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The effect of silicia concentration on the time of set of constant pH

Walter Otto Gerber

Union College - Schenectady, NY

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THE EFFECT OF SILICA CONCENTRATION ON THE
TIME OF SET AT CONSTANT pH

THE EFFECT OF SILICIA CONCENTRATION ON
THE 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 Walter O. Gerber Jr.

Approved by Charles B Hurd

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INTRODUCTION

When an aqueous solution of sodium silicate is treated with an acid, the mixture will become increasingly viscous and opalescent, and will finally set, if the silica concentration exceeds 2% and if the gel is not too acid or too alkaline. The time of set is determined by the pH, concentration of silica, concentration of certain foreign substances, and the temperature.

HISTORICAL

Work on silicic acid gels has been performed in order to discover the mechanism of the reaction and the structure of the gel. In fact, much of this work has been done in this laboratory by studying the effect of various factors on the time of set. In particular, Sheffer¹ has made a study of the effect of silica concentration on the time of set, and it is this problem with some variation, to which this thesis is devoted.

Sheffer kept the silica concentration constant, varied the amount of acetic acid added, and diluted each mixture up to a certain constant volume. In order to obtain the relation between silica concentration and time of set, he plotted several curves (time of set vs. pH), silica concentration being constant on each. Then, he chose a certain abscissa, say pH 5, erected a line parallel

to the time axis cutting each curve. The intersection of this line with each curve gave a series of points which, when replotted, resulted in a curve of silica concentration vs. time of set at constant pH.

This procedure was of course a good beginning to the problem of keeping all factors constant except the silica concentration in order to discover its independent effect on the time of set. Whether Sheffer was aware of the fact or not, he has however, neglected two factors which undoubtedly are significant, namely the sodium ion concentration and the acetate ion concentration. Each time that he added a different amount of silica which was introduced into the reaction as sodium silicate, he was varying his sodium ion concentration, and each time that he added a different amount of acetic acid, he was varying the acetate ion concentration.

Later, Hurd got the idea of actually varying the sodium silicate and acetic acid each time keeping a constant difference between the milli-equivalents of acetic acid and milli-equivalents of sodium hydroxide in the silicate, and then adding sufficient sodium acetate to keep the sodium ion concentration constant as well as the acetate ion concentration and also to maintain constant pH.

EXPERIMENTAL

In accordance with the statement of the problem, three standardized solutions were needed, sodium silicate, acetic acid and a sodium acetate solution. The standardization of the latter was the most difficult and time consuming. Sodium acetate is not a primary standard; it does not take up a definite amount of water of crystallization. Thus it was not advisable to trust making up a solution gravimetrically. The method used was, in essence, that proposed by Hurd and Fiedler². A ten milliliter pipet was calibrated by weighing the amount of water which it delivered, for each of three trials. A rather concentrated solution of reagent grade sodium acetate was made up. Two portions of this solution were delivered by the calibrated pipet, one into each of two previously weighed platinum crucibles. Platinum was used to avoid the trouble of getting the crucibles to constant weight. Each platinum crucible was placed on a steam bath for each of which a sheet iron central ring was made to avoid the contamination of the platinum by particles of copper from the copper rings. Later the crucibles were to be placed in a flame and copper is known to alloy with platinum. The crucibles were left on the steam bath for two

successive days. One must be careful in this evaporation because, when the solution becomes very concentrated, a scale of sodium acetate forms over the surface, making one think that the material is already dry. If the solution is then placed over a flame it will bump and sodium acetate will be lost. The evaporation takes about twelve hours. Then the crucibles were placed in an oven at about 110°C for about five hours to be sure of the preliminary drying. Occluded water was observed to be given off. After removing the crucibles from the oven they were placed in silica triangles and heated gradually, the clamps holding the triangles being lowered toward the Bunsen flame. The sodium acetate melted and turned into a viscous brown colored liquid, which was evaporated carefully to a black residue which turned white upon ignition to sodium carbonate.

When the last traces of blackness were gone, the crucibles were allowed to cool for a minute and then placed into a calcium chloride dessicator to further cool. The crucibles were then weighed, reheated for five minutes, allowed to cool as before, and then reweighed. There was no change in weight. The initial weight of the crucible subtracted from the final weight gives the weight of sodium carbonate formed. From this the corresponding amount of

sodium acetate can be calculated, and knowing the volume of the pipet, the molarity of the original solution can be found.

An approximately 1N sodium hydroxide solution was standardized against weighed amounts of potassium acid phthalate using phenolphthalein as an indicator. Then a 1N hydrochloric acid solution was made up and compared with the sodium hydroxide solution using methyl orange-xylene cyanol as an indicator. The color change for this indicator was more favorable than that for methyl orange alone, the color change being from green to pink, instead of orange to pink, as the solution becomes acid. Then, an approximately 1N aqueous sodium silicate solution was made up by diluting 4.6 liters of E-brand silicate* to about twenty liters, and was titrated with the 1N hydrochloric acid solution using methyl orange-xylene cyanol again as the indicator. After the sodium hydroxide equivalent of the silicate has been determined, the amount of silica can be calculated from the soda:silica ratio given by the manufacturers who guarantee it to about one percent accuracy. For the purposes of this experiment, however, the exact amount of silica need not be known, as the silica concentration

* Manufactured by the Philadelphia Quartz Company.

in each run is proportional to the number of milliliters of silicate solution used, because the total volume is kept the same for each run. Next an approximately 2N acetic acid solution was made up by diluting 2.17 liters of glacial acetic acid to about 20 liters. The distilled water used in making up the acetic acid, silicate and sodium acetate solutions was previously boiled to remove carbon-dioxide.

