	29 days	-188	
4	4.0	72.0	29 days	-182	
4	3.5	72.5	29 days	-186	

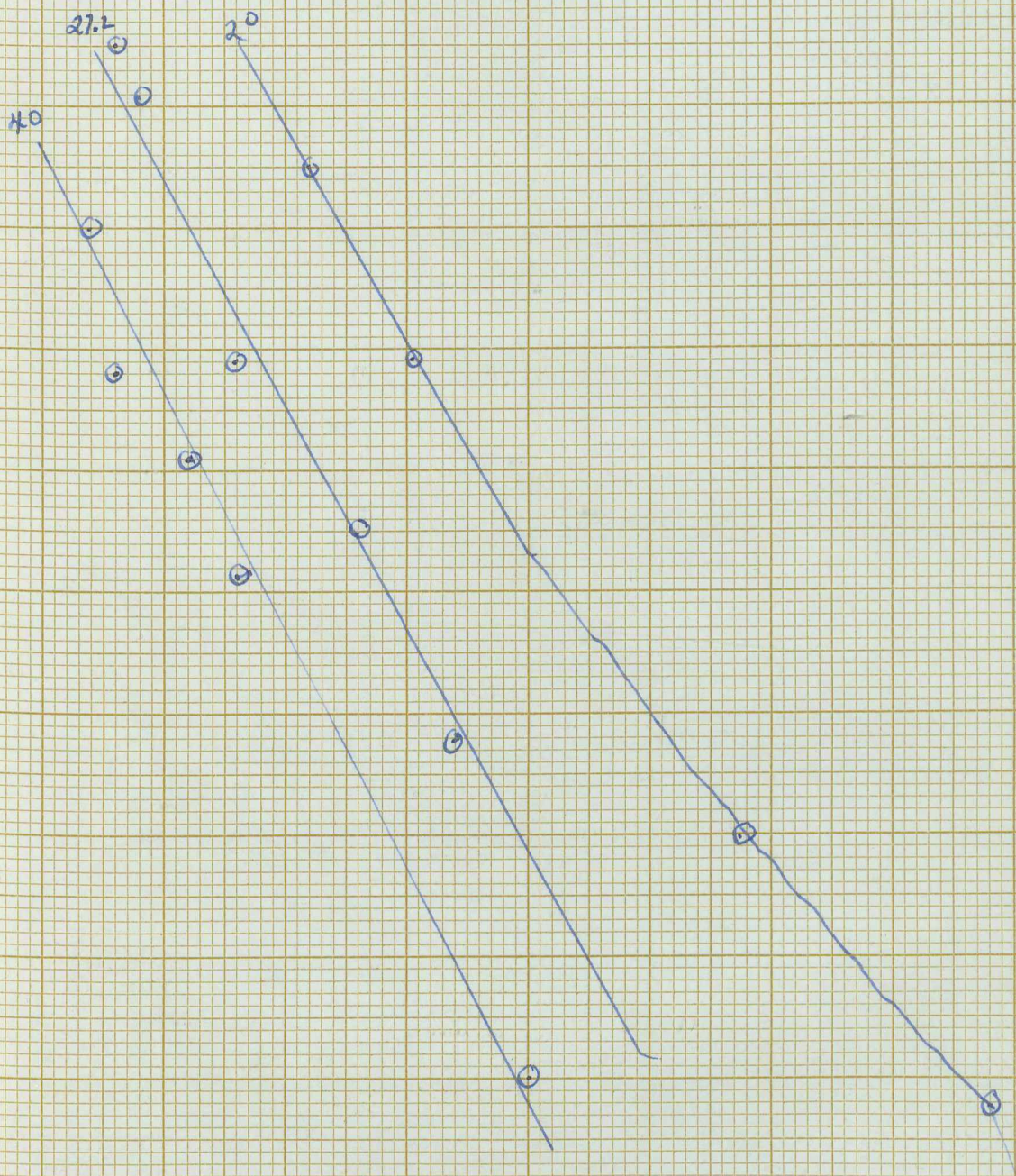


DATA FOR CURVE III - TEMPERATURE 58.2° C.

