A STUDY OF THE VOLUME CHANGE DURING THE SETTING OF SILICIC ACID GEL

BY

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TABLE OF CONTENTS

Abstract:

An investigation of the volume change during the setting of silicic acid gel was made using a precision mercury dilatometer. The effects of varying the silicate and acid concentrations were studied. The heat of neutralization of the acetic acid and sodium silicate was compensated for to prevent any heat expansion in the gel. Also discussed are the theories of the setting of the gel.

Introduction and Historical:

While a large amount of work has been done on the properties of silicic acid gel in the past, there is a dearth of information in the literature about the volume change connected with the setting process of the gel. The little work that has been done contains many discrepancies.

The first recorded work done on volume changes during the setting of gels was conducted by E. Heymann (3), (4) in 1936 in England. Heymann experimented with several different gels with the following results: For gelatin and agar gels he found a decrease in volume; with ferric hydroxide gel, he observed no volume change at all, and for methyl cellulose and silicic acid, Heymann found an increase in volume. He attributed this increase to a decrease in the hydration of the silicic acid on setting. To explain this more fully, the bound water, he said, is held tightly to the silicic acid molecule by Van der Waal's forces and is compressed very slightly. When this water is freed, its volume increases with the relaxation of these forces, and the total volume of the gel is increased. Freundlich (2), in a later paper, discussed Heymann's results, saying that the volume change phenomenon provides one of the most characteristic tests for classifying gels. According to Freundlich, gels can be placed in three classes, those which decrease in volume on setting, those which increase, and lastly thixotropic gels, or those whose volume remains constant. (The term thixotropy defines a <u>reversible</u> sol-gel transformation.)

Three years later, A. Riad Tourkey (9) worked with silicic acid and found increases in volume with the exception of one run which increased at first and then decreased. However, both Tourkey and Heymann ignored the heat developed in the reacting of the reagents. In precision measurements heat expansion can have a large effect on results. It is likely that this heat had an adverse effect on Tourkey's and Heymann's work.

The heat of reaction was compensated for in the study of Stratta (8) at Union College in 1957. Stratta measured the heat of neutralization of the acetic acid and sodium silicate used, which is approximately equal to that developed in the neutralization of a strong base and weak acid. His volume change measurements were probably more accurate than those of previous experimenters because of these compensations. However, Stratta worked with gels of one concentration only.

The work described in this paper is an attempt to investigate the effects of varying the pH and also the silicate concentration on the volume, while holding other factors constant.

Theory:

Colloidal silicic acid, or sol of hydrated silica, is formed by the action of an acid, acetic acid in this case, on a soluble silicate, usually sodium silicate.

Sodium silicate is commonly written as Na_2SiO_3 or sodium meta silicate. It is really not a compound as written but rather a mixture of compounds of Na_2O and SiO_2 in variable proportions. The ratio of soda to silica in the meta silicate is obviously 1:1

from the formula. The silicate used in this series of experiments had a ratio of 1:3.29.

Practically any sol of hydrated silica will set with lapse of time. There are three important theories which have been set forth in an attempt to explain the setting process. First, we will consider the emulsion theory, postulated by Ostwald (7). He assumed the gel to be a liquid-liquid system with an emulsoid structure. However, the theory fails for silicic acid when one considers two factors, the viscosity and elasticity of the gel. An emulsion could have a high viscosity but would still flow. Dilute silicic acid gels have good flow properties but as the silica concentration increases, flow disappears. Also stress-strain curves for silicic acid gels bear no resemblance to those of true emulsion such as rubber in benzene. These two inconsistancies lead to the abandonment of the emulsion theory.

Second is the cellular theory, credited to Bütchli (1). It assumes a solid in the form of a cellular structure and the liquid in the form of small droplets trapped in the cells. This theory accounts for the elasticity of the gel but cannot satisfactorily explain syneresis, which occurs some time after the gel has set. Syneresis is the squeezing out of liquid containing the salts and acids present in the gel. It is not obvious how liquid could be squeezed out of the gel without inflicting damage to the cell walls. Finally, as the gel sets there should be an increase of electrical resistance as the liquid is subdivided by the non-conducting solid. This increase in resistance does not occur.. Therefore, there are serious doubts as to the validity of the cellular theory.