Other workers in this field had used, as gel containers, 100ml. beakers covered with watch glasses and held in place by lead weights. This method seemed a little troublesome, because, if the beakers were submerged deep enough in the water of the thermostat to insure constant temperature throughout the gel, the buoyancy of the beaker and contents is greater than its weight and there is danger of its dumping over, especially when the experimenter attempts to remove the watch glass and weight. Furthermore, if one hand were used to hold the beaker, and the other to remove the watch glass and insert a testing rod, there would not be a free hand to click a stop-watch. Even if the beaker were removed from the thermostat for testing, there is danger of dumping the beaker over when removing it, as it is a rather clumsy affair with a watch glass and weight superposed, and there is also opportunity for a temperature change.

After looking at several different containers, the flat mayonnaise jar was selected for several reasons. The mouth was wider than that of the 100 c.c. beaker, thus providing more gel surface to rupture, and allowing for more frequent testings. The jar and contents was heavy enough to submerge to the proper depth in the thermostat without danger of being easily tipped over. The jar had a screw top which prevented contamination by splattering and by materials in the air and also stopped evaporation which causes serious errors in long setting gels. Furthermore, the jars held a convenient amount of solution when filled to the same height as the 100 ml. beaker containing 80 ml. of solution, which corresponds to the proper height of gel for the tilt rod testing method. This standard height was conveniently indicated by a structural bend in the side of the jar. When filled to this bend the jar held exactly 160 c.c.. Since 65 c.c. of gel mixture were needed for a p H determination, it was decided to use $160+65$ or 225 c.c. as the total volume, which was to be the same for each run.

In order to make the most of one's time, it was necessary to work out a procedure for running a number of gel reactions. Since the proper cleaning of four burets (one for measuring silicate, one for acetic acid, one for sodium acetate, and another for distilled water) required a considerable amount of time, it was found advisable to perform the volumetric

work for several runs all at once. If it were desired to make six runs, twelve jars were needed, two for each run. The silicate solution was put into one, and the sodium acetate and acetic acid into the other; about half of the water required for dilution to constant volume, was added to each. The sodium acetate had to be put into the acetic acid, as it formed a precipitate when added directly to the silicate. While making up the solutions to be mixed, one could intermittently tinker with the thermostat until it was observed to maintain the desired temperature.

The thermostat consisted of a well insulated copper tank, which holds about fourteen pails of water and contains a motor driven fan shaped propeller for stirring. The actual temperature control was maintained by a Thyatron tube circuit, electric knife heater, and a thermoregulator with a toluene filled bulb and an adjustable mercury contact.

The following procedure for measuring out solutions for various runs was found expedient. First, the calculated amount of silicate was added to each of six numbered jars (1A, 2A etc.) Then the acetic acid was added to each of another six jars (numbered 1B, 2B, etc) which were placed in a row behind the corresponding jars containing the silicate. Next, the sodium acetate was added to each jar of the acid set. Then the amount of water necessary for dilution to

to 225 ml. was added to each. After the water was added to each number one jar, these two jars (1A and 1B) were placed in the thermostat. The jars were numbered in order of decreasing time of set. Thus the longer setting gels were started first to minimize the time required to make a set of runs. After the water had been added to each set of two jars, they were immediately placed in the thermostat, which was bringing them to the desired temperature while the operator was adding water to the rest of the jars. After the water had been added to the last set of two jars, the first two were just about at the proper mixing temperature.

If it were desired to make a set of runs at 25° C., the mixing temperature was always kept below 25° C. The first set of gels were mixed at 23.5° C. and the temperature rise measured. This temperature rise which was due to the heat of neutralization was found to be dependent on the number of ml. of silicate present, as was to be expected, and a rough calibration curve was drawn (temperature rise vs. ml. of silicate). Thereafter when gels were to be run at 25° C., the reactants were brought to the proper temperature as observed from the calibration curve before mixing. Nevertheless, the temperature was taken after mixing, and the gel was cooled or heated to the desired temperature before placing in the thermostat. There were so many factors

involved that one had to be very careful in order to prevent additive errors from obscuring the possibility of obtaining any worthwhile results at all.

All 0° gels were cooled in an ice and salt water bath to below zero degrees, mixed, allowed to come to zero and then buried in wet snow or chopped ice. When the estimated time of set had elapsed, the snow was removed down to the cover, the cover removed and the gel tested and recovered with cap and snow, at intervals judged from the rigidity of the gel.

Some preliminary trial runs were made to determine the difference between the milli-equivalents of sodium hydroxide in the silicate and the milli-equivalents of acetic acid which would give a pH in the buffer range of sodium acetate which is between 3.5 and 5.5. Gels in this region were found to have barely observable pH drift if any and also to have such a long setting time as to be impracticable to run in one day. It could not always be arranged so that the experimenter could be present when the gel was about to set, and there was a waste of time involved when this situation occurred. So the writer decided to investigate the reaction at a slightly higher pH, where the setting time would be more convenient.

While gel reactions were being run, a quinhydrone

potentiometer with platinum and calomel electrodes and a 100 ml. beaker containing a pinch of quinhydrone and a stirring rod were maintained on the edge of the thermostat ready for use. A testing rod 3 mm. in diameter and 10 cm. long, a stopwatch, a concentrated sodium hydroxide solution and a wash bottle for cleaning the electrodes were kept near-by.

