

6-1937

# The Effect of the Change of pH during the Time of Set, upon the Time of Set of Silicic Acid Gels

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## Recommended Citation

Paton, Harris W., "The Effect of the Change of pH during the Time of Set, upon the Time of Set of Silicic Acid Gels" (1937). *Honors Theses*. 2123.

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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

HARRIS W. PATON

Approved by Charles B. Hurd

June 1937

TITLE

The Effect of the Change of pH  
during the Time of Set, upon the Time  
of Set of Silicic Acid Gels.

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## INTRODUCTION

The study of this particular subject was made in the hope that it might lead to a more complete explanation of the manner of setting of gels. It was thought that by changing the pH during the time of set irregularities in the course of the setting of the gel might be found. It was thought, for example, that there might be a period during which the addition might have less effect than average, or a period where it would have a much greater than average effect. These periods might possibly have occurred at any part of the time of set.

## HISTORICAL

It has been determined that the time of set of gels is dependent upon seven different factors.

1. The concentration of the silica.
2. The concentration of the acid.
3. Agitation.
4. Temperature
5. The pH of the mixture.
6. The presence of additional soluble materials.
7. The size of container, or relative amount of surface exposed to the air.

Prased and Hattiangadi (1) stated that the process of setting of mixtures of solutions of sodium silicate and acetic acid consists of three stages:

- (1) The formation of silicic acid by the interaction of the acid with sodium silicate.
- (2) The formation of the colloidal solution of silicic acid.
- (3) The coagulation of the colloidal solution by the electrolytes liberated by the first reaction.

Flemming (2), H. N. Holmes (3), H. A. Fells (4), J. B. Firth (5), and Letteron (6) studied the time of set of silicic acid gels as a function of the temperature, water glass, and acid.



The study of the effect of the Hydrogen ion concentration has been made by Prased and Hattiangadi (1a); and Hurd, Raymond, and Miller (7).

The effect of additional materials has been studied by Prased and Hattiangadi (1b), P. H. Dewey (8), and D. H. Carver (9).

As far as I was able to determine, no work has ever been done in the line of charging the factors, in the time of set, during the time of set. However, viscosity, surface tension, and conductivity measurements during the time of set have been carried out at Union College.

## EXPERIMENTAL

### Solutions:

The sodium silicate used in the entire investigation was the "E" brand silicate produced by the Philadelphia Quartz Company. Its  $\text{Na}_2\text{O}_2:\text{SiO}_2$  ratio by weight was 1/3.19. This silicate solution was diluted with freshly boiled distilled water to the approximate normality 1.25.

The acetic acid used in the entire investigation was prepared from 99.5% glacial acetic acid by dilution with distilled water. This dilution was made to the approximate normality of 2.00.

In the A run, the first or trial run, the solutions were prepared by Fredericks. These were standardized by him October 1935 as sodium silicate 1.2536N, and acetic acid 2.0035N. Restandardization February 1937 found that they had changed slightly, as was to be expected, to sodium silicate 1.2500N and acetic acid 2.010N.

In the B run, the solutions were prepared as described, and standardized by titrations. The sodium silicate was titrated with Hydrochloric acid using Methyl Orange as indicator, and the acetic acid was titrated with Sodium Hydroxide using phenolphthalein as indicator. The Hydrochloric acid and Sodium Hydroxide had previously been standardized in the usual manner.



The sodium silicate used in the B run was found to be 1.2583N and the acetic acid 2.008N.

#### Apparatus:

##### Temperature Control

The most important apparatus was the constant temperature water baths. These were thermostatically controlled. Several of these were used during the year, and quite a bit of work was necessary to keep them in running condition. One regulator was completely taken down and reassembled, and one relay system was built. One bath was used for thermostating the gels before mixing. This bath was held at  $23.5^{\circ}\text{C}$ . The bath for after mixing, and in which the time of set was determined, was held at  $25^{\circ}$ . These baths were constant to  $.05^{\circ}\text{C}$ .

##### Determination of the Time of Set

The method of determining the time of set used was the tilting rod method described by Hurd & Letteron (10). This method consists of inserting a small glass rod about 3 mm. in diameter 8 cm. long, and drawn to a rounded point. It has been determined that this is the most practical method, and gives results accurate to two percent.