The third and generally accepted theory is the fibrillar theory of Nägeli (6). There are three types of structure which are covered by it. They are:

a. Structure formed by agglomeration of the colloid.

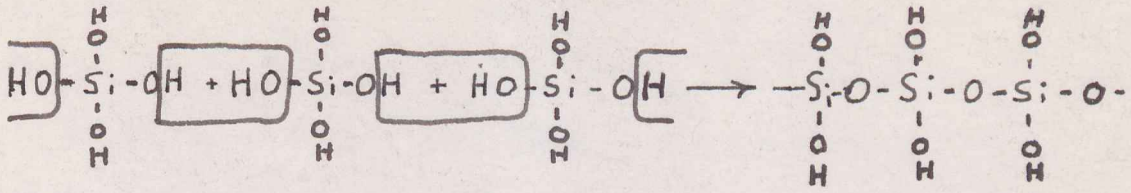
b. Mats of fine crystals.

c. Polymers formed by condensation.

Electrolytes are generally ineffective in coagulating silicic acid and moreover, divalent electrolytes are less effective than monovalent. Therefore, we may say that the gelation process does not proceed by agglomeration. There is only one gel, myricyl alcohol, which is known to form mats of fine crystals.

The third structure, condensation polymers, seems to apply best to silicic acid. Water is split out of neighboring molecules of silicic acid forming long chain molecules with the water enmeshed between them. These molecules are probably very highly hydrated. The theory is supported by the fact that the molecular weight of silicic acid is quite low at first and rises to about 8000 as the gel sets (5). The theory explains the lack of increase of electrical resistance since the liquid phase remains continuous. After the gel has set, any further contraction should squeeze out liquid; hence, syneresis occurs.

Assuming the fibrillar theory to be correct, we can see why a volume change is possible. Water is split out of two silicic acid molecules as shown below, and the formation of the shorter silicon-oxygen bonds draw the molecules closer together than in the ordinary silicic acid grouping.



The tendency for the freed water to polymerize leads to a further reduction in volume.

Apparatus:

A dilatometer of about 73 cc. capacity was constructed (see diagram). The change in volume of the gel was measured in the capillary tube which was calibrated by weighing columns of mercury whose length in the capillary was known. The volume of the dilatometer was determined by weighing it empty and filled with water at 25°C. and calculating the volume of the water. The instrument was held at constant temperature within 0.013°C. The dilatometer was constructed with two stopcocks, one attached to the side, on the filling tube, and one on top as an exit for air.

Procedure:

Compensations were required for the heat developed by the neutralization reaction which is similar to that of a weak acid and a strong base. The heat of condensation of the gel, which is distinct from that of neutralization, was developed over such a long period of time, i.e. the time of set, that all heat due to it was considered to be dispersed into the constant temperature

bath without causing any error. The temperature rise to be expected for each run was calculated. The reactants were kept at a temperature lower than that of the dilatometer by the temperature rise to be expected on mixing. Therefore, when the reactants were mixed, their temperature rose to that of the dilatometer and when introduced into it, no heat effect on the volume occurred.

The reactants and the dilatometer were kept in two constant temperature baths with the correct temperature difference between them. The acid and silicate were kept in separate 50 cc. beakers until they reached constant temperature. They were then mixed by pouring silicate into the acid and introduced into the dilatometer as quickly as possible. Readings could usually be taken 30 seconds after mixing but the first one or two readings were usually uncertain because of small fluctuations in temperature before equilibrium was established.

The acetic acid used contained 60 cc. of glacial acetic acid per liter which gave a normality of 0.951. The sodium silicate contained 240 cc. of "Brand E" silicate per liter. This resulted in a normality of 0.831, calculated as equivalent in sodium hydroxide.