After the contents of the two number one jars had come to the proper temperature, the silicate of the no. 1A jar was poured into the 1B jar containing the acetic acid and sodium acetate, the stop watch started and the solution poured from one jar to the other three times to insure thorough mixing. Then a sufficient amount of the mixture was poured into one jar to fill it to the head, and the rest into the 100 ml. beaker containing quinhydrone which was immediately stirred and placed under the calomel and platinum electrodes which held the beaker in the thermostat. The potentiometer reading was taken at various intervals for long setting gels, while sometimes only one reading could be taken for rapidly setting gels. A second run could then be started if the operator desired to repeatedly wash the electrodes and transfer them from one reaction to the other. This procedure was actually carried out in the case of long gels.

It was also found helpful to estimate when to start the tilt rod testing on the gel by observing the portion of the gel being used for the pH determination, since the operator is at the potentiometer most of the time. This simple expedient saved undue rupturing of the gel surface on setting, a practice which should always be avoided as it increases the time of set and, in some cases, causes one to believe that a certain gel will never set, which if left undisturbed would support the rod in a short time after mixing. This is especially true of gels low in silica concentration which correspondingly exhibit a weak structure. The above described situation became really important during a 35° C. run at a pH of 7. All gels of this pH and temperature, that will support the rod, set in less than twenty minutes. It was desired to lengthen the time of set to get further points for a graph of silica concentration against time of set. The only way to lengthen the time of set in this situation was to decrease the silica concentration. Accordingly, the silica concentration was decreased to 15 ml. per 225 ml. of solution. By visual extrapolation on the above mentioned curve, the time of set should have been in the neighborhood of four minutes. Consequently, the gel was tested at quarter minute intervals starting at three minutes. After four testings, the gel had not set. The gel was tested at 15 minutes and

at thirty five minutes. The gel never did set. This run was repeated and the rod inserted after four minutes as judged from the portion being used for a pH determination. After a second insertion at four minutes and 30 seconds, the gel supported the rod at the proper angle. The practice of too frequent testing, which may lead to serious errors, can be avoided by judging approximately when to test by practicing on the gel being used for the pH determination.

It was also found advisable to wash the gel containers immediately after the gel had set, as the silicate attacks the glass and adheres so firmly that it cannot be completely removed by washing. The interior surface may appear to be washed clean, but the next day a white powdery film will be observed on the interior of the glass. These tiny particles composing the film form excellent nuclei for gel formation and may cause unobserved errors. Thus it is wise to wash gel containers immediately after the gel has set.

In short, the experimental procedure consisted of making up and standardizing 5 gallons of silicate, 5 gallons of acetic acid and four liters of sodium acetate solution, of performing trial runs to find the proper difference to be maintained between milli-equivalents of acid and ml. equivalents of silicate to maintain the desired pH, of making calculations for a set of runs at constant pH,

volume, temperature, sodium ion concentration and acetate ion concentration, finally of mixing the proper amounts of reactants and taking the pH, and the time of set by the tilt rod method. The results were as follows.

DATA

Units for reactants are in milliliters. pH readings are given only at 25° C. pH's were taken at other temperatures, but were found to be meaningless as the quinhydrone and saturated calomel electrodes were at 25° C. and the gel at some other temperature. This temperature difference was observed to cause a variable error of about .3 of a pH unit. Identical gel mixtures were assumed to have the same pH at 25° C. as at 35° C. and at 0° C.. The only way of actually measuring the pH at a temperature other than 25° C. would be to have the electrodes thermostated and recalibrated at this new temperature.

1. Zero degree runs.

A. pH-6

<u>Silicate</u>	<u>HAc</u>	<u>NaAc</u>	<u>H₂O</u>	<u>Time</u>
149.0	75.23	0	.77	25'
110.0	56.46	12.72	45.82	54'
90.0	46.82	19.82	68.36	89'
77.8	40.96	23.23	83.01	137'
70.0	37.20	25.78	92.02	170'
50.0	27.58	32.30	115.12	396'

B. pH-6.3

<u>Silicate</u>	<u>HAc</u>	<u>NaAc</u>	<u>H₂O</u>	<u>Time</u>
69.3	33.60	0	122.10	43.5'
60.0	29.11	3.05	132.85	59.8'
54.0	26.23	5.00	139.78	88.3'
45.0	21.89	7.93	150.18	117.0'
40.0	19.48	9.57	155.95	146.5'

C. pH-7

<u>Silicate</u>	<u>HAc</u>	<u>NaAc</u>	<u>H₂O</u>	<u>Time</u>
149.0	70.76	0	5.24	*
110.0	51.98	12.73	50.29	7.0'
74.5	32.80	25.80	96.40	13.7'
60.0	27.91	29.05	108.04	18.0'
50.0	23.09	32.30	119.61	25.5'
40.0	18.28	35.55	131.17	36.0'
30.0	13.47	38.82	142.71	69.0'

* Curdled on mixing

25°C. runs

A. pH-6

<u>Silicate</u>	<u>HAc</u>	<u>NaAc</u>	<u>H₂O</u>	<u>Time</u>	<u>Temp. rise on mixing</u>	<u>pH variation</u>		
149.0	75.23	0	.77	1'20"	3.5°	3'	6.15	
110.0	56.46	12.72	45.82	3'31"	2.8°	3'	5'	5.91 5.95
90.0	46.82	19.82	68.36	7'18"	2.4°	5'	8'	6.05 6.15
70.0	37.20	25.78	92.02	13'41"	2.0°	5'	6.5'	9'-14' 6.07 6.15 6.15
60.0	32.39	29.02	103.53	20'52"	1.5°		19'	21' 5.84 6.24 6.27
50.0	27.58	32.30	115.12	31'19"	1.1°	5.68	5.8	5.83