## Determination of the pH

The Quinhydrone method of determining pH was used. Hurd and Griffeth (11) made a careful study of the applicability and reliability of this method, and they found that it gave reliable results. Laskin (12) found close agreements between measurements of a Pt-H<sub>2</sub> electrode and the Quinhydrone method. Some trouble was encountered at first due to the fact that the Quinhydrone did not dissolve easily, but this was overcome by thorough mixing. Work was done this year by A. Marotta (13) comparing the Quinhydrone method with the glass electrode. In some cases in this investigation there was a slight pH drift. In such cases the final reading was taken.

The Pt electrode used in the Quinhydrone determinations of the pH was frequently cleaned with hot, concentrated sodium hydroxide in order to remove any coating of silica which might have collected on the Pt. A saturated calomel electrode was used. It was made by placing a paste, made by mixing mercury and calomel in a mortar, in the bottom of the glass cell. Mercury was placed above this, and the rest of the cell filled with saturated potassium chloride.

## PROCEDURE

As it was desired to vary only one of the seven known factors in the time of set of gels the others were held constant in the following manner:

1. Concentration of the silica--by using 25 cc. of the sodium silicate solution for every gel.
2. Concentration of the acid--by using the same acid in all gels.
3. Agitation--There was as little agitation as possible, and where it could not be avoided every attempt was made to give the same agitation to every gel. For example:--in mixing the gels the sodium silicate in beaker (1) was always poured into the acetic acid in beaker (2), the entire mixture was then poured back to (1) and then back again to (2) where it remained. Additions were made in the same manner except that the acid or distilled water was always poured from beaker (1) to the mixture in beaker (2),



back to (1) and then back to (2) in order to assure thorough mixing. This procedure was developed as the simplest and best after several others had been tried.

Thorough mixing was especially important in the addition, both that full effect of the addition might be felt, and in order to get definite time of sets.

4. Temperature--The temperature was controlled as described by placing the beakers in water baths.
5. The pH--This was the variable.
6. Additional materials--None were added.
7. Size of containers, etc.--All gels were run in 100 cc. K beakers, and the total amount of solution in nearly every case was 60 cc.

#### Method of Changing the pH (#5 the variable)

The pH was varied during the time of set by the addition of measured (all volume measurements were made with pipettes) amounts of acid which had been thermostated at 25°C. This, however, changed the volume another variable. In order to know the dilution effect

similar runs were made adding like amounts of distilled water. There was a small change in pH due to the dilution but this was smaller than was expected because of the buffering effect of the acetic acid and sodium acetate present in solution.



## RESULTS

The results of run A which was in reality a trial run to devise and test a method of procedure are tabulated on Data I. Table I is the listing of the average of four complete runs of the same gels. It shows their change in time of set due to the addition of acid at successive intervals. Table II is also an average, and lists the change in time of set due to the addition of distilled water at successive intervals. Table III lists the pH of the various solutions.

In run B the procedure perfected in B runs followed with three different proportions of solutions. Data II--Table I lists the average change adding 5 cc. of acid. Table II lists the average change adding 10 cc. of acid. Table III lists the average change adding 15 cc. of acid. Data III--Table I introduces a final and better method than averaging. It consists of addition more frequently with no repetition, and thus gives more points with less tendency to anticipate the results. This Table lists the results of adding 5 cc. of distilled water to the proper solution. Table II lists the average change caused by the addition of 10 cc. of distilled

water to the proper solution. Table III lists the average change caused by the addition of 15 cc. of distilled water to the proper solution. Data IV--Table I lists the pH of the various solutions in B run.

Figure I is a graph of the results listed in Data I--Table I corresponds to #1 and Table II to #2.

Figure II is a graph of the results listed on Data II--Table I corresponds to #1; Table II to #2, Table III to #3.

Figure III is a graph of the results listed on Data III, Table I again corresponding to #1, Table II to #2, Table III to #3.