Using data from Stratta's work on the heat of neutralization of the acid and silicate, the molar heat was calculated to be 4610 calories. From this was calculated the temperature rises for each run.

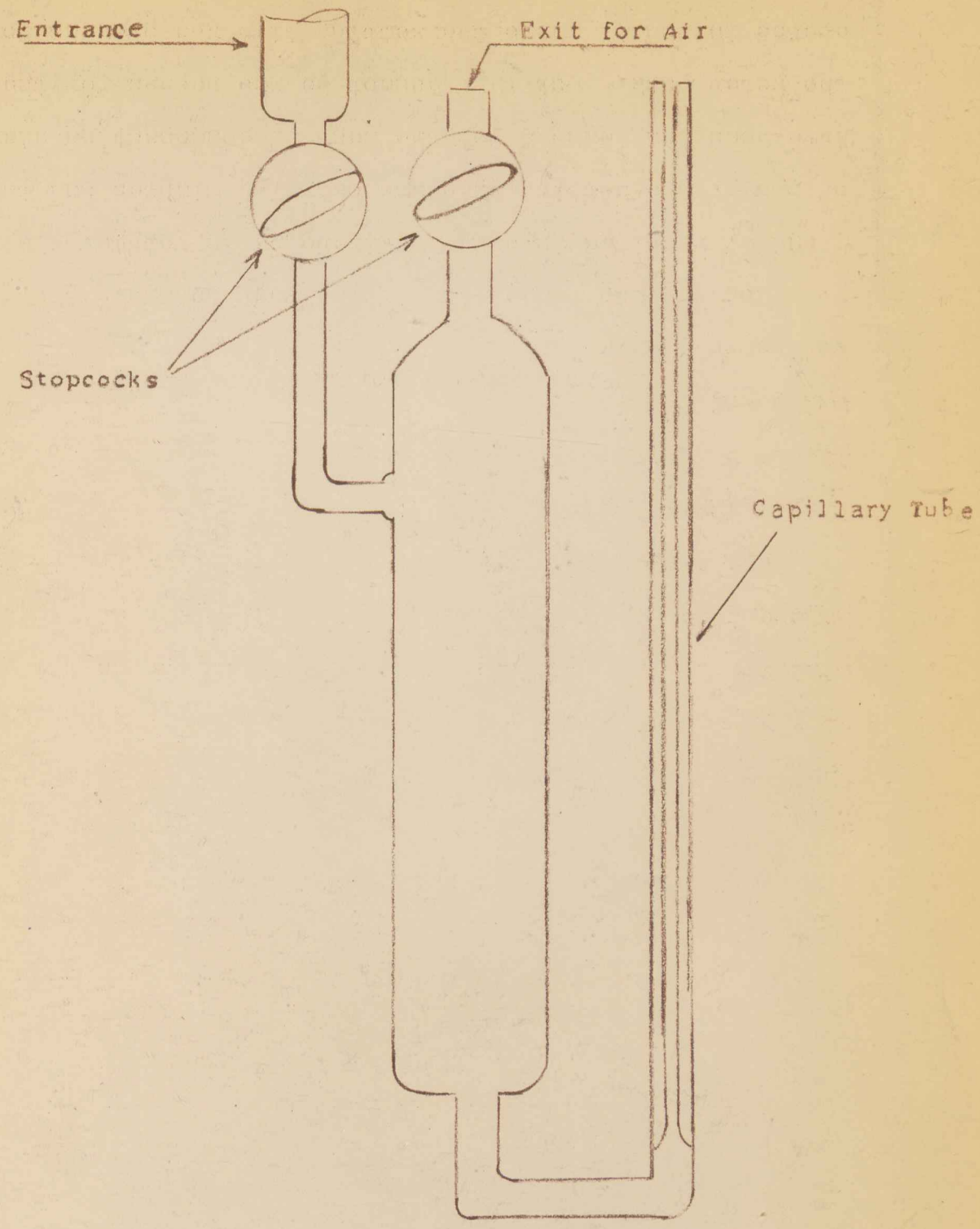


DIAGRAM OF DILATOMETER

Data:

Volume of dilatometer - 72.94 cc.