B. pH-6.3

<u>Silicate</u>	<u>HAc</u>	<u>NaAc</u>	<u>H₂O</u>	<u>Time</u>	<u>pH</u>
69.30	33.60	0	122.10	5'50"	6.2
54.00	26.23	4.99	139.76	8'00"	6.2
45.00	21.89	7.93	150.18	11'01"	6.3
40.00	19.48	9.57	155.95	12'50"	6.3
38.55	18.80	10.04	157.61	16'50"	6.3
35.00	17.07	11.18	161.75	23'00"	6.3
30.00	14.67	12.82	167.51	34'00"	6.3
27.50	13.16	13.65	170.69	39'02"	6.6
25.00	12.26	14.46	173.28	44'49"	6.3-6.5
22.50	11.05	15.28	176.17	58'00"	6.5

C. pH-7

<u>Silicate</u>	<u>HAc</u>	<u>NaAc</u>	<u>H₂O</u>	<u>Time</u>	<u>pH</u>
110.0	51.98	12.73	50.29	56'2"	6.7
74.5	34.89	24.32	91.29	1'33.4"	6.8
60.0	27.91	29.05	108.04	1'56.8"	7.0
40.0	18.28	35.55	131.17	2'18.0"	6.9-7.0
30.0	13.47	38.82	142.71	2'35.5"	7.3
25.0	11.06	40.50	148.44	3'26.0"	7.4
20.0	8.65	42.10	154.25	5'27.0"	7.2
15.0	6.24	43.76	160.00	9'35.0"	6.8-6.7
10.0	3.84	45.30	165.86	*	6.7

* Too weak to support the tilted rod.

3. 35° C. Runs

A. pH-6.0

<u>Silicate</u>	<u>HAc</u>	<u>NaAc</u>	<u>H₂O</u>	<u>Time</u>
110.0	56.46	12.72	45.82	20"
90.0	46.82	19.82	68.36	2'31"
70.0	37.20	25.78	92.02	5'10"
60.0	32.39	29.08	103.53	6'00"
50.0	27.58	32.30	115.12	10'25"

B. pH-6.3

<u>Silicate</u>	<u>HAc</u>	<u>NaAc</u>	<u>H₂O</u>	<u>Time</u>
69.30	33.60	0	122.10	2'10"
45.00	21.89	7.93	150.18	5'64"
35.00	17.08	11.18	161.75	5'34.2"
22.50	11.05	15.28	176.17	14'12"
20.00	9.85	16.12	179.03	15'03"

C. pH-7.0

<u>Silicate</u>	<u>HAc</u>	<u>NaAc</u>	<u>H₂O</u>	<u>Time</u>
30.0	13.47	38.82	142.71	1'10.8"
25.0	11.06	40.50	148.44	1'43.0"
20.0	8.65	42.10	154.25	2'18.0"
15.0	6.24	43.76	160.00	4'30.0"

DISCUSSION OF RESULTS

Data as a mere series of tabulations is uninteresting, but when a column of figures assumes the form of a smooth curve, the data becomes picturesque and significant. Curve 1 shows a plot of all data obtained that was established by at least two checks. One would say, on first thought, that, when too many curves are plotted on one graph, there is danger of confusion. This thought bothered the writer for some time until he decided that a better study of the curves and their interrelation could be made if they were placed on one graph even if there were danger of confusion.

Since there were so many curves to be plotted on a single sheet, different color ink and a variation in line type was used for purposes of distinguishing between curves. The color determines the pH, red for pH-7, white for 6.3, and blue for 6.0. The type of line tells the temperature, full line stands for 0° C., long dash for 25° C., and the short dash for 35° C. Each curve bears out the fact, that a decrease in silica concentration, other factors constant, causes an increase in the time of set. The acid curves flatten out gradually on both ends and approach certain limiting values asymptotically, the asymptotes depending on the method of determining when the gel is set. The curves for acid gels near the neutral point, when run at 35° C., seem to stop

rather abruptly. This is due to an idiosyncrasy of the testing method. In order to proceed along these curves in the x-direction, one must continue to decrease the silica concentration. Eventually, the gel structure becomes so weak that it will no longer support the tilted rod. For these rapidly setting gels, it is difficult to get values for points close enough together with sufficient accuracy to tell whether the curve bends gradually toward a horizontal asymptote or abruptly. The latter seems to be the case.

The curves for gels run at higher pH* and higher temperatures lie closer to the origin. This means that the time of set decreases with an increase of temperature, and also with an increase of pH, a result which bears out the findings of previous workers in this field. One would also think that if the silica concentration were increased without limit, that the curves would approach the concentration axis asymptotically. This point cannot be tested experimentally, as there is no such thing as zero time of set, because a certain length of time is required for mixing, and the resulting agitation prolongs the setting. If the silica concentration is very high, the gel cannot be thoroughly mixed before chunks of gel begin to form, and consequently there is an upper limit to the curves.

* All discussion refers to the pH range 5.8-7.3 unless otherwise indicated.

Furthermore, in this experiment, the silica concentration could not be made high enough so as to cause the constant sodium ion concentration to be exceeded. For example, suppose we had decided to make a run at a pH of 7. We could use no more than 153 ml. of silicate, since this amount required 72 ml. of acid for neutralization. The sum of these two volumes would then be equal to the constant volume which was chosen to be 225 ml.. Consequently, there could be no further increase in the amount of sodium silicate added. Therefore, no sodium acetate was added to this mixture, and the concentration of sodium ion and acetate ion present was chosen as the concentration to be kept constant throughout the remainder of reactions of that set. For the upper white curve, which represents the first run, this predicament was not foreseen. A gel containing 70 ml. of silicate at a pH of 6.3 at 25° C. was observed to set within a convenient space of time, so the sodium ion concentration corresponding to 70 ml. of sodium silicate per 225 ml. of solution was chosen as the constant sodium ion concentration; consequently the white curve and its mates which were to be compared with it had their upper limit predetermined. This situation was changed in the remaining determinations so as to extend the curves upward as far as possible.