## DISCUSSION OF RESULTS

It is evident in this experiment that in every run there are two very definite points that are easily determined. Let us call these the principal points. The point where the time of addition is 0 minutes after mix or coincides with the mix is the first point. The <sup>second</sup> ~~second~~ point is where the gel would set without any addition, as it is obvious that this point would be the same if an addition were made at that time.

It was found that the points determined by addition between these two times lie in general upon the straight lines connecting these two points. This is so generally true that the relation

$$T_c = K T_a$$

$T_c$  = Time change

$K$  = Constant

$T_a$  = Time of addition

may be used to calculate the  $T_c$  if the principal points are known in order that  $K$  may be determined.

<sup>There are</sup>  
The several points that are off the straight lines a bit, perhaps some attention should be paid



to them. Let us consider them. Those in Figure I with the additions at 30 minutes. In this case the gel was so far advanced in the process of setting that it was impossible to get the proper mixing upon addition, and therefore an exact time of set. For these reasons these points may quite possibly be in error. This error was avoided in subsequent runs. That the points on graph #3 of Figure III do not fall on the line, but fall consistently above it, I cannot exactly account for.

This straight line would be the effect expected in this experiment, but was not exactly the most advantageous one to further explanation of the method of setting of gels.

There are some minor variations which may explain why the points are not more exactly on the straight lines. First, the solution of the principal points did not receive the added agitation due to additions. Second, the addition was always poured into the solutions, which means pouring acid into silicate which is the reverse of the correct



procedure. This would have more effect in some cases than in others. Third, the total amount of solution in some cases, especially the second principal points, was different than <sup>4.5</sup> varying factor (7).

From the results of other measurements during the time of set such as viscosity measurements it is regretted that points near the time of set could not be obtained, for it is here that the greatest changes take place.

## SUMMARY

It was found that by determining the so-called principal points the amount of change caused by an addition during the time of set can be simply and rather accurately calculated by the formula:

$$T_c = KT_a$$

From these results it would seem that the setting of a gel is a continuous, straight line process.



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## Data I

## Run A

Table I - Acid Addition

#1 on graph Fig. I

cc. of silicate 25	cc. of Acid 25	cc. of Acid Added 10	Time of Addition min. after mix 0	Time of Set in Minutes 104
"	"	"	10	86
"	"	"	20	67
"	"	"	30	45
"	"	-	-	37½

Table II - Water Addition

#2 on graph Fig. I

cc. of silicate	cc. of Acid	cc. of H <sub>2</sub> O added	Time of Addition min. after mix	Time of Set in Minutes
25	25	10	0	53
"	"	"	10	50
"	"	"	20	46
"	"	"	30	43
"	"	-	-	37½

Table III - pH Measurements

Really only three different solutions

cc. of silicate	cc. of Acid	cc. of H <sub>2</sub> O	pH
25	35	0	4.45
"	25	0	4.7
"	25	10	4.7



## Data II

## Run B

## Acid Addition

Table I #1 on graph Fig. II

cc. of Alkalate	cc. of Acid	cc. of Acid Added	Time of Addition min. after mix	Time of Set in Minutes
25	30	5	0	88
"	"	"	15	79
"	"	"	26	75
"	"	"	39	65½
"	"	-	-	57

Table II #2 on graph Fig. II

cc. of Alkalate	cc. of Acid	cc. of Acid Added	Time of Addition min. after mix	Time of Set in Minutes
25	25	10	0	88
"	"	"	8	74
"	"	"	15	60
"	"	"	22	49
"	"	-	-	32

Table III #3 on graph Fig. II

cc. of Alkalate	cc. of Acid	cc. of Acid Added	Time of Addition min. after mix	Time of Set in Minutes
25	20	15	0	88
"	"	"	3	67½
"	"	"	6	47½
"	"	"	8	36
"	"	-	-	11