Calibration of capillery - 1 cm. = 0.01376 cc.

Normality of acetic acid - 0.951

Normality of acetic acid II - 2.84

Normality of sodium silicate - 0.831

I VARIATION OF ACID CONCENTRATION:

Run 1. 50 cc. silicate pH - 4.89

30 cc. 2.84 N. HAc Set in 121 min.

30 cc. H_2O *Temp. difference 1.74°C.

Time (min.)	**Capillary reading (cm.)	Time	Capillary reading
0	5.80	30	12.97
1	6.42	40	13.38
2	7.18	50	13.53
3	7.75	60	13.60
4	8.30	70	13.67
5	8.85	80	13.67
10	10.28	90	13.70
12	10.89	100	13.70
15	11.65	150	13.57
20	12.25		

* between reactants and dilatometer; rise expected on mixing.

** scale runs backwards; level is actually falling.

Run 2. 50 cc. silicate pH 4.80

30 cc. 2.84 N. HAc Set in 120 min.

30 cc. H_2O Temp. difference 1.74°C.

Time (min.)	Capillary Reading (cm.)	Time	Capillary Reading
0	6.50	40	13.65
1	7.00	50	13.78
2	7.46	60	13.85
3	7.92	70	13.87
4	8.42	80	13.92
5	8.86	90	13.92
8	10.15		
10	10.75	100	13.92
15	11.82	110	13.85
20	12.58	120	13.83
30	13.30	130	13.76

Run 3. 50 cc. silicate — pH 5.28

50 cc. 0.951 N. HAc — Set in 49 min.

10 cc. H_2O — Temp. difference 1.74°C.

Time (min.)	Capillary reading (cm.)	Time	Capillary reading
0	5.70	15	8.68
1	5.95	20	9.28
2	5.85	30	10.27
3	5.95	40	10.70
4	6.15	49	10.67
5	6.35	60	10.64
8	7.00		
10	7.45	70	10.60
12	7.88	80	10.50

Run 4. 50 cc. silicate pH - 5.40

50 cc. 0.951 N. HAc Set in 69 min.

15 cc. H_2O * Temp. difference 1.59°C.

Time (min.)	Capillary reading (cm.)	Time	Capillary reading
0	5.05	15	3.25
1	4.92	20	3.10
2	4.50	30	2.96
3	4.25	40	2.87
4	4.03	50	2.80
5	3.89	137	2.60
8.	3.60	170	2.50
10	3.48	261	2.45

*In error, should have been 1.66°C., calculated from the heat of reaction.

Run 5. 50 cc. silicate pH - 5.35

48 cc. 0.951 N. HAc Set in 48 min.

12 cc. H_2O Temp. difference 1.74°C.

Time (min.)	Capillary reading (cm.)	Time	Capillary reading
0	6.80	12	8.75
1	7.20	15	9.14
2	7.22	20	9.54
3	7.30	30	9.86
4	7.53	40	9.86
5	7.70	50	9.77
8	8.22	60	9.75
10	8.53	70	9.73

Run 6. 50 cc. silicate pH 5.40

48 cc. 0.951 N. HAc Set in 45 min.

12 cc. H_2O Temp. difference 1.74°C.

Time (min.)	Capillary reading (cm.)	Time	Capillary reading
0	7.55	12	9.25
1	8.10	15	9.65
2	7.92	20	10.20
3	7.95	30	10.74
4	7.97	40	10.85
5	8.10	45	10.80
8	8.65	50	10.77
10	8.95	55	10.77

Run 7. 50 cc. silicate — pH 5.45

45 cc. 0.951 N. HAc — Set in 30 min.

15 cc. H_2O — Temp. difference 1.74°C.