The next observation which one may make is that there

are two crossings of the curves. This means that two gels each containing 65 ml. of 1.178 N E-brand silicate per 225ml. of solution, one gel at a pH of 7 and at 0° C. and each containing the proper amount of sodium acetate (which can be found in the data) will set in the same length of time. A similar statement may be made for the other crossing.

One might next ask what sort of equation these curves follow. The writer had tried to fit a simple exponential, an equilateral hyperbola and a parabola to these curves with very little success except in the latter case. The parabola was observed to fit very roughly. Somewhat later, however, the writer plotted curves 2,3, and 4, which seemed to show a linear relation between the reciprocal of concentration squared and the time of set, the criterion for a third order reaction. This meant that $1/c^2 = KT$ or, taking the square root of both sides, that $C\sqrt{T} = K$. This constant was determined for the upper white curve, and an empirical curve plotted which fit the experimental curve within the limits of experimental error. This was also done for the second white curve with a fair amount of success. The writer does not propose the equation $C \times \sqrt{T} = K$ as the truth; it may be, if pH temperature, sodium ion concentration and acetate ion concentration are better controlled, nevertheless, this equation serves as a good working rule.

All of this discussion of the silica equation emanates from a study of the curves drawn to show the order of the reaction, which was really what I was seeking. When the various criteria for zero, first, and second order reactions were plotted, there was no semblance of linearity, but when the reciprocal of concentration squared was plotted against time of set, the curve seemed to be fairly linear. The circles, spotting the points, are drawn with radii equal to the estimated probable error. In the case of all pH's, the results were very good at 0° C. and only fair at 35° C. where the temperature control was not as good as it might have been. The pH control was better at 6 and 6.3, and the curves are more nearly linear. On the number 2 graph, the 35° C. run was plotted merely for completeness, also to show the effect of temperature. The curves, of course, may be straight lines, if the pH, were better controlled. The temperature rise on mixing was hard to judge at 35° C. and the gels set so rapidly that it was difficult to get any satisfying accuracy at all. One might also ask why the curves do not pass through the origin. One answer is that possibly these extrapolations do not hold for gels with very high silica concentration, that is, the reaction is very likely not a third order in this neighborhood. Secondly, if the extrapolations are assumed to hold, we may draw certain conclusions as follows. Considering the graph number one, we

may conclude that the gel will theoretically set in zero time with a finite concentration of silica, which can be read from the curve. By studying curve 4, we could say that at 0° C. and a pH of 7, a gel will not set in zero time no matter how much silicate is present. Since we have no experimental right to assume that the reaction is third order in the neighborhood of the origin, conclusions such as these are merely interesting and not necessarily valid.

From curves 2, 3 and 4, we can come to an important conclusion after the following assumptions are made:

1. That the reaction is concerned with like molecules of silica in some form which result from the rapid interreaction of sodium silicate and acetic acid.
2. That the time of set represents a definite fraction of the original concentration converted during the reaction.

One may derive* the relation $1/c^2 = kt$ as follows:

$$\frac{dx}{dt} = k(c - x)^3 \quad \int_0^x \frac{dx}{(c - x)^3} = \int_0^t k dt$$

$$\frac{1}{(c - x)^2} - \frac{1}{(c - 0)^2} = k(t - 0)$$

Where c = the original concentration of silica.
 x = the amount converted in time t .

Now, let $x_s = f \cdot c$, where f = the fraction reacted at the time of set (t_s), and x_s = the amount of silica converted at the time of set. Substituting, we have,

$$\frac{c^2 - (c - x_s)^2}{c^2(c - x_s)^2} = kt \quad , \quad \frac{c^2 - (c - f \cdot c)^2}{c^2(c - f \cdot c)^2} = kt_s$$

* Originally derived by Hurd.

$$\frac{2fc^2 - f^2c^2}{c^2(c - fc)} = kt_s, \frac{2f - f^2}{c^2(1 - f)^2} = kt_s, 1/c^2 = k't_s \text{ or,}$$

dropping subscripts, $\frac{1}{C^2} = KT$.

Since the volume was kept constant, C is proportional to the number of ml. of silicate added. Accordingly, a plot of time of set vs. (ml. of silicate)⁻² would serve just as well as T vs. 1/C² and would eliminate further calculations. What was actually plotted was time of set vs. (ml. of silicate)⁻² x 10⁴ to make the units more convenient. Although the writer does not feel justified in proposing that the reaction is a third order type, he will say that, in the range studied, it is closer to a third order than any other, and presumably, that the reaction might follow the equation for the third order, if conditions were better controlled.

