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# The effect of polyvalent electrolytes on the viscosity of silicic acid gel mixtures

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THE EFFECT OF POLYVALENT ELECTROLYTES  
ON THE VISCOSITY OF SILICIC ACID GEL MIXTURES

THE EFFECT OF POLYVALENT ELECTROLYTES  
ON THE VISCOSITY OF SILICIC ACID GEL MIXTURES

A thesis presented to the Department of Chemistry  
at Union College in partial fulfillment of the  
requirements for the degree of Bachelor of Science  
with a Major in Chemistry, by

David J. Smiler

Approved by \_\_\_\_\_

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## INTRODUCTION

Von Weimarn has shown that the degree of supersaturation at the time of formation, and the viscosity of the medium account, qualitatively at least, for the resulting character of the precipitate from a solution, whether it be crystalline or amorphous. When fairly concentrated solutions form precipitates they are usually colloidal in nature and may even be gelatinous, or a jelly may be formed. When a precipitate, thus formed, retains an appreciable quantity of the liquid in which it was dissolved in the form of a semi-rigid mass, it is termed a "gelatinous precipitate", and if all the liquid is initially retained a jelly or gel is produced. In the latter case Von Weimarn's ratio,  $\frac{P}{L} = U$ , is very high or the percentage supersaturation at the beginning of the precipitation is very large. Where  $P$  = the instantaneous concentration,  $L$  = the solubility of coarse crystals,  $U$  = the percentage supersaturation at the beginning of precipitation.

Jellies result when a gelatinous material separates sufficiently slowly and uniformly. An aqueous inorganic jelly consists of myriads of highly hydrous or gelatinous particles enmeshed into a network of sponge structure that entrains all the liquid phase. Both the solid and liquid phases are continuous in this case.

Many of the organic gels are formed simply by the cooling of a colloidal solution of the substance. Such substances as gelatin, agar and pectin are of this type.

However, inorganic gels are usually produced by the precipitation from solution of highly hydrated oxides or any insoluble substance which adsorbs water readily. Ferric oxide,

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chromic oxide, silica, alumina, arsenic trisulfide, stannic and cupric oxides will form either gelatinous precipitates or jellies by precipitation from colloidal solution. Uniform jellies can be formed from sols in this way in the absence of a medium that would produce an appreciable solvent or peptizing action. The concentration of the sol must be fairly high and the velocity of precipitation must be fairly slow. Salts in the mixture may determine the velocity by the stabilizing action of their ions.

Gels and jellies may be produced also by metathesis, as when an acid is mixed with sodium silicate solution in suitable concentrations. This would be the direct precipitation from solution instead of the sol.

The factors governing the gelation of hydrated silica have been summarized by Flemming(1), Hurd and Carver (2), and Hurd and Hallstrom (3). These are:

1. The silica concentration
2. The acid concentration
3. pH
4. The temperature
5. Agitation
6. Added soluble materials
- 7 Type of silicate

During the course of the experiments, factors (4) and (6) were studied while the other factors were kept as nearly constant as possible.

The process of gelation was studied with an Ostwald-Vensky viscometer. This instrument has been used by Prasad, Mehta, and Desai (4), Dhar and Chakravarti (5), and Santora (6) in the study

of silicic acid gels.

The effect of several electrolytes on the viscosity and time of set of the silicic acid gels was studied. By using polyvalent electrolytes, namely, salts of the alkaline earth group metals, it was hoped to further study their effect. Both Santora (6) and Rhoades (7) have already reported the effects of various univalent salts.

### HISTORICAL

Prasad, Mehta, and Desai (4) found that when silicic acid gels form in an alkaline medium, the initial rate of increase of viscosity is more rapid and the acceleration of increase of viscosity is smaller than when the gels form from the same concentrations of  $\text{SiO}_2$  in acid media. Increase in the concentration of alkali increases the rate of increase in viscosity, Increase in concentration of acid decreases the rate of increase in viscosity. These facts have been explained by assuming that the initial increase in viscosity is due to the number of small colloidal particles formed and the later increase in viscosity is due to the increased hydration of the particles.

Dhar and Chakravarti (5) report that the viscosity of the silicic acid solution decreases immediately upon addition of a little electrolyte; then it increases rapidly, and it finally reaches a maximum before it starts to fall again. They have shown that by increase of a colloidal particle charge, the surface and consequently the degree of hydration and the viscosity are reduced.

Prakash and Dhar (8) have shown that viscosity measurements of jelly-forming mixtures reveal: (1) the passage of the crystal-



loidal substance into the colloidal state, (2) the gradual neutralization of the charge on the colloidal micelles and (3) the formation of the specific structure of jellies.

Hatschek (9) has suggested that the viscosity of a colloidal particle can be obtained from  $\frac{\eta'}{c}$ , where  $c$  is the concentration of the colloidal solution by weight and  $f$ , the ratio of the volume of the disperse phase to the total, given by:

$$f = \left( \frac{\eta' - \eta}{\eta} \right)^3$$

where  $\eta'$  and  $\eta$  are the viscosities of the colloidal solution and the dispersion medium respectively.

### THEORIES OF GEL STRUCTURE

The assumption that jellies are solid-liquid systems is the oldest and is generally looked upon as the most satisfactory of the three general theories that have been proposed. There is, however, still a considerable difference of opinion as to the exact nature of the solid framework which is assumed to entrain the liquid phase and the manner in which this framework is formed. The earliest view was that a distensible body was porous, and that swelling resulted from water penetrating the pores and being held by capillarity or by molecular attraction. In 1858, Nägeli pointed out that porous bodies and gels have such widely different properties that a theory based on their apparent similarity is untenable. As a substitute theory, he suggested that distensible bodies are made up of small anisotropic, crystal-like, molecular aggregates which retain their identity even when the substance goes into (colloidal) solution. The micelles, as Nägeli called them take up water in such a manner that they are surrounded by a water layer, the thickness of which is determined by the relative

intensity of the attraction of the micelles for water and for each other. Jellies are thus considered to possess an interlacing or sponge structure. This conception was opposed by Bütschli (10) and Van Bemmelen (10), who suggested that the droplets of liquid were held in a cell-like framework comparable to a honeycomb.