<u>Silicate</u>	<u>HAc</u>	<u>H<sub>2</sub>O</u>	<u>Time</u>	<u>Galv.</u>	<u>pH</u>
40	40.0	0.0	205	-140	5.38
40	38.0	2.0	185	-137	5.38
30	38.0	12.0	1820	-174	4.78
30	35.0	14.0	1882	-164	4.93
30	32.0	18.0	900	-157	5.05
30	30.0	20.0	480	-148	5.19
20	25.0	35.0	6680	-190	4.48
20	24.0	36.0	2880	-170	4.82
20	23.0	37.0	990	-150	5.18
20	20.0	40.0	80	-70	5.50
10	14.0	58.0	1860	-170	5.67
10	12.0	48.0	4680	-152	5.31
10	10.0	60.0	9300	-120	4.82
8	8.5	67.5	96000	-179	4.87
8	8.0	68.0	41000	-159	5.01
8	5.5	68.5	18000	-147	5.26
8	5.5	69.5	40700	-157	5.04
8	5.0	70.0	18000	-140	5.33
4	4.5	71.5	120000	-183	4.94
4	4.0	72.0	14000	-128	5.58
3	3.5	73.5	399000	-188	4.55
3	3.0	74.0	clear after 1 mo.	-17	7.30
2	2.5	75.5	cloudy after 1 mo.	-204	4.25
2	2.0	76.0	clear after 1 mo.	-155	5.08
1	1.0	78.0	clear after 1 mo.	-179	4.85