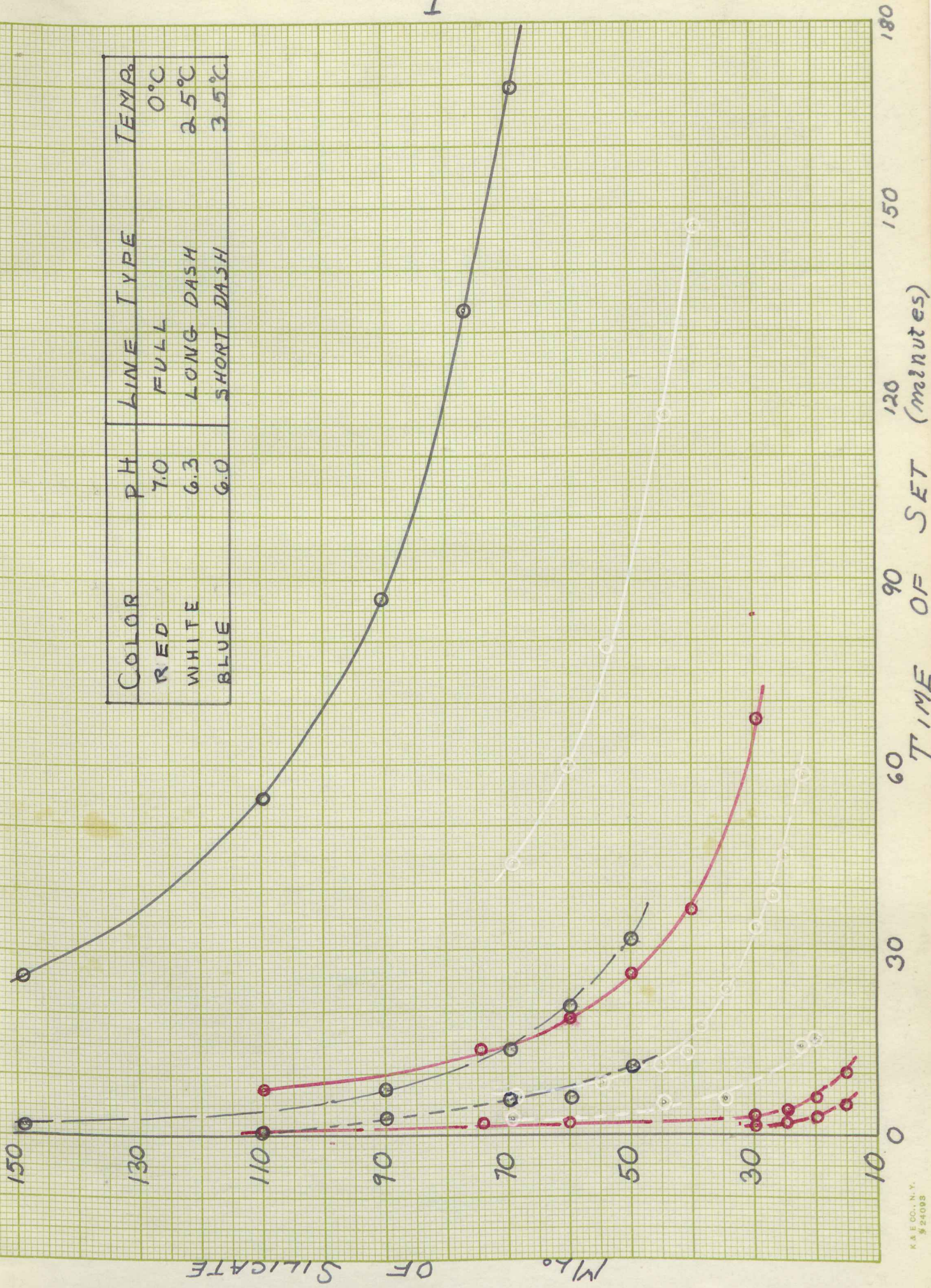
An effort has been made to maintain all factors constant except the silice concentration, to discover its independent effect on the time of set. Even when all other factors are properly controlled, there is still trouble with the pH. The initial pH's were satisfactorily constant, but there was a slight drift toward a higher pH. At 6.3, there was little or no observable pH drift, and the pH was maintained fairly constant from one run to another. At 7, the pH drifted appreciably and continued even after the gels had set. Nevertheless, curves of silica concentration vs. time of set were

obtained having the same general shape as those obtained by Sheffer, who neglected the variation of the sodium and acetate ion concentrations. If the pH's which were taken with a gel at 0° C. and the electrode at 25° C. mean anything, there was less pH variation at this lower temperature. In fact, if the reaction is inherently third order in the range studied, the curves, (time vs. $1/C^2$) being more nearly linear at 0° C., indicate better control, as the writer believes is the case.

Judging from the plots of time vs. $1/C^2$, the reaction appears to be of the third order. Presumably, better control could be maintained in the pH range 3.5-5.5 which should be studied. In addition, a study of gels made by mixing sodium silicate, hydrochloric acid and sodium chloride, would also be interesting and perhaps easier, since the difficulty of standardizing the sodium acetate solution could be avoided as a sodium chloride solution could be made up gravimetrically.

I

COLOR	P.H.	LINE TYPE	TEMP.
RED	7.0	FULL	0°C
WHITE	6.3	LONG DASH	2.5°C
BLUE	6.0	SHORT DASH	3.5°C



II

25°C

0°C

pH = 6.0

TIME OF SET (MINUTES)