Later, Zsigmondy and Bachmann (10) pointed out that, in addition to the apparently grainy structure met with in diluted gels of gelatin, agar, and silica, there is also a fibrillar structure. These fibrils or threads are sharply defined in soap jellies studied by Bachmann and later by McBain and his co-workers (10) and in barium malonate jellies studied by Flade (10). The latter noted that the fibrils were of a crystalline character and suggested that jellies in general probably consisted of a network of crystalline threads.

While in certain cases the colloidal particles -- the molecular aggregates, or micelles -- may possess the thread-like characteristic essential for forming an entangling mesh in which each particle is discrete, in other cases it is probable that the micelles actually become stuck together or oriented into loose aggregates which may take the form of chance granules, threads or chains. Such a linking together of the particles to form an enmeshing network seems essential in some of the extremely dilute inorganic jellies.

### PROCEDURE

#### Preparation of Solutions

Approximately three liters of E brand sodium silicate, a product of the Philadelphia Quartz Company, was diluted with



recently boiled, distilled water and titrated with a standard sulfuric acid solution. The normality in NaOH equivalents was determined as 1.245 N., using methyl orange as an indicator.

A quantity of acetic acid was prepared by diluting 99.5% glacial acetic acid with recently boiled, distilled water. The solution was titrated against a standard sodium hydroxide solution, using phenolphthalein as an indicator and was found to be 1.999 N.

Solutions of alkaline earth salts in water were prepared; for the most part, being 0.9 M.

The standard sulfuric acid solution was titrated against the standard sodium hydroxide, using phenolphthalein as the indicator and the sodium hydroxide solution was titrated against a weighed amount of oxalic acid, using phenolphthalein as the indicator.

#### Thermostat Control

A large glass battery jar filled with water and kept at constant temperature by means of a de Khotinsky thermo-regulator and heated with a knife heater with a neon tube indicator was used for all determinations. The accuracy of the regulator was approximately  $\pm 1^{\circ}\text{C}$ . A metal stirrer was used for uniform circulation of the water.

#### The Ostwald Viscometer

The Ostwald-Vensky viscometer is a U-tube with fine capillary in one arm above which are two small bulbs. in the other

arm as a small reservoir. About 10 c.c. of the liquid is placed in the instrument and drawn up past two reference marks, one above and one below the first bulb. The time that it takes for the meniscus of the liquid to pass from the upper to the lower mark is determined. Only hydrostatic pressure of the liquid is involved.

The viscometer is calibrated with pure distilled water as viscometers vary in the size of their capillary bore.

#### Measurement Of Time

An accurate stopwatch was used for the time of efflux of each solution. The time after mixing of the solutions was noted with an electric clock.

#### pH Measurements

Measurements of pH of all gels were found to be in the acid region and reliable results were obtained by use of the quinhydrone potentiometer using a saturated calomel electrode employing saturated KCl solution and a polished platinum wire electrode. All pH measurements were made in 250 c.c. beakers with approximately 40 c.c. of gel mixture. Hurd and Griffeth (//) found that accurate and reliable results maybe obtained with pH measurements on silicic acid solutions in the acid range.

#### Preparation Of The Silicic Acid Solutions

50 c.c. of the standardized sodium silicate solution was pipetted into a clean, dry 250 c.c. beaker and 50 c.c. of the standardized acetic acid solution was pipetted into another 250 c.c.



beaker with 50 c.c. of pure distilled water or 50 c.c. of a salt solution made 0.18 M. with respect to the salt. In all cases the total volume was 150 c.c. These beakers were placed in a thermostated bath and allowed to come to the bath temperature.

At a convenient time, they were removed and the silicate solution was poured into the acid solution. The mix was then poured back and forth three or four times. Approximately 100 c.c. of this mix was poured into a 100 c.c. beaker, 10 c.c. were pipetted into the viscometer and the remainder was used for pH measurements. The solution in the 100 c.c. beaker was placed in the thermostat and allowed to gel. A measurement of the time of set by the tilted rod method was made on this.

#### Tilted Rod Method For Time Of Set

Hurd and Letteron (12) have presented a new method in measuring the time of set of the silicic acid solution. They employ a glass rod 3 mm. in diameter and 10 cm. long, one end of which has been drawn to a stubby point. The rod is inserted into the gel at intervals after the characteristic opalescence is observed, at an angle of about  $20^{\circ}$  to the vertical. The gel is set when the rod just fails to fall and the gel structure holds it. The complete gel structure is formed at this moment. All times of set are longer than the time elapsed when the solution is too viscous to flow through the capillary tube.

# EXPERIMENTAL

The effect upon the time of set and the formation of a gel by adding electrolytes to the silicic acid solution was studied. Sodium acetate formed in the simple metathesis reaction has some effect upon the time of set but as all concentrations were kept constant, the concentration of this salt in solution was also kept constant.

Salt solutions of the alkaline earth group elements were added so that the final concentrations were 0.06 M. with respect to the salts. A concentration of salt very much higher than this would have coagulated the sol almost immediately. I used 10 c.c. of the mix in the viscometer for measurements and part (100 c.c.) was used for measurement of the time of set as already described. The electrolytes used were:  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$ , using a 50 c.c solution of each made 0.18 M. with respect to each salt. One run was made using 50 c.c. of water added to the gel mixture.

Viscosity measurements during gelation were also made varying the temperature. Pure distilled water was used instead of salt solutions for all these runs and measurements were made at  $20^\circ$ ,  $25^\circ$ ,  $30^\circ$ ,  $35^\circ$ ,  $40^\circ$  and  $45^\circ\text{C}$ .

The pH of all solutions was measured with the quinhydrone potentiometer.

All times of set were noted with the tilted rod method.

The viscosity curves were drawn by plotting the time of



efflux as the ordinate and the time after mixing as the abscissa. All viscosity curves show the characteristic up-sweep to an almost vertical line.

The energy of activation of the solution as it set at various temperatures has been calculated by the equation:

$$\frac{d \ln t'}{d (1/T)} = \frac{Q}{R}$$

where  $t'$  is the time of set and  $T$  is the absolute temperature.  $Q$ , the energy of activation was found to be 15,695 cal.