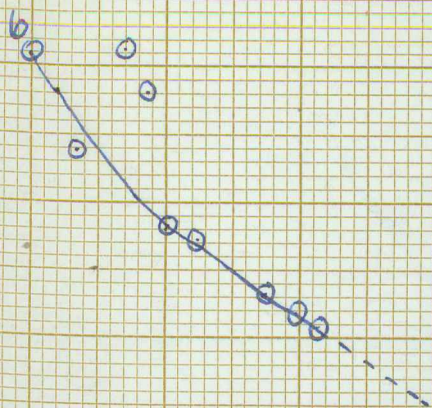


Temp. °C



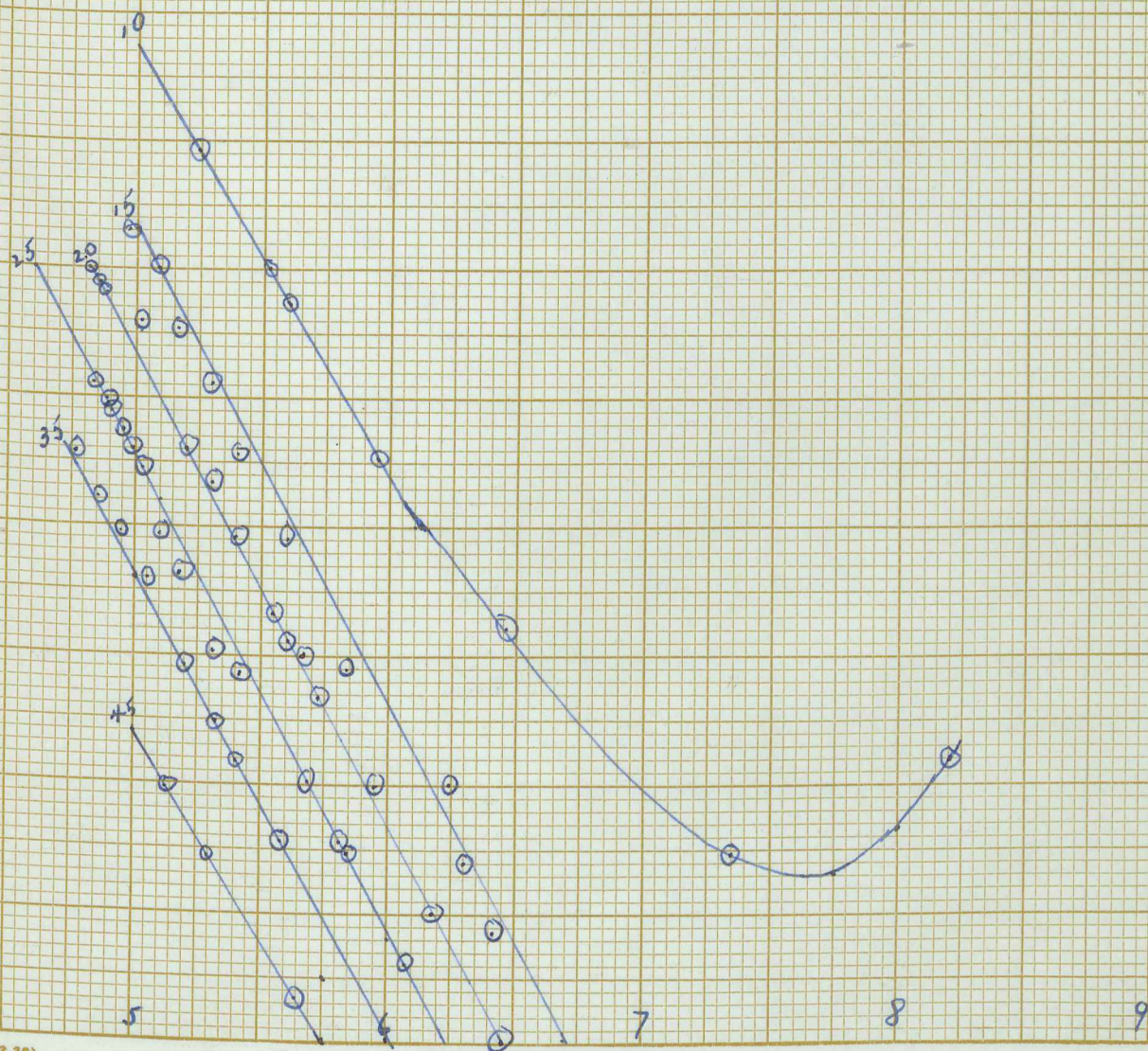


Temp 25°C



6, 10, 15, 20, 25, 35, 45 cc  
1.21 N silicate / 80cc of  
solution

6	- .93	gmals $\text{SiO}_2$
10	- 3.10	"
15	- 4.65	"
20	- 6.20	"
25	- 7.75	"
35	- 10.85	"
45	- 14.00	"