36

180

30

160

24

140

18

100

12

80

6

60

0

20

0

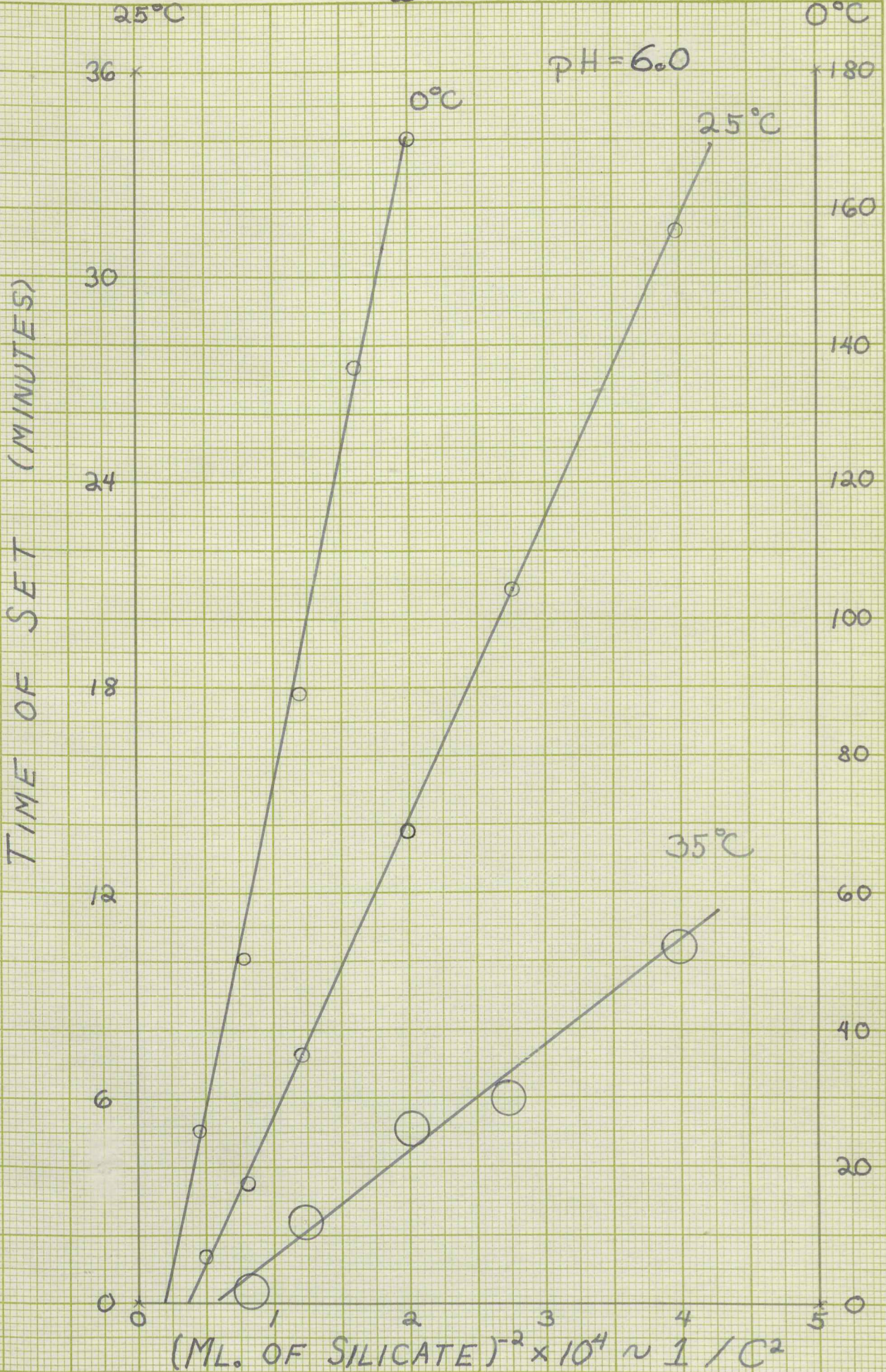
0

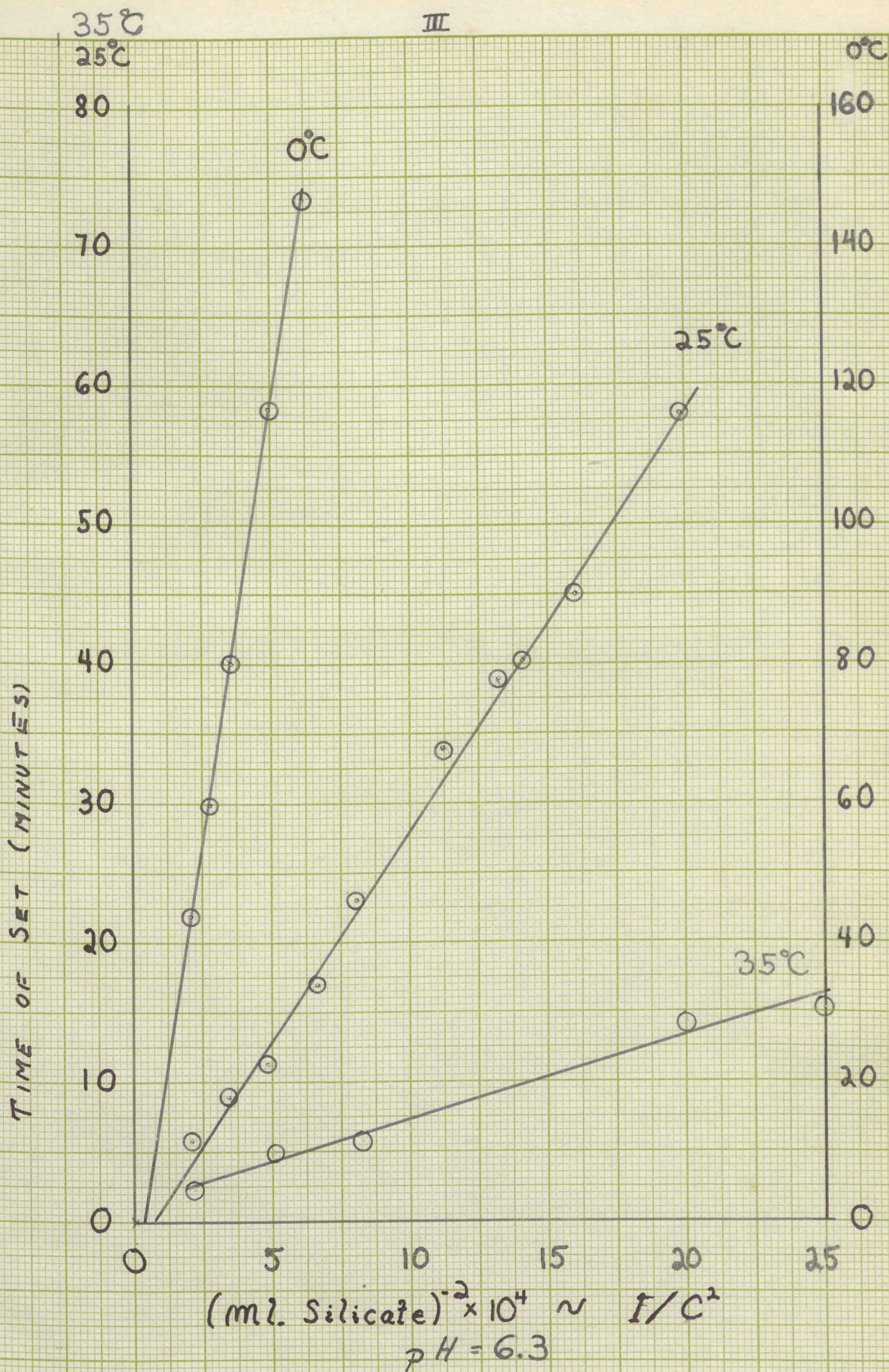
(ML. OF SILICATE)⁻² × 10⁴ ~ 1/C²

0°C

25°C

35°C





25°C

35°C

pH = 7

0°C

TIME OF SET (minutes)