The viscosity curves are represented by graphs I-IV and the energy of activation curve by graph V.

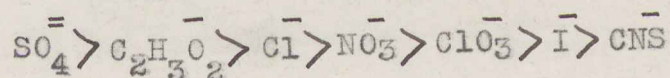
### RESULTS AND DISCUSSION

All the salts used have a marked effect on the viscosity and time of set. They decrease the time of set and increase the rate of increase of viscosity.

As a rule, much larger amounts of electrolytes are necessary to coagulate hydrophilic sols than are needed to coagulate hydrophobic sols. Because of the high electrolyte concentrations that maybe required for coagulation, the process has come to be termed salting out.

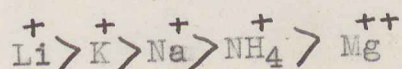
Hofmeister (13) found in experiments of the coagulation of negative albumin sol with alkali salts that the following order of coagulating power applies:

a.) for the anions:

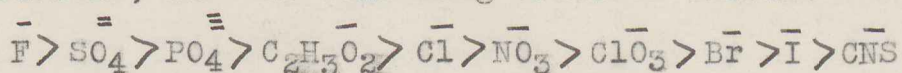


and

b.) for the cations:

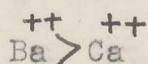


Pauli (13) investigated this phenomenon and found the same order of cations, but the following order of anions:

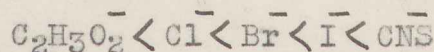


The order for salts of the alkaline earths is:

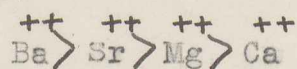
a.) for the cations:



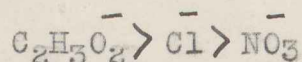
and b.) for the anions:



The order of the coagulating power of the cations as found in the experiments is:



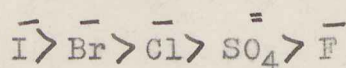
and for the anions:



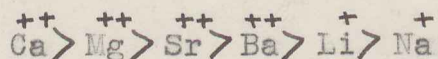
The order for the anions does not agree with Pauli's results but rather seem to be reversed.

Gortner and his co-workers (13) found the order of the peptizing action of ions on the globulins of wheat flour to be:

a.) for the anions :



and b.) for the cations:



As we are interested in the coagulation of the sol instead of peptization, the reverse of this order should agree with our results; which it does.

The lyotropic order of ions is, in general, the same as the order of hydration of the ions. Since water associated with the ions is not available as a solvent, the lyotropic influence may be



traced in some instances to removal of solvent. This would account, in part at least, for the effect of salts on the solubility of non-electrolytes and on the rate of inversion of cane sugar.

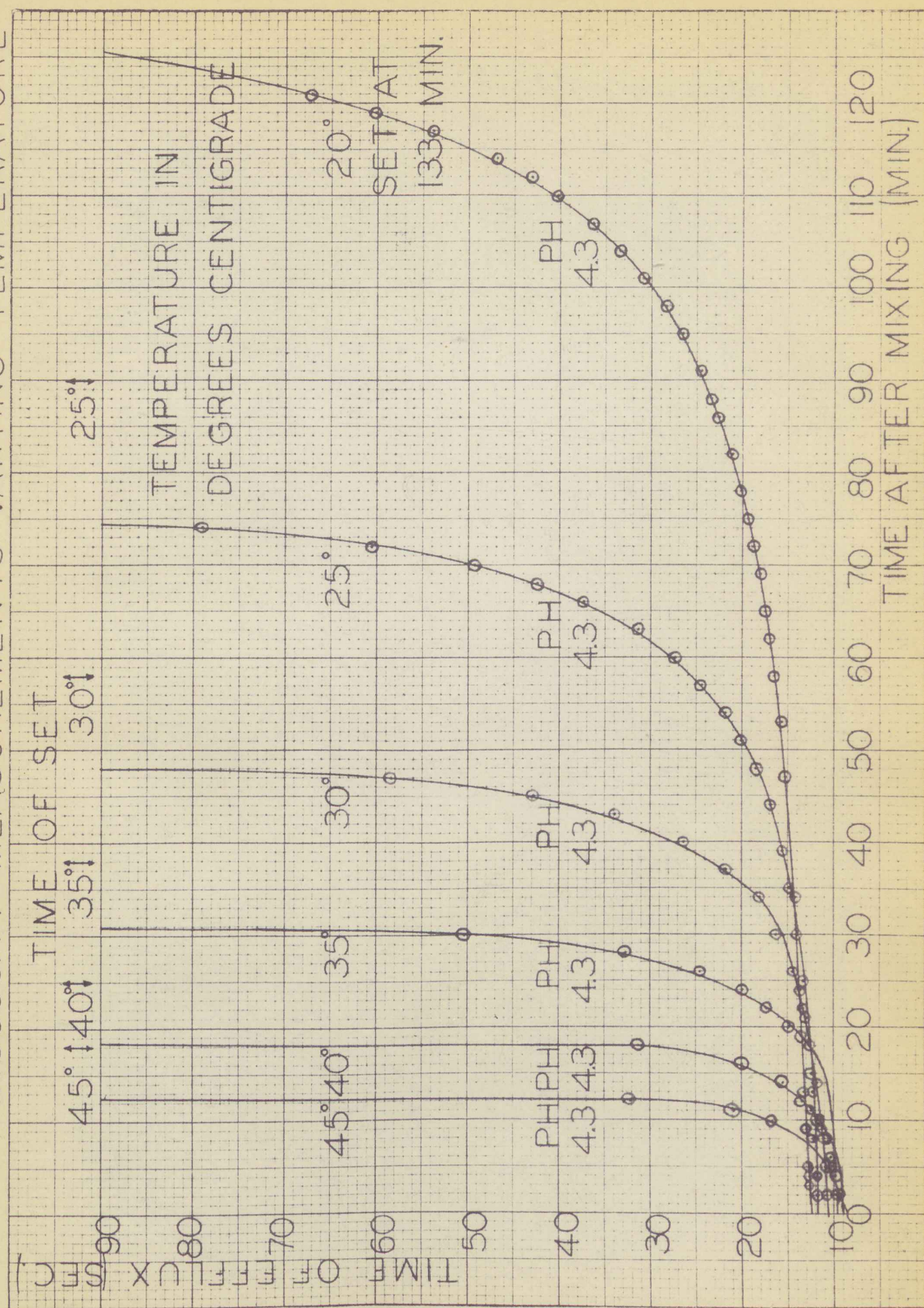
Bancroft (13) assumes that the presence of ions influences the association equilibrium of water:  $n\text{H}_2\text{O} \rightleftharpoons (\text{H}_2\text{O})_n$ , the ions at one end of the series favoring association, and that the other end, dissociation, of the solvent. Adsorption of ions by particles of the sol may supplement the coagulation effect which is attributed to taking up water for modifying the water equilibrium. In coagulating positively charged sols, anions will have a precipitating and cations a stabilizing effect, whereas, in coagulating negatively charge sols, cations will have a precipitating and anions a stabilizing action. Adsorption of ions follows essentially the same order as their hydration or their effect on the water equilibrium.

