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THE EFFECT OF SODIUM AND POTASSIUM IONS
ON THE TIME OF SET OF SILICIC ACID GELS



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 Arin C. ^{ter} Hansen Jr. UC 1946
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Approved by _____

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HISTORICAL

It has been demonstrated by various investigators that the addition of an electrolyte to a silicic acid gel mixture, other factors remaining constant, will produce a change in the time of set of the mixture. Graham (1) considered the sodium chloride formed in the reaction between sodium silicate and hydrochloric acid to be responsible for the setting of the gel. Hurd, Miller and Raymond (2) reported that sodium chloride, sulphate, and nitrate decreased the time required for gelation. Yajnik and Haksar (3) showed the relative effect of various ions on the transparency of gels, those ions producing the clearest gels having the least accelerating effect on the setting process. Prasad and Hattiangadi (4) studied the effects of several sodium and potassium salts and showed that the potassium salts produced a greater accelerating effect in all cases. Rhoades (5) also determined the relative accelerating effects of the alkali metal ions and numerous anions. Werner (6) performed extensive tests to determine the effects of a large number of anions and cations.

INTRODUCTION

This paper will deal with the relative effect of the potassium and sodium ions on the time of set. To determine this effect, gels were prepared using potassium silicate in place of the sodium silicate used in the previous experiments on the effects of electrolytes in this laboratory. The heat of activation for the setting of the potassium silicate gels was determined by the method used by Hurd and Letterton (7) in which the logarithm of the time of set was plotted against the reciprocal absolute temperature, the heat of activation being computed from the slope

of the resulting line by means of Arrhenius' equation. Runs were then made in which the potassium silicate was replaced in steps by a sodium silicate solution of equivalent alkali and silica concentrations. The effect of sodium and potassium chlorides on the potassium silicate gels was compared with the effect on sodium silicate gels.

EXPERIMENTAL

The silicate solutions used in these experiments were made from "E Brand" sodium silicate and "K-Sil #6" potassium silicate both of which are produced by the Philadelphia Quartz Company. These were diluted with freshly boiled distilled water to obtain solutions which were 1.25 N with respect to NaOH and KOH respectively. The solutions were standardized by titration with sulphuric acid using methyl orange indicator. The acid employed was 2.00 N acetic acid standardized with sodium hydroxide solution. The sodium, potassium, and lithium chloride solutions which were used in the gel mixtures were 2.00 molar.

The gel mixtures, except those which were set at 0° C., were mixed in 100 ml. beakers. The silicate solutions were placed in one set of beakers while the mixtures of acetic acid, the electrolyte if any, and the amount of water required to bring the mixture to the desired volume were placed in another set of beakers. The two sets of beakers were thermostated at the desired temperature before the mixing of the two solutions. The thermostat used was a water bath equipped with a knife type heating unit, a DeKhotinsky thermal regulator and an electric stirrer. The solutions were then mixed by pouring the silicate solutions into the acid solutions and pouring the mixture from one beaker to the other four times. The solutions were then placed back in the thermostat

during the gelation period. The total volume of all the gel mixtures mixed by this method was 80 ml., the difference between the volume of the silicate, acid and the electrolyte solutions being made up by water. In the case of the gels which were set at 0° , the same general procedure was followed, but the beakers were replaced by stoppered, 250 ml. Erlenmeyer flasks, and the amounts of the constituents were doubled, making a total volume of 160 ml. These gels were kept at 0° by packing them in snow in a thermostat insulated by sawdust. The tilted rod test used by Hurd and Letterton (7) was used to determine the point of setting. This test consists of inserting a 10 cm. pointed stirring rod into the gel mixture until the time is reached when the rod is supported by the gel at an angle of approximately 20° .

In the series of experiments to determine the energy of activation of the potassium silicate gels, mixtures containing 25 ml. of 1.22 N potassium silicate and 35, 40, 45, and 50 ml. of 2.00 N acetic acid were set at 25° , 35° , and 45° C.; gels containing twice these amounts were set at 0° C.