## Data III

## Run B

## Distilled Water Addition

ble I #1 on graph Fig. III

c. of licate	cc. of Acid	cc. of H <sub>2</sub> O	Time of Addition min. after mix	Time of Set in Minutes
25	30	5	0	67½
"	"	"	8	66½
"	"	"	15	64½
"	"	"	20½	63
"	"	"	30	61
"	"	"	40	60
"	"	"	45	58
"	"	"	46	59
"	"	-	-	57

ble II #2 on graph Fig. III

c. of licate	cc. of Acid	cc. of H <sub>2</sub> O	Time of Addition min. after mix	Time of Set in minutes
25	25	10	0	46
"	"	"	10	42
"	"	"	15	39½
"	"	"	20	37½
"	"	-	-	32



ble III #3 on graph Fig. III

c. of licate	cc. of Acid	cc. of H <sub>2</sub> O	Time of Addition min. after mix	Time of Set in minutes
25	20	15	0	21
"	"	"	3	20
"	"	"	6	17½
"	"	"	8	15½
"	"	-	-	11

Data IV

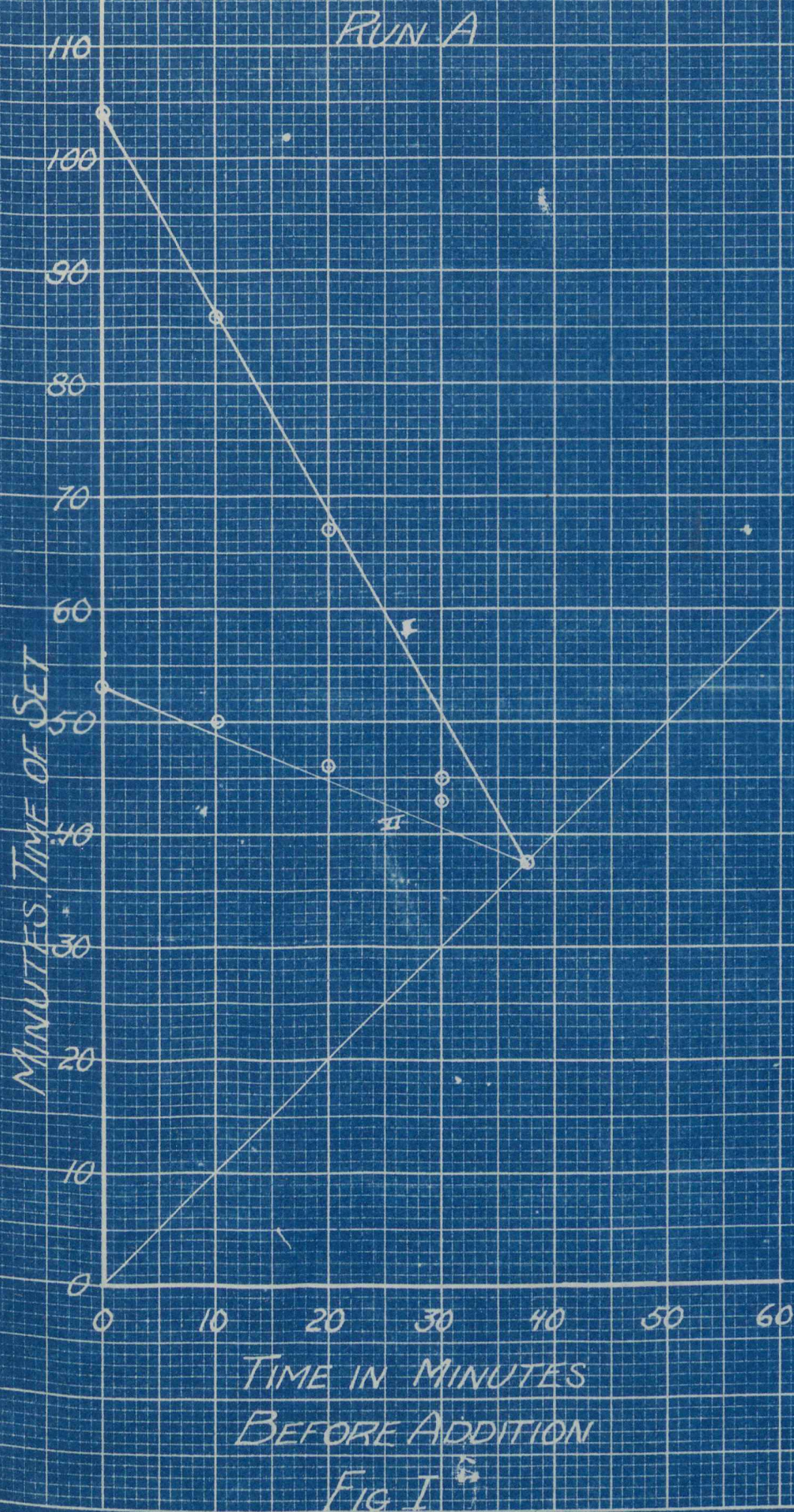
pH of solution in run B

In reality only seven different solutions

ble I

	cc. of Silicate	cc. of Acid	cc. of H <sub>2</sub> O	pH
I	25	35		4.57
I	"	30		4.82
I	"	25		4.98
V	"	20		5.08
V	"	30	5	4.82
I	"	25	10	5.03
I	"	20	15	5.42