SUMMARY

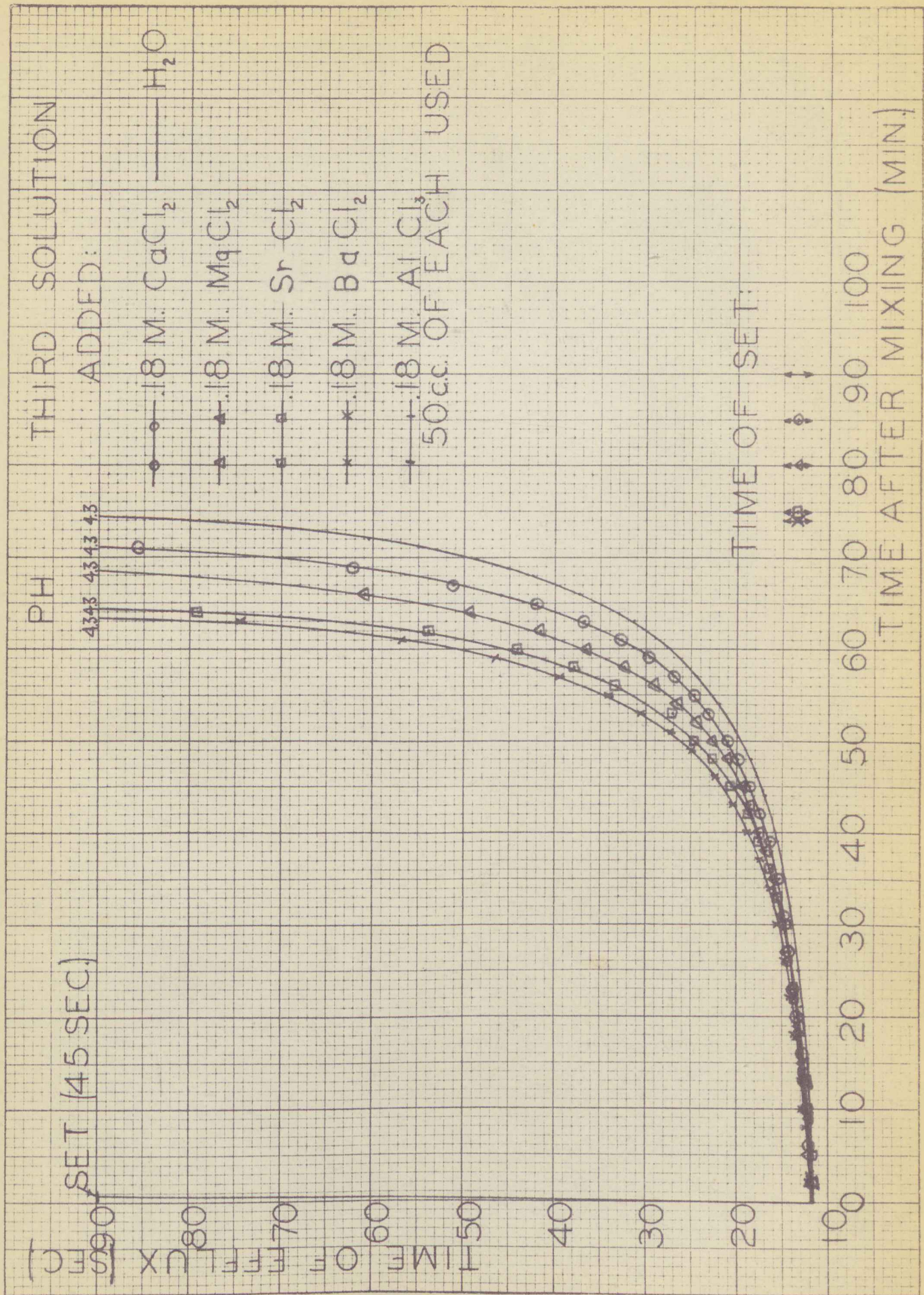
1. The Ostwald-Vensky viscometer has been used to study the process of gelation of certain silicic acid gel mixtures.
2. The effect of typical salts of the alkaline earths on coagulation of the silicic acid sol and decrease in the time of set has been noted.
3. A typical lyotropic series for the power of coagulation of these salts has been presented.
4. The energy of activation of the pure silicic acid gel as it set has been determined.