Time (min.)	Capillary reading	Time	Capillary reading
0	5.85	15	10.35
1	6.20	20	10.70
2	6.49	25	10.76
3	6.92	30	10.66
4	7.42	40	10.65
5	7.81	50	10.50
8	8.92	60	10.45
10	9.45	80	10.36
12	9.86	100	10.30

Run 8. 50 cc. silicate
40 cc. 0.951
20 cc. H_2O

pH 6.20
Set in 7.5 min.
Temp. difference 1.59°C.

Time (min.)	Capillary reading (cm.)
0	8.05
0.5	8.00
1	7.67
2.5	7.58
3	7.56
4.5	7.58
7.5	7.56
10	7.50
12	7.47
15	7.40
20	7.32
30	7.20
96	6.92

Run 9. 50 cc. silicate pH 10.5

21.5 cc. 0.951 N.HAc Set in 6 hours 30 min.

38.5 cc. H_2O Temp. difference 0.80°C.

Time (min.)	Capillary R reading (cm.)	Time	Capillary reading
0	6.73	30	8.66
1	6.84	40	9.10
2	6.77	50	9.46
3	6.80	60	9.66
4	6.80	80	9.92
5	6.95	115	10.30
8	7.16	158	10.64
10	7.30	180	10.75
12	7.45	210	11.00
15	7.68	271	11.00
20	8.04	360	11.00
		390	11.00

Run 10. 50 cc. silicate — pH 10.70

20 cc. 0.951 N. HAc — Set in 9 hrs. 30 min.

20 cc H_2O — Temp. difference 0.80°C.

Time (min.)	Capillary reading (cm.)	Time	Capillary reading
0	6.95	90	9.85
1	7.02	110	10.33
2	6.92	130	10.67
3	6.92	150	11.02
4	6.95	170	11.20
5	6.98	205	11.52
8	7.06	240	11.75
10	7.13	270	11.95
12	7.20	340	12.26
15	7.30	360	12.35
20	7.48	420	12.48
30	7.90	480	12.58
40	8.27	510	12.55
50	8.65	540	12.55
60	8.96	570	12.55

II VARIATION OF SILICATE CONCENTRATION:

Run 11. 30 cc. silicate pH 5.33

30 cc. 0.951 N. HAc Set in 210 minutes

50 cc. H_2O Temp. difference 1.04°C.

Time (min.)	Capillary reading (cm.)	Time	Cappilary reading
0	7.20	20	13.60
1	8.23	30	13.70
2	9.37	40	13.72
3	10.20	50	13.74
4	10.90	60	13.75
5	11.25	70	13.75
8	12.45	85	13.75
10	12.90	150	13.75
12	13.15	210	13.65
15	13.41	330	13.60

Run 12. 30 cc. silicate pH 5.40

30 cc. 0.951 N. HAc Set in 210 min.

50 cc. H_2O Temp. difference 1.04°C.

Time (min.)	Capillary reading	Time	Capillary reading
0	6.90	22	13.68
1	7.18	35	13.90
2	8.30	40	13.95
3	9.18	50	14.01
4	9.76	60	14.05
5	10.40	71	14.09
8	11.65	80	14.09
10	12.25	90	14.05
13	12.80	125	14.00
15	13.05	210	13.85

Run 13. 40 cc. silicate — pH 5.25

40 cc. 0.951 N. HAc — Set in 91 min.

30 cc. H_2O — Temp. difference 1.39°C.

Time (min.)	Capillary reading (cm.)	Time	Capillary reading
0	6.80	15	12.05
1	7.28	21	12.72
2	7.68	32	13.28
3	8.12	40	13.45
4	8.60	50	13.48
5	9.00	60	13.50
8	10.17	70	13.45
10	10.82	80	13.40
12	11.43	90	13.34

Run 14. 55 cc. silicate pH 5.20

55 cc. 0.951 N. HAc Set in 49 min.

Temp. difference 1.91°C.