14 x

12

10

8

6

4

2

0

70

60

50

40

30

20

10

0

10

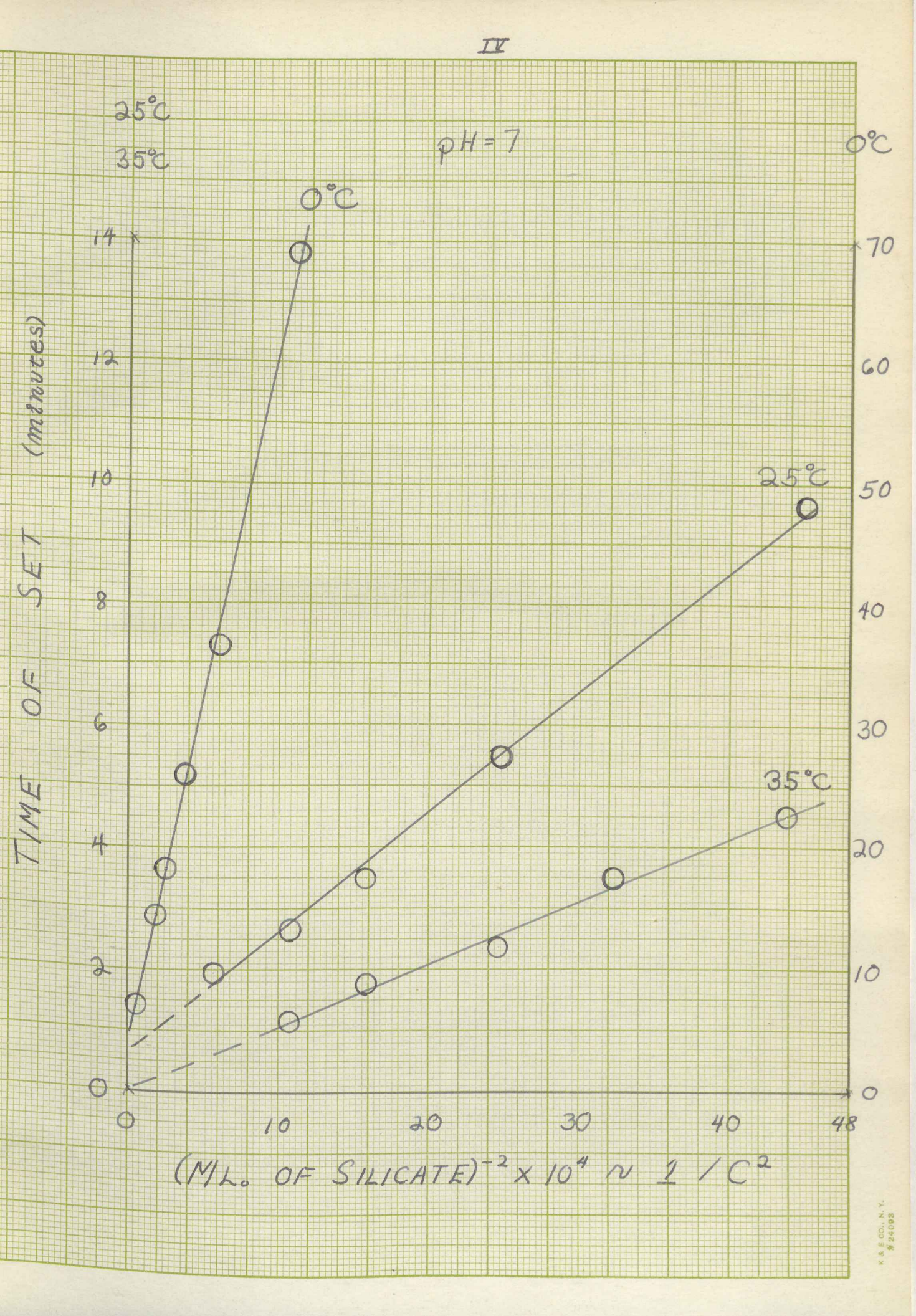
20

30

40

48

$(\text{M/L. OF SILICATE})^{-2} \times 10^4 \sim 1 / C^2$



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