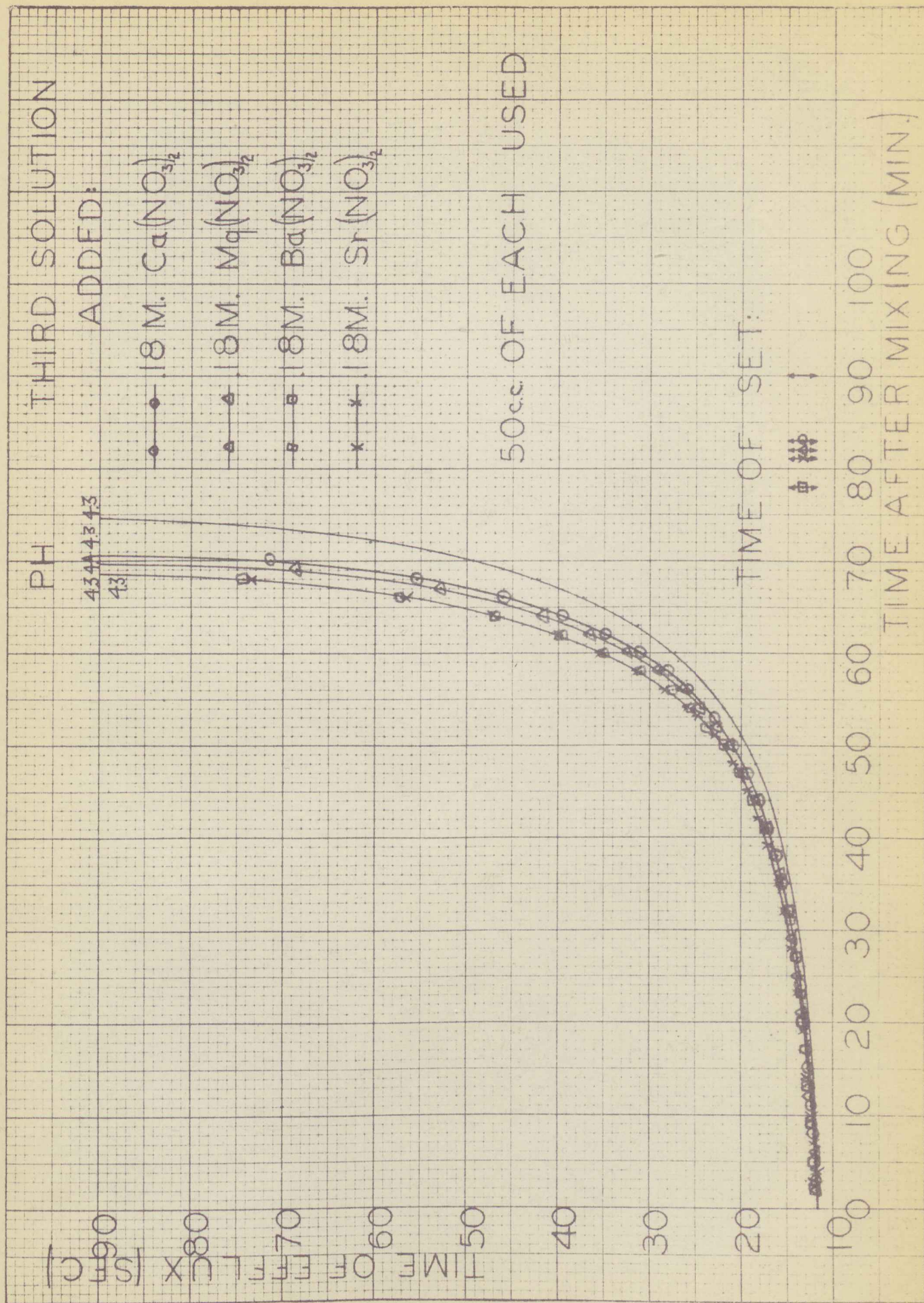
VISCOSITY MEASUREMENTS VARYING TEMPERATURE