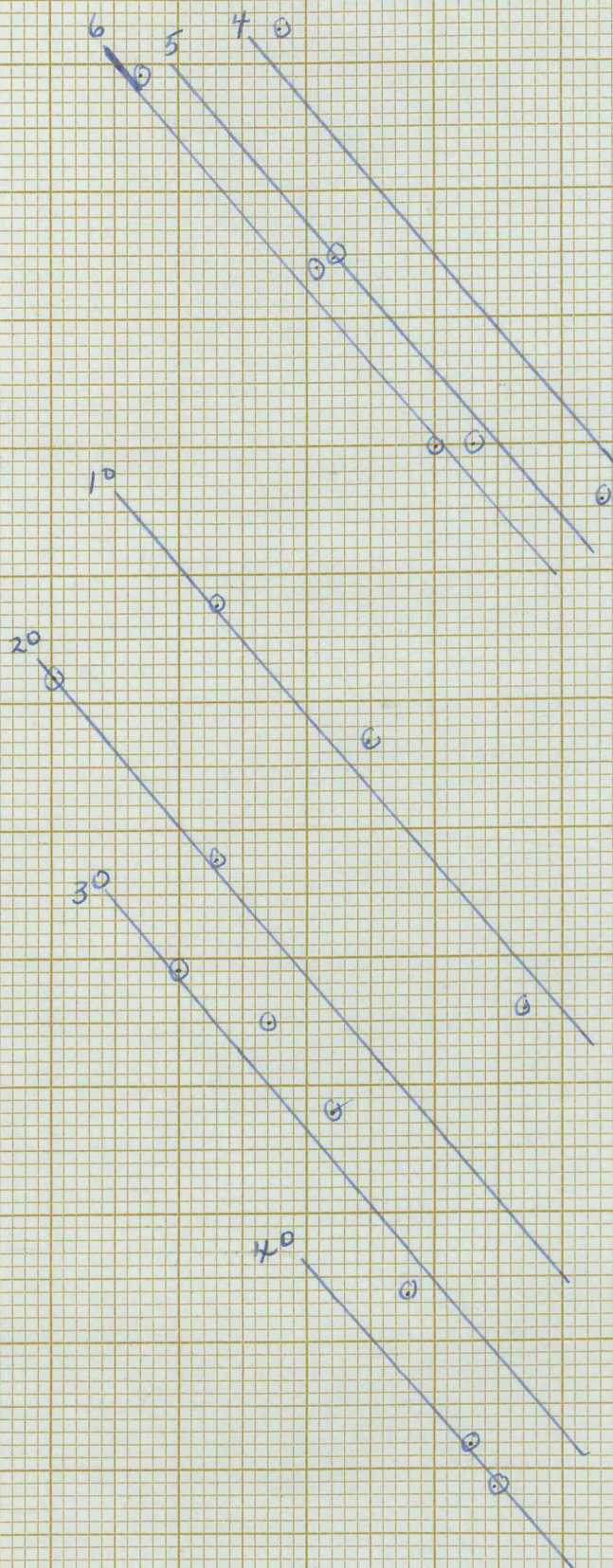
4

5

6

III

Temp 38.2°C

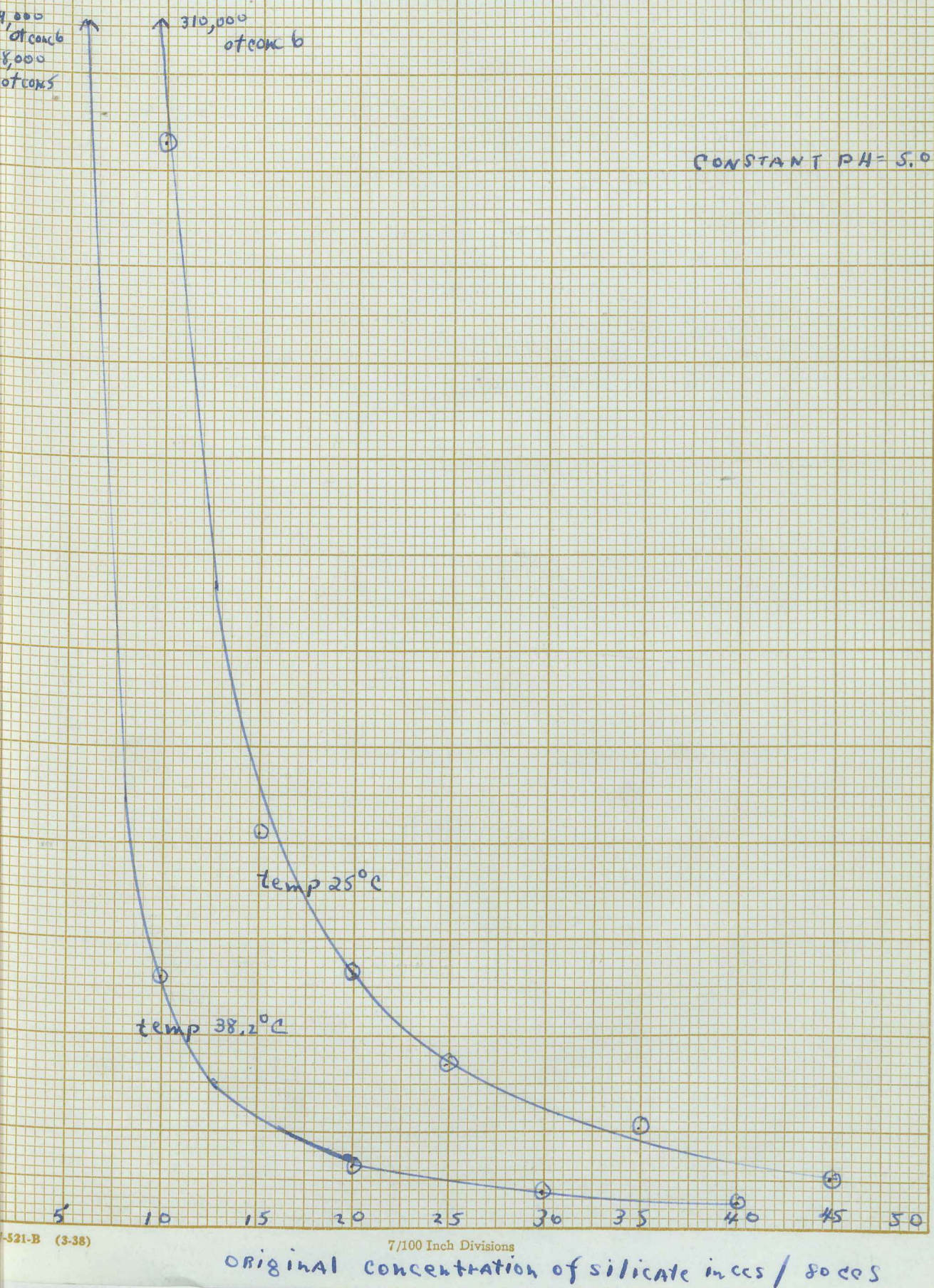


4

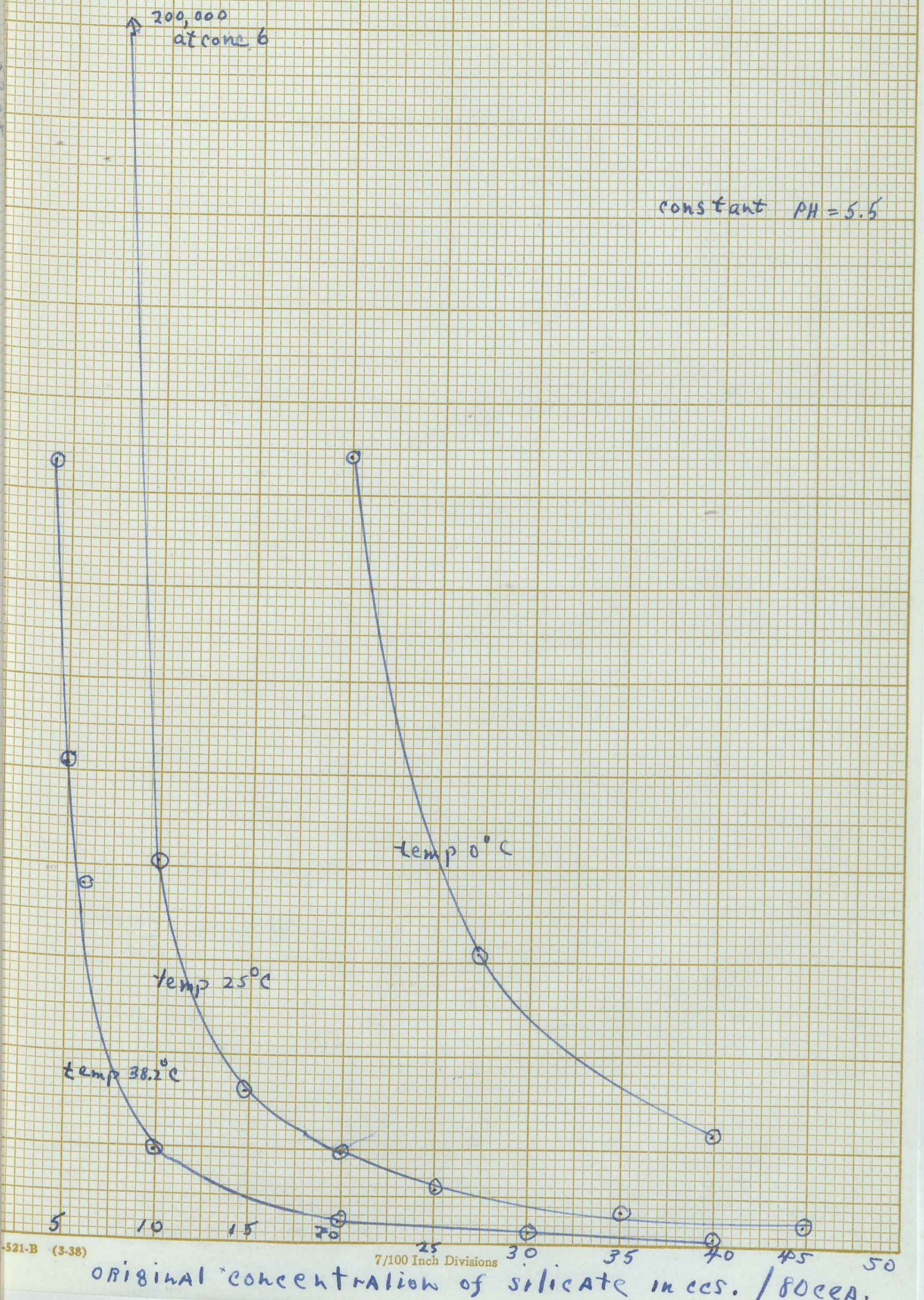