RUN B

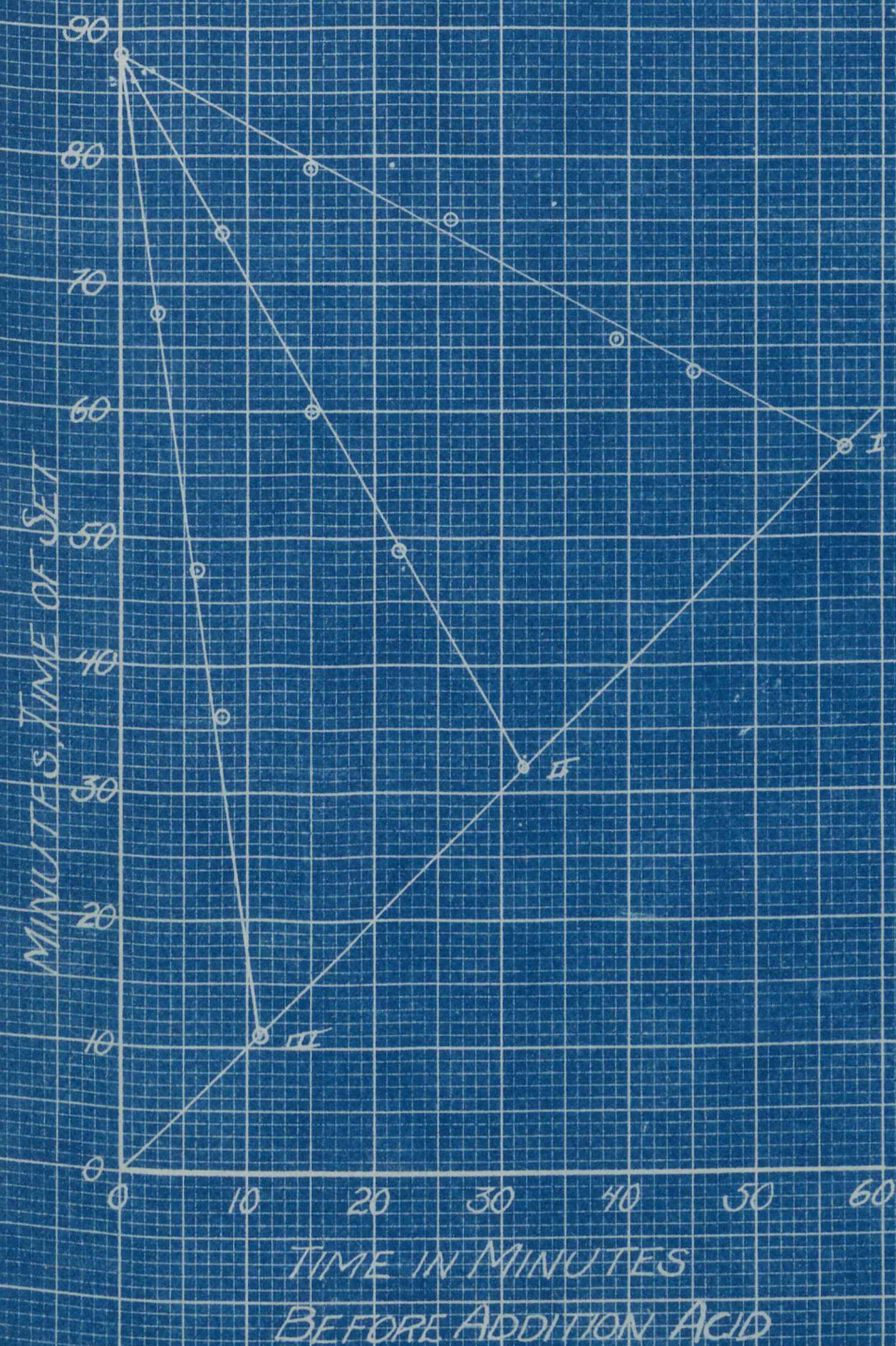
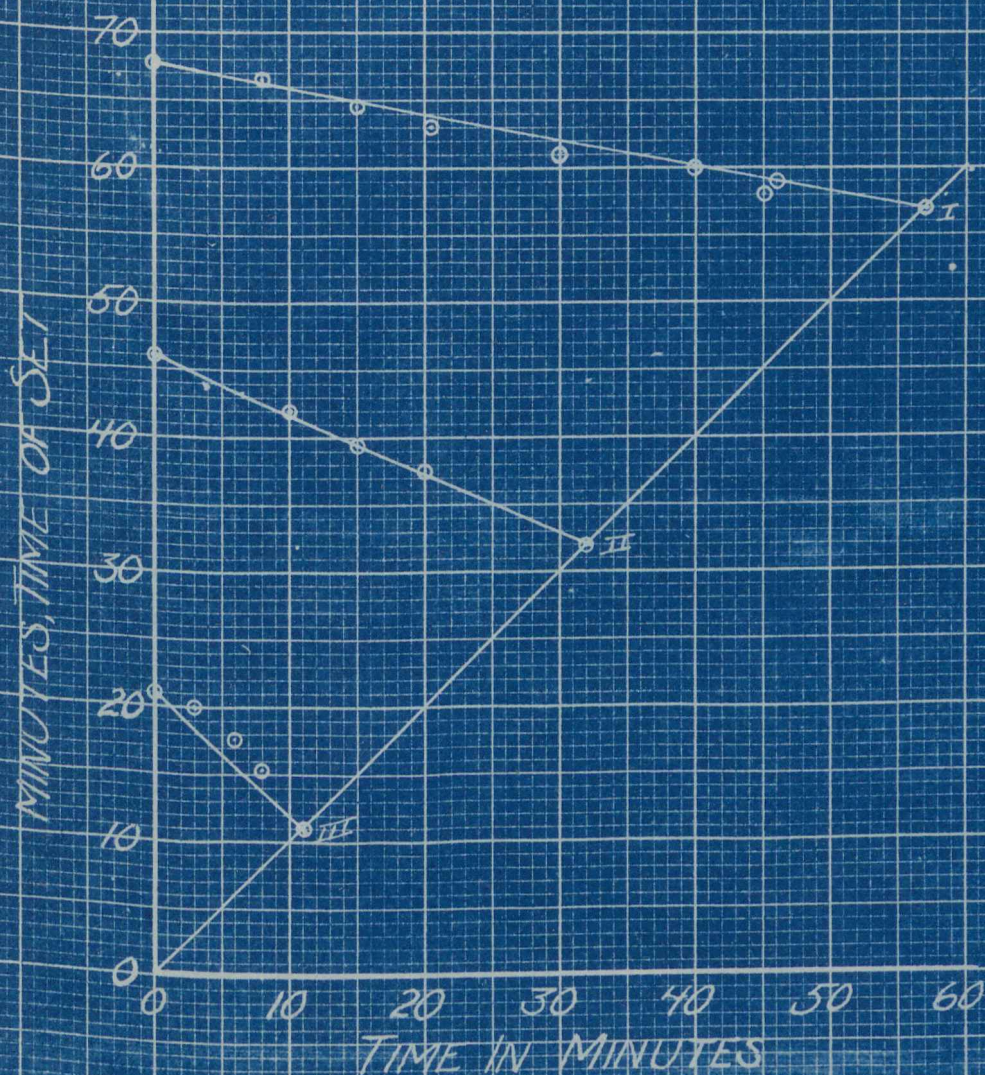


FIG. II



RUN B



BEFORE ADDITION OF WATER  
FIG. III