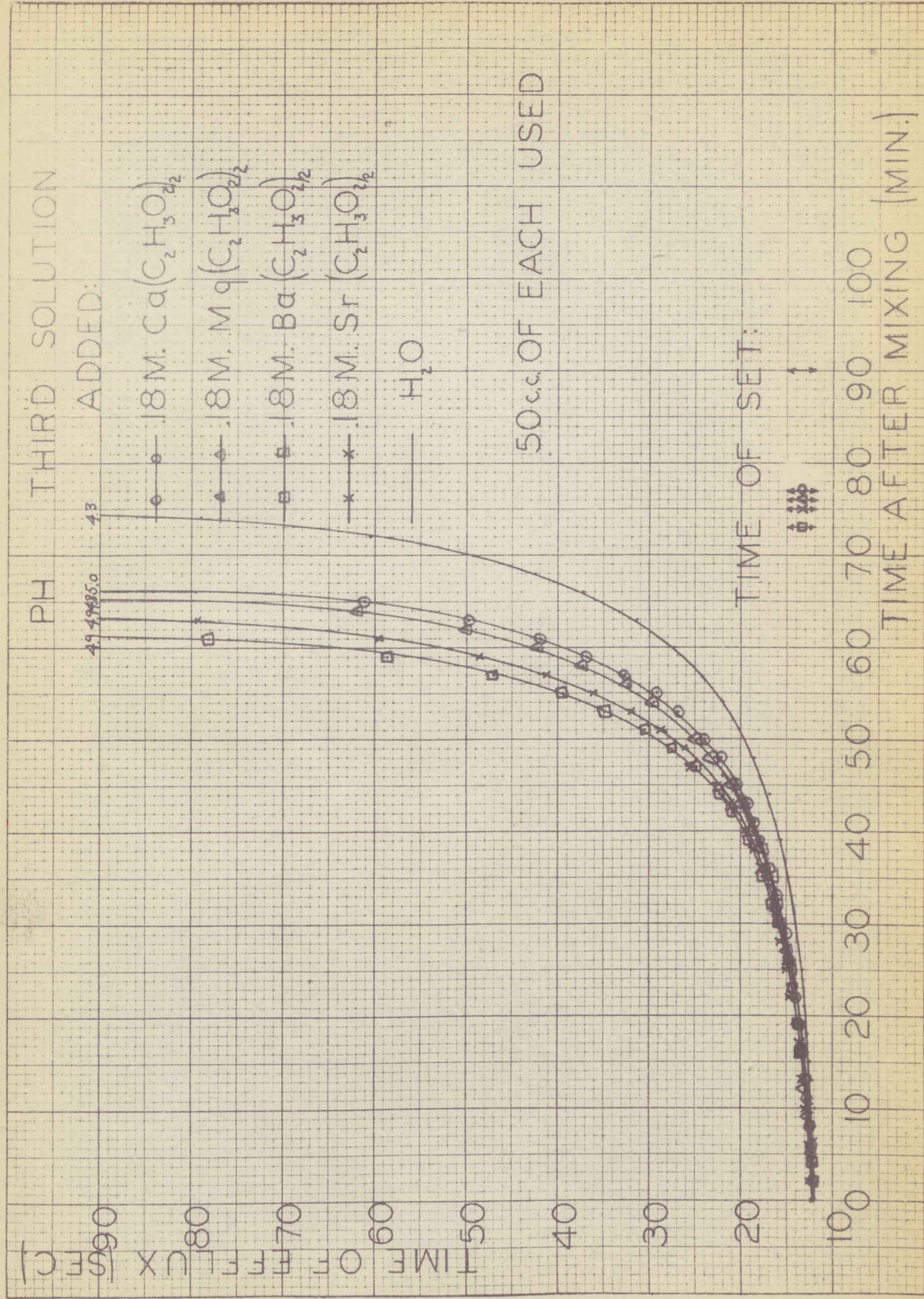






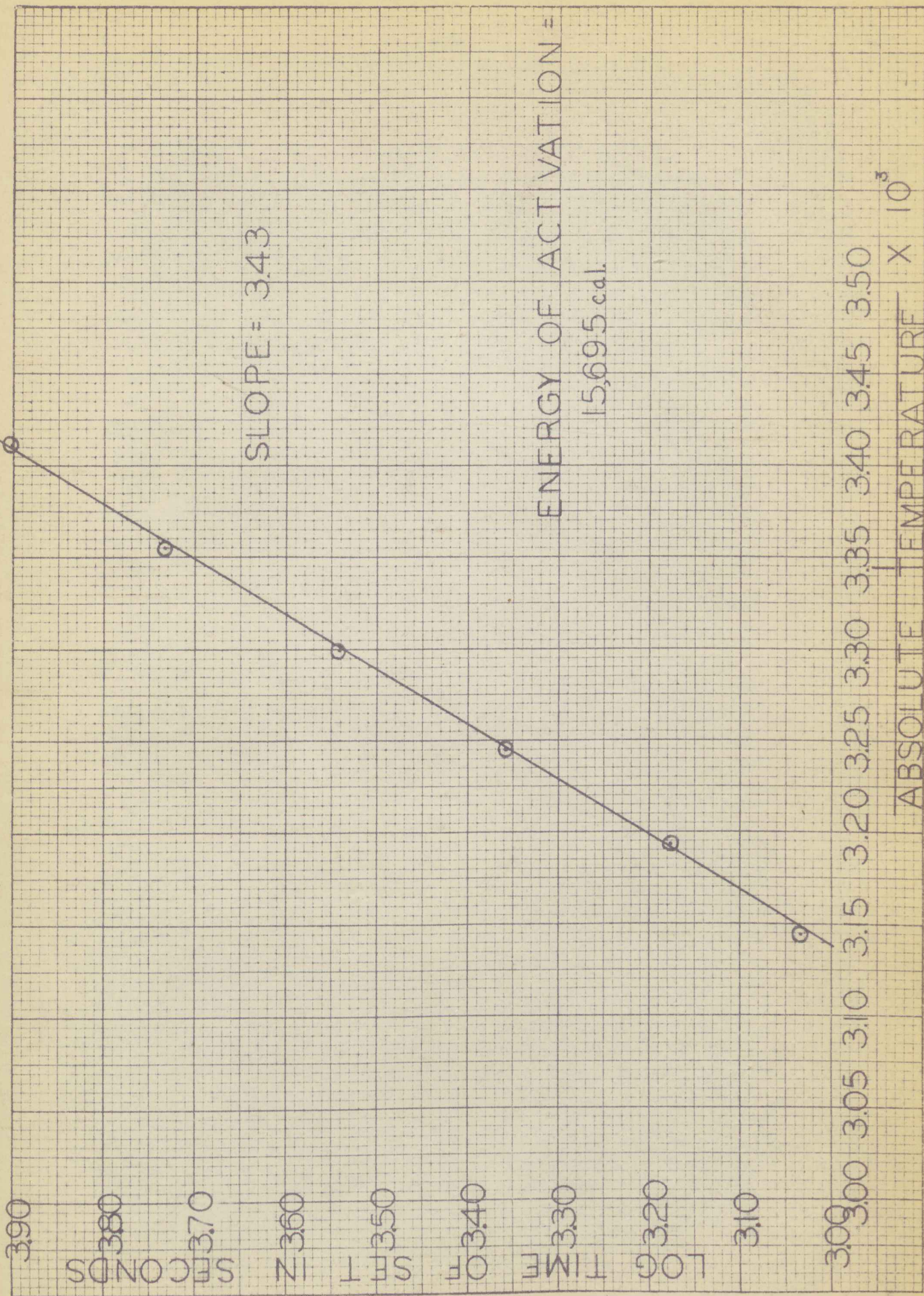








GRAPH V  
CALCULATION OF ENERGY OF ACTIVATION





DATATABLE I

Calibration of Viscometer	Time of Efflux (sec.)
Pure distilled H <sub>2</sub> O - 25° C.	10.0
	10.0
	9.9
	10.0
	10.0
Average	<u>10.0</u>

In each of the following runs, the total volume was kept at 150 c.c. For each run 10. c.c. was pipetted into the viscometer and the pH was noted.

TABLE II

Gel mixture as follows:

50 c.c. HAc - 1.999 N. 25° C.  
 50 c.c. Sodium Silicate - 1.026 N.  
 50 c.c. Water  
 pH 4.1

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
2.5	11.4
7	11.4
10	11.6
12	11.6
17	11.7
20	11.7
27	11.9
29	12.0
32	12.0
37	12.2
43	12.4
45	12.5
48	12.5
52	12.7
55	13.0
57	13.0
59	13.1



Time after Mix (min)

Time of Efflux (sec.)

61	13.1
63	13.1
66	13.3
68	13.5
71	13.6
73	13.7
76	14.0
78	14.2
80	14.2
82	14.3
86	14.7
88	15.0
91	15.0
94	15.3
103	16.3
105	16.4
108	16.8
110	17.2
112	17.4
114	18.0
116	18.1
118	18.5
120	18.9
122	19.3
125	19.8
128	20.7
130	21.2
132	21.5
134	22.3
136	22.9
138	23.4
140	24.0
142	25.1
144	25.9
146	27.0
148	28.1
150	29.1
152	30.5
154	31.8
156	33.3
158	34.8
160	36.2
162	37.9
164	40.5
166	44.0
168	46.9
170	51.5
172	55.5
174	61.8
176	70.7
178	88.7
180	153.8
208	Set

TABLE III

Gel mixture as follows:

50 c.c. HAc - 1.999 N.  
50 c.c. Sodium Silicate - 1.245 N.  
50 c.c. Water  
pH 4.3

25°C.