5

6











CONSTANT PH=6

100,000 at conc 6



temp 35°C

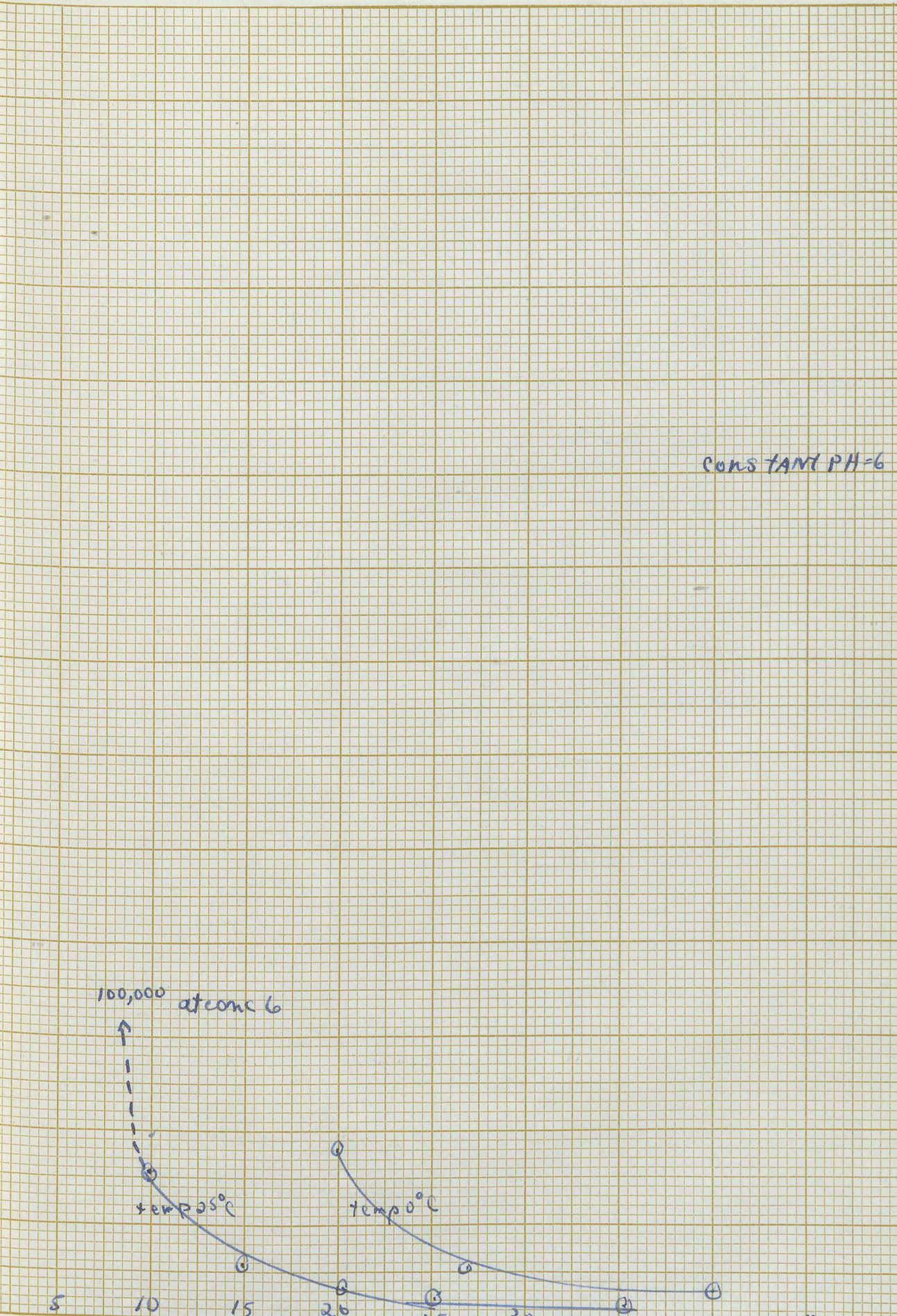
temp 0°C

5 10 15 20 25 30 35 40 45 50

521-B (3-38)

7/100 Inch Divisions

ORIGINAL concentration of silicate mcs. / 80ccs





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