Time (min.)	Capillary reading (cm.)	Time	Capillary reading
0	5.90	13	12.16
1	6.35	15	12.50
2	7.32	20	12.95
3	8.20	31	13.32
4	9.17	40	13.37
5	9.80	50	13.35
8	11.00	114	12.93
10	11.55		

Compilation of Results:

Run	cc. HAc	cc. Sil.	cc. H_2O	pH	Time of set (min.)	Volume Change %
1	50	*30	30	4.89	121	-0.148
2	50	*30	30	4.80	120	-0.138
3	50	50	10	5.28	49	-0.0937
4	50	50	15	5.40	69	+0.0313
5	50	48	12	5.35	48	-0.0565
6	50	48	12	5.40	45	-0.0633
7	50	45	15	5.45	30	-0.0906
8	50	40	20	6.20	7.5	+0.0111
9	50	21.5	38.5	10.5	390	-0.0805
10	50	20	40	10.7	570	-0.0948
11	30	30	50	5.33	210	-0.120
12	30	30	50	5.40	210	-0.0955
13	40	40	30	5.25	91	-0.124
1	50	50	10	5.28	49	-0.0906
14	55	55	0	5.20	49	-0.142

*Using 2.84 N. HAc. All other runs use 0.951 N. Hac.

Sample Calculations:

Run 3. 50 cc. silicate (0.831 N)

50 cc. HAc (0.951 N)

10 cc. H_2O

a. temperature rise.

50/1000 x 0.831 = 0.0415 mole in 50 cc.

4610 cal./mol. x 0.0415 mol. = 192 cal.

$$\frac{192 \text{ cal.}}{110 \text{ gm.} \times 1 \frac{\text{cal.}}{\text{gm. deg.}}} = 1.74^{\circ}$$

b. volume change.

capillary change = 4.97 cm. x 0.01376 cc./cm. = 0.0682 cc.

Since the dilatometer was calibrated with a reading of 15.00, the volume of the capillary between the reading at time = 0 and 15.00 must be added to the total volume of the dilatometer.

9.28 x 0.01376 = 0.128 cc. + 72.94 cc. = 73.07 cc.

0.0682/73.07 x 100 = 0.0937 % decrease.

Discussion of Results:

A review of the results showed that identical runs varied as much as 10%. The first thing to be suspected was temperature but experiment showed that one degree rise in temperature resulted in an increase of only 0.91 cm. on the capillary. Since temperature control and calculation of temperature rise was accurate to approximately .06 degree, the small errors in temperature could not have caused such large errors in the volume change. The discrepency must be due primarily to some other factor. In general, errors seem larger when there is a very large initial change, i.e. during the first five minutes.

The volume change seems generally to vary with the time of set. Also, the variation of volume change with pH resembles that of setting time with pH. A minimum in setting time occurs at a pH of about 7, but it could not be determined whether a minimum in volume change occurred there, because the gel set before it could be completely poured into the dilatometer.

The curves of capillary reading vs. time are in general similar. The volume decreases rapidly at first and then gradually levels off. The volume remains at a minimum for a short while and then, usually about ten minutes before the gel sets, begins to increase very slightly.

However, an inspection of the results shows that two runs, 4 and 8, resulted in a marked increase in volume. In the case of run 8, the setting time was only 7.5 minutes and this may not have been long enough for the heat of condensation to dissipate into the water bath. But this cannot be the reason for the volume increase in run 4, where the setting time was over an hour. (This

time seems out of line with other runs.) Since 5 cc. too much water was used in run 4, runs 5 and 6 were done using the same proportions of acid and silicate as 4 but with the total volume maintained at 110 cc. Here, a decrease rather than an increase resulted and the data fits the general trend of the other results.

Next, experiments were carried out to observe the effect on the volume change of varying the silica concentration. The ratio of silicate to acid was kept constant for all runs in an attempt to keep the pH constant. With increasing silicate concentration one would expect the volume change to increase. The results show a rough increase but there is some uncertainty. All data is included on this set of runs, however.

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