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
2	11.7
4	11.8
10	11.9
13	12.3
15	12.4
18	12.7
21	13.0
25	13.3
30	14.0
35	14.8
39	15.6
44	16.8
48	18.5
51	20.1
54	21.9
57	24.3
60	27.3
63	31.3
66	37.3
68	42.4
70	49.3
72	60.5
74	79.0
90	Set

TABLE IV

Gel mixture as follows:

50 c.c. HAc - 1.999N  
50 c.c. Sodium Silicate - 1.245 N.  
50 c.c. Water  
pH 4.3

20°C.

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
3	12.7
4	12.7
5	12.7
9	13.0
13	13.2



<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
19	13.4
24	13.6
30	13.9
34	14.2
47	15.2
53	15.7
58	16.4
62	17.0
65	17.4
69	18.0
72	18.8
75	19.3
78	20.1
82	21.1
86	22.6
88	23.3
91	24.4
95	26.6
98	28.3
101	30.8
104	33.3
107	36.3
110	40.2
112	43.1
114	46.9
117	53.9
119	60.2
121	67.2
133	Set

TABLE V

Gel mixture as follows:

50 c.c. HAc - 1.999 N.  
 50 c.c. Sodium Silicate - 1.245  
 50 c.c. Water  
 pH 4.3

30°C.

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
2	10.8
5	10.9
9	11.3
14	11.8
18	12.5
22	13.3
26	14.4
30	16.2
34	18.1
37	21.8

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
40	26.3
43	33.9
45	42.8
47	58.3
58	Set

TABLE VI

Gel mixture as follows :

50 c.c. HAc - 1.999 N. 35° C.  
 50 c.c. Sodium Silicate - 1.245 N.  
 50 c.c. Water  
 pH 4.3

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
2	9.7
5	10.2
8	11.0
11	11.4
14	12.3
17	13.3
20	14.9
22	17.2
24	19.9
26	24.5
28	32.7
30	50.3
38	Set

TABLE VII

Gel mixture as follows:

50 c.c. HAc - 1.999 N. 40° C.  
 50 c.c. Sodium Silicate - 1.245 N.  
 50 c.c. Water  
 pH 4.3

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
2	9.4
4	9.9
6	10.3
8	10.9
10	11.8
12	13.2
14	15.5



<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
16	19.9
18	31.2
25	Set

TABLE VIII

Gel mixture as follows:

50 c.c. HAc - 1.999 N. 45°C.  
 50 c.c. Sodium Silicate - 1.245 N.  
 50 c.c. Water  
 pH 4.3

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
2	9.0
4	9.7
6	10.5
8	12.4
10	16.7
11	20.9
12	32.2
18	Set

TABLE IX

Gel mixture as follows:

50 c.c. HAc - 1.999 N. 25°C.  
 50 c.c. Sodium Silicate - 1.245 N.  
 10 c.c. 0.9 M. CaCl<sub>2</sub> (CaCl<sub>2</sub>·2H<sub>2</sub>O)  
 40 c.c. Water  
 pH 4.3

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
2	11.8
6	12.0
10	12.3
13	12.6
16	12.8
20	13.4
23	13.8
27	14.2
31	14.8
35	15.3
39	16.3

Time after Mix (min.)

Time of Efflux (sec.)

42	17.4
45	18.5
48	19.9
50	21.00
53	23.1
55	24.7
57	26.9
59	29.6
61	32.7
63	36.8
65	42.1
67	51.2
69	62.0
71	85.4
85	Set

TABLE X

Gel mixture as follows:

50 c.c. HAc - 1.999 N.  
 50 c.c. Sodium Silicate - 1.245 N.  
 10 c.c. 0.9 M.  $MgCl_2$  ( $MgCl_2 \cdot 6H_2O$ )  
 40 c.c. Water  
 pH 4.3

25°C.

Time after Mix (min.)

Time of Efflux (sec.)

2	11.7
5	12.0
9	12.2
13	12.6
15	12.8
19	13.1
23	13.7
27	14.4
30	14.9
33	15.4
35	15.9
38	16.8
40	17.4
43	18.5
45	19.3
48	21.0
50	22.7
52	24.3
54	26.5
56	29.0



<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
58	32.3
60	36.5
62	41.5
64	49.3
66	60.9
80	Set

TABLE XI

Gel mixture as follows:

50 c.c. HAc - 1.999 N. 25°C.  
 50 c.c. Sodium Silicate - 1.245 N.  
 10 c.c. 0.9 M.  $\text{SrCl}_2$  ( $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ )  
 40 c.c. Water  
 pH 4.3

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
2	11.8
5	12.0
10	12.3
14	12.8
18	13.2
22	13.6
26	14.1
30	14.8
33	15.5
36	16.4
39	17.5
42	18.7
45	20.6
48	22.7
50	24.6
53	27.0
56	33.3
58	37.9
60	44.1
62	53.9
64	79.1
75	Set

TABLE XII

Gel mixture as follows:

50 c.c. HAc - 1.999 N. 25°C.  
 50 c.c. Sodium Silicate - 1.245 N.  
 10 c.c. 0.9 M.  $\text{BaCl}_2$  ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ )  
 40 c.c. Water  
 pH 4.3

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
2	12.1
3	12.2
8	12.4
10	12.6
13	12.7
18	13.3
22	13.9
26	14.6
30	15.4
34	16.3
37	17.4
40	18.8
43	20.3
46	22.3
49	24.9
51	27.3
53	30.6
55	34.1
57	39.5
59	46.4
61	56.9
63	74.3
74	Set

TABLE XIII

Gel mixture as follows:

50 c.c. HAc - 1.999 N. 25°C  
 50 c.c. Sodium Silicate - 1.245 N.  
 10 c.c. 0.9 M.  $\text{Ca}(\text{NO}_3)_2$  ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ )  
 40 c.c. Water  
 pH 4.3

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
3	11.8
5	12.0
8	12.2
11	12.4
15	12.8
20	13.2
24	13.5
27	13.9
32	14.8
35	15.4
38	16.1
41	17.0
44	18.0
47	19.3



Time after Mix (min.)