The gel mixtures containing varying amounts of both sodium and potassium silicates were made of solutions which were 1.25 N with respect to NaOH and KOH respectively. The soda-silica ratio of the sodium silicate was 1:3.32 and the potash-silica ratio of the potassium silicate was 1:3.29. Since this means a difference of less than 1% which is about the same as the experimental error involved in the methods used, the silica concentration was assumed to remain constant when the potassium silicate was replaced by the sodium silicate. pH readings were taken with a calomel electrode for the mixtures in the series containing 50 ml. of acid and very little difference in pH was observed in the mixtures. Thus

the only factor influencing the time of set which was varied in these runs was the concentration of the individual cations, the total cation concentration remaining constant. These solutions were also used in the determinations in which 2.00 N sodium and potassium chlorides were included in the sodium silicate gel mixtures and sodium, potassium, and lithium chlorides were included in the potassium silicate mixtures.

DISCUSSION OF RESULTS

When the logarithm of the time of set was plotted against the reciprocal absolute temperature for each of the potassium silicate gel mixtures (Graph 1), a straight line resulted as in the case of the sodium silicate gel mixtures prepared by Hurd and Letterton (7). The value obtained for the time of set at 45° was found to be high in each case probably because of the cooling of the mixtures below 45° by the colder air during the setting period. When the slopes of the resulting lines were measured, the average value obtained was 3520 degrees which corresponds to an energy of activation of 16,200 calories per gram mol. This is slightly less than the average value for the energy of activation for the setting of sodium silicate mixtures which is 16,600 according to Hurd and Miller (8). A more accurate value would probably be obtained by making this determination on a series of gels having a variety of potash-silica ratios and taking the average. The difference between the values is not large, however, indicating that the acceleration by temperature of the setting process is not greatly affected by the presence of the potassium ions in place of the sodium ions and that these ions are probably not involved in the fundamental reaction taking place.

When the logarithms of the times of set for the gel mixtures containing varying amounts of potassium and sodium silicates were plotted against either the sodium or potassium ion concentration, a straight line resulted (Graph 2). The equation representing this line would be:

$$\log T = K C_{Na^+} + K'$$

which can be derived from the assumption that the fractional change in the time of set brought about by a small change in the concentration of a positive ion is proportional to the change in concentration. This may be represented by:

$$\frac{dT}{T} = K'' dC_{Na^+} + K''' dC_{K^+}$$

where T is the time of set and C represents the concentration of the ion indicated. Since in these experiments the total positive ion concentration remained constant we may substitute:

$$C_{Na^+} + C_{K^+} = K''''$$

giving:

$$\frac{dT}{T} = K'' dC_{Na^+} - K''' dC_{Na^+}$$

which yields upon integration:

$$\log T = (K'' - K''') C_{Na^+} + K''''$$

which is the equation of the lines obtained.

Graph 3 shows the effect of sodium, potassium, and lithium chlorides on potassium silicate gels and of sodium and potassium chlorides on sodium silicate gels. These salts all produced acceleration, potassium chloride showing the greatest effect in both cases. It might be expected that a straight line would result if the logarithm of the time of set were plotted against the ion concentration as it did in the substitution experiments. This, however did not occur, but a straight line did result when the logarithm of the time was plotted against the logarithm of the total ion concentration. A possible explanation for this result may be

obtained as follows: In these experiments the total cation concentration did not remain constant as it did in the case of the substitution of the silicates. As the total cation concentration increased, the effect caused by a unit change in concentration became less and the coefficient of the differentials of the concentrations in the equations above did not remain constant. If this coefficient is assumed to be inversely proportional to the total cation concentration, the following equation is obtained for a potassium silicate gel mixture containing varying amounts of sodium chloride:

$$\frac{dT}{T} = \frac{K'' dC_{Na+}}{K''(C_{Na+} + C_{K+})}$$

Since the potassium ion concentration is constant:

$$d(C_{Na+} + C_{K+}) = dC_{Na+}$$

and the resulting integral is the equation of the line obtained.

$$\log T = \frac{K''}{K'''} \log(C_{Na+} + C_{K+}) + K'''$$

Consequently each line thus produced has a slope which depends upon the differential coefficient of the ion present in varying proportions. This coefficient has a different value for each ion. This is shown in Graph 4 for the effect of potassium and sodium ions on sodium silicate gel mixtures and potassium, sodium, and lithium ions on potassium silicate mixtures.

CONCLUSION

The setting of potassium silicate and sodium silicate mixtures has been studied and it was found that the energy of activation for the potassium silicate gel mixtures was slightly lower than that of the sodium silicate gel mixtures. Future work might be done with potassium silicates of different potash-silica ratios to obtain an average value. The effect of varying the ion concentrations in the sodium and potassium silicate gel mixtures was studied and the assumption has been made that the fractional change

in the time of set of the gels brought about by a change in the concentration of a cation is proportional to that change in concentration and inversely proportional to the total cation concentration thus producing linear logarithmic curves.

REFERENCES

- (1) Graham - Trans. Roy. Soc. Lond. 151, 183 (1861)
- (2) Hurd, Miller & Raymond - Studies on Silicic Acid Gels
J. Phys. Chem. 38 663 (1933)
- (3) Yajnik & Haksar - Die Lichtwirken von Elektrolyten und Nicht-elektrolyten auf das Durchlässigkeitsvermögen von Kiesel-säuregelen - Kolloid Zeit. 49 303 (1929)
- (4) Prasad & Hattiangadi - The Effect of Electrolytes on the Time of Setting of the Gel-forming Mixtures (Studies on Silicic Acid Gels Part IV) - Journ. Ind. Chem. Soc. VII 341 (1930)
- (5) Rhoades - Effect of Electrolytes on the viscosity and Time of set of Silicic Acid Gel - Thesis, Union College (1942)
- (6) Werner - The Effect of various Ionogens on the Time Period Required for the Gelation of Colloidal Silica - Journ. Amer. Pharm. Ass'n. 9 501 (1920)
- (7) Hurd and Letterton - Studies on Silicic Acid Gels I -
Journ. Phys. Chem. - 36 604 (1932)
- (8) Hurd and Miller - Studies on Silicic Acid Gels II
J. Phys. Chem. 36 2194 (1932)

DATA FOR GRAPH 1

Time of set and log time for mixtures containing 25 ml.
1.22 N potassium silicate solution, 35, 40, 45, and 50 ml.
2.00 N acetic acid and having a total volume of 80 ml. The
mixtures set at 0° contained twice these amounts and had a
total volume of 160 ml.

Ml. Acid	Temp.	Time	Log Time	Slope of line
35	45°	23.8 min	1.38	3571°
"	35°	53.6	1.73	
"	25°	132	2.12	
"	0°	1612	3.21	
40	45°	30.0	1.48	3485°
"	35°	66.9	1.83	
"	25°	160.5	2.21	
"	0°	1918	3.28	
45	45°	36.0	1.56	3514°
"	35°	78.3	1.89	
"	25°	188.0	2.27	
"	0°	2241	3.35	
50	45°	42.3	1.63	3514°
"	35°	89.1	1.95	
"	25°	217.5	2.34	
"	0°	2611	3.42	

Average slope - 3521°

Reciprocal absolute temperatures

0° - 3.662×10^{-3}
25° - 3.355
35° - 3.246
45° - 3.144

GRAPH I

LOGARITHM OF TIME OF SET IN

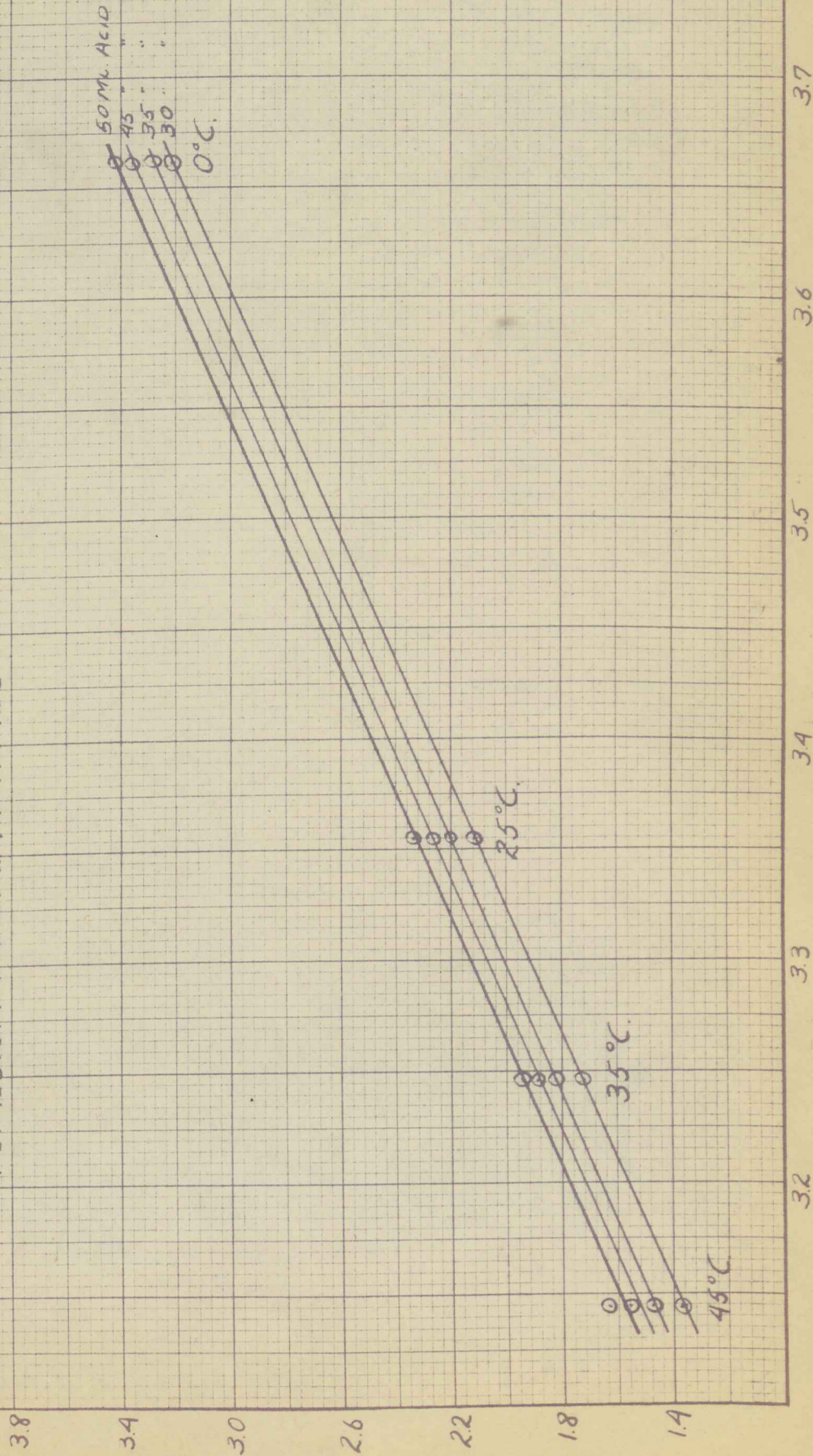
MINUTES

VS.

RECIPROCAL ABSOLUTE TEMPERATURE $\times 10^3$

FOR

POTASSIUM SILICATE MIXTURES



DATA FOR GRAPH 2

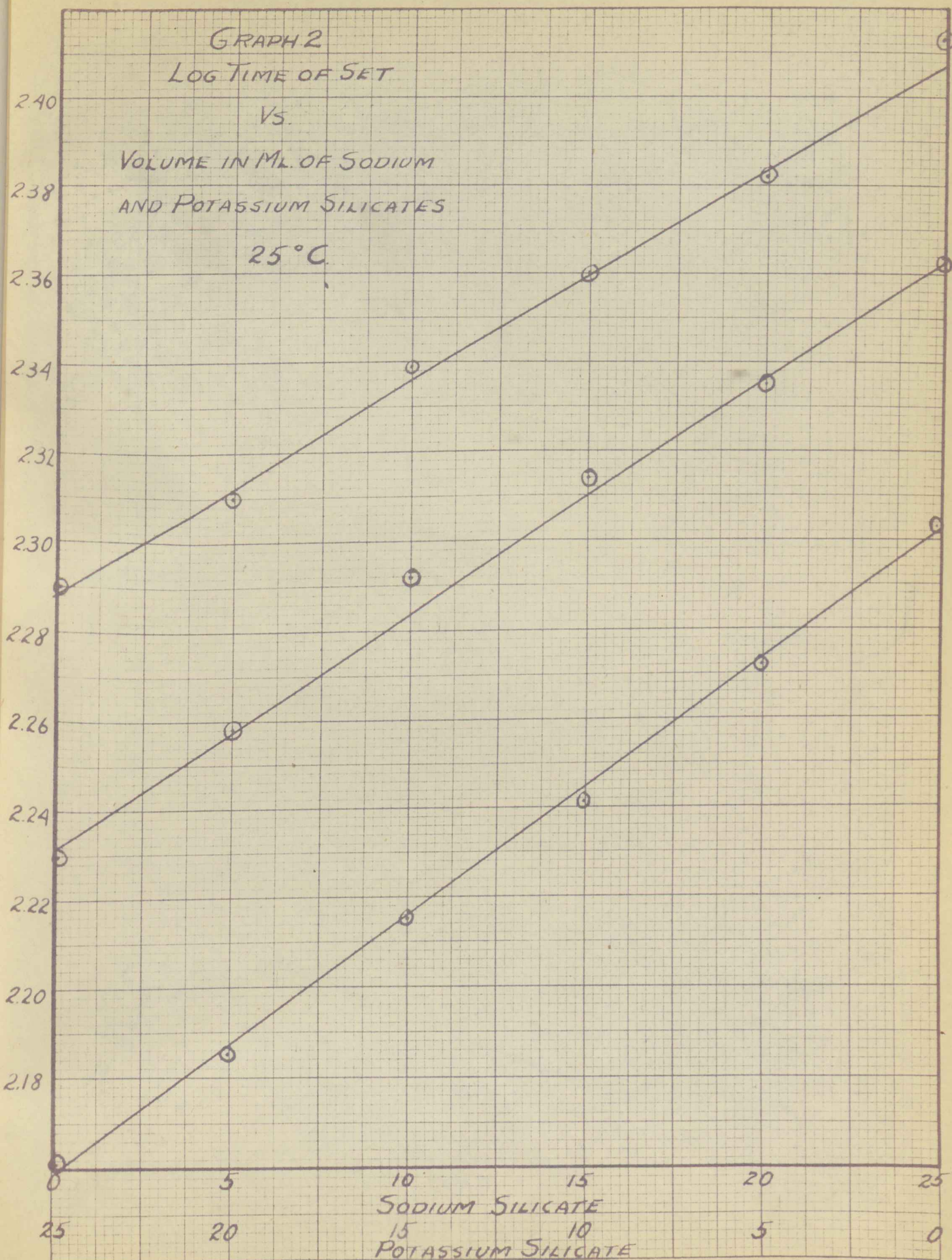
Time of set and log time for mixtures containing varying amounts of 1.25 N sodium and potassium silicates, 40, 45, and 50 ml. 2.00 N acetic acid and having a total volume of 80 ml.

Temperature - 25° Times are in minutes

Ml. Silicate		50 ml. acid		45 ml. acid		40 ml. acid	
Na	K	Time	Log	Time	Log	Time	Log
0	25	195	2.290	170	2.230	145	2.161
5	20	204	2.310	181	2.258	153	2.185
10	15	218	2.339	196	2.292	164	2.215
15	10	229	2.360	206	2.314	174	2.241
20	5	241	2.382	216	2.335	187	2.272
25	0	259	2.413	230	2.362	201	2.303

GRAPH 2
LOG TIME OF SET
VS.

VOLUME IN ML. OF SODIUM
AND POTASSIUM SILICATES
25°C.



DATA FOR GRAPHS 3 AND 4

Time of set and log time for sodium silicate and potassium silicate mixtures containing 25 ml. 1.25 N silicate solution, 35 ml. 2.00 N acetic acid, varying amounts of 2.00 N electrolyte solution, and having a total volume of 80 ml.

Temperature - 25° Times are in minutes.

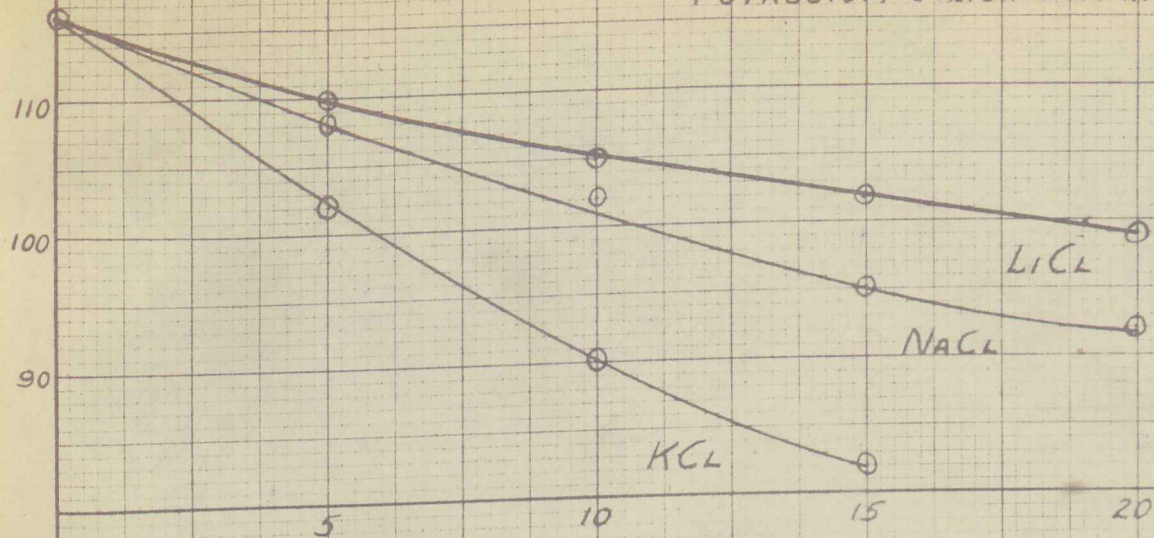
SODIUM SILICATE MIXTURES

Ml. Electrolyte	Log total cation Concentration	NaCl		KCl	
		Time Log		Time Log	
0	-.409	167	2.223	167	2.223
5	-.288	139	2.143	123	2.090
10	-.194	120	2.079	102	2.009
15	-.116	111	2.045	85	1.929
20	-.051	102	2.009	77	1.887

POTASSIUM SILICATE MIXTURES

		LiCl		NaCl		KCl	
		Time Log		Time Log		Time Log	
0	-.409	116	2.061	116	2.061	116	2.061
5	-.288	110	2.041	108	2.033	102	2.009
10	-.194	105	2.021	102	2.009	90	1.954
15	-.116	102	2.009	95	1.978	82	1.914
20	-.051	99	1.996	92	1.964	-	-

POTASSIUM SILICATE MIXTURES

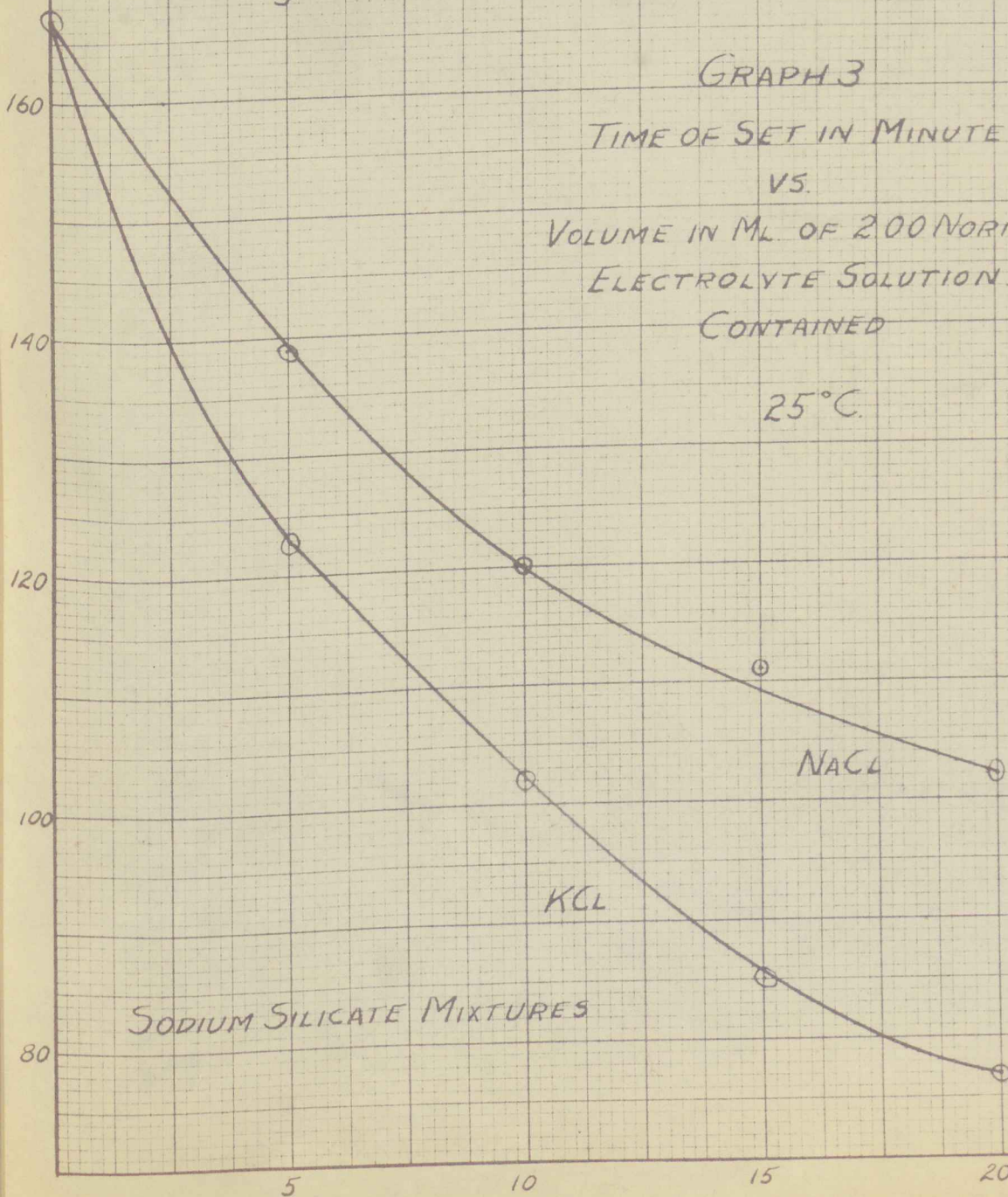


GRAPH 3

TIME OF SET IN MINUTES
VS.

VOLUME IN ML. OF 200 NORMAL
ELECTROLYTE SOLUTION
CONTAINED

25°C.



SODIUM SILICATE MIXTURES