Time of Efflux (sec.)

50	20.9
53	23.0
56	25.7
58	28.1
60	31.1
62	34.9
64	39.5
66	46.1
68	55.5
70	71.6
83	Set

TABLE XIV

Gel mixture as follows:

50 c.c. HAc - 1.999 N. 25°C.  
 50 c.c. Sodium Silicate - 1.245 N.  
 10 c.c. 0.9 N.  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$   
 40 c.c. water  
 pH 4.4

Time after Mix (min.)

Time of Efflux (sec.)

2	11.7
6	11.9
9	12.2
12	12.5
13	12.6
17	12.9
21	13.3
25	13.8
29	14.3
32	14.7
36	15.6
41	17.0
44	18.1
47	19.8
50	21.1
52	22.4
54	24.4
56	26.2
58	29.1
60	32.5
62	36.6
64	41.7
67	52.9
69	68.6
82	Set

TABLE XV

Gel mixture as follows:

50 c.c. HAc - 1.999 N.  
50 c.c. Sodium Silicate - 1.245 N.  
10 c.c. 0.9 M.  $\text{Sr}(\text{NO}_3)_2$  ( $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ )  
40 c.c. Water  
pH 4.3

25°C.

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
3	12.0
4	12.1
7	12.2
10	12.3
14	12.8
19	13.2
23	13.6
28	14.4
32	14.9
35	15.6
39	16.8
42	17.9
45	19.1
48	21.0
51	22.9
53	24.7
54	25.6
56	28.0
58	31.3
60	35.1
62	39.9
64	46.9
66	56.7
68	73.5
81	Set

TABLE XVI

\* Gel mixture as follows:

50 c.c. HAc - 1.999 N.  
50 c.c. Sodium Silicate - 1.245 N.  
50 c.c. 0.18 M.  $\text{Ba}(\text{NO}_3)_2$  ( $\text{Ba}(\text{NO}_3)_2 \cdot \text{OH}_2\text{O}$ )  
pH 4.3

25°C.

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
2	11.8
5	12.0
9	12.2
13	12.4



<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
17	12.8
20	13.2
23	13.4
27	13.9
31	14.6
35	15.4
38	16.2
41	17.3
44	18.4
47	19.9
50	21.8
52	23.6
54	25.4
56	27.6
58	31.0
60	34.9
62	39.7
64	46.9
66	57.2
68	74.3
78	Set

TABLE XVII

Gel mixture as follows:

50 c.c. HAc - 1.999 N.  
 50 c.c. Sodium Silicate - 1.245 N.  
 10 c.c. 0.9 M.  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$   
 40 c.c. Water  
 pH 5.0

25°C.

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
2	12.1
6	12.3
8	12.5
11	12.8
16	13.2
19	13.6
22	14.0
26	14.6
29	15.0
33	16.0
36	16.8
39	17.8
41	18.4
43	19.1
45	20.3
48	22.2

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
50	23.9
53	26.9
55	29.2
57	32.7
59	36.9
61	42.0
63	49.7
65	61.1
77	Set

TABLE XVIII

Gel mixture as follows:

50 c.c. HAc - 1.999 N. 25°C.  
 50 c.c. Sodium Silicate - 1.245 N.  
 50 c.c. 0.18 M.  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$   
 pH 4.8

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
2	12.0
5	12.2
9	12.8
12	13.0
16	13.3
19	13.6
25	14.3
27	14.8
30	15.4
32	15.8
35	16.5
38	17.6
40	18.6
43	19.4
45	20.8
48	22.9
50	24.6
54	29.4
56	32.3
58	37.2
60	42.2
62	49.9
64	61.8
76	Set



TABLE XIX

Gel mixture as follows:

50 c.c. HAc - 1.999 N. 25°C.  
 50 c.c. Sodium Silicate - 1.245 N.  
 50 c.c. 0.18 M.  $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$  ( $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ )  
 pH 4.9

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
2	12.2
6	12.6
10	12.8
13	13.2
17	13.6
19	13.8
22	14.3
25	14.8
28	15.6
31	16.1
34	16.8
36	17.5
38	18.5
40	19.1
43	21.1
45	22.6
47	25.1
49	26.1
51	28.7
53	31.9
55	36.1
57	41.2
59	48.7
61	59.6
63	79.3
75	Set

TABLE XX

Gel mixture as follows:

50 c.c. HAc - 1.999 N. 25°C.  
 50 c.c. Sodium Silicate - 1.245 N.  
 50 c.c. 0.18 M.  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  ( $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ )  
 pH 4.9

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
2	12.0
4	12.2

<u>Time after Mix (min.)</u>	<u>Time of Efflux (sec.)</u>
8	12.5
13	13.0
16	13.4
19	13.6
23	14.4
26	14.7
30	15.8
32	16.5
35	17.6
39	19.1
42	21.0
44	22.3
47	24.8
49	27.6
51	30.5
53	34.8
55	39.5
57	47.1
59	58.7
61	78.2
73	Set

TABLE XXI

Gel mixture as follows:

50 c.c. HAc - 1.999 N.  
 50 c.c. Sodium Silicate - 1.245 N.  
 10 c.c. 0.9 M.  $\text{AlCl}_3$  ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ )  
 40 c.c. Water  
 pH 4.3

25°C.

Time of set - 45 sec.



CALCULATION OF THE ENERGY OF ACTIVATION

A graph was plotted with the log of the time of set as ordinates and the reciprocal of the absolute temperature as abscissae. The slope of the straight line obtained was multiplied by  $2.303 \times 1.987$ . This gave  $Q$ , the calculated energy of activation, as 15,695 cal. The slope is 3.43.

<u>Log t'</u>	<u><math>1/T \times 10^3</math></u>
3.0334	3.144
3.1761	3.193
3.3579	3.245
3.5416	3.299
3.7324	3.355
3.9020	3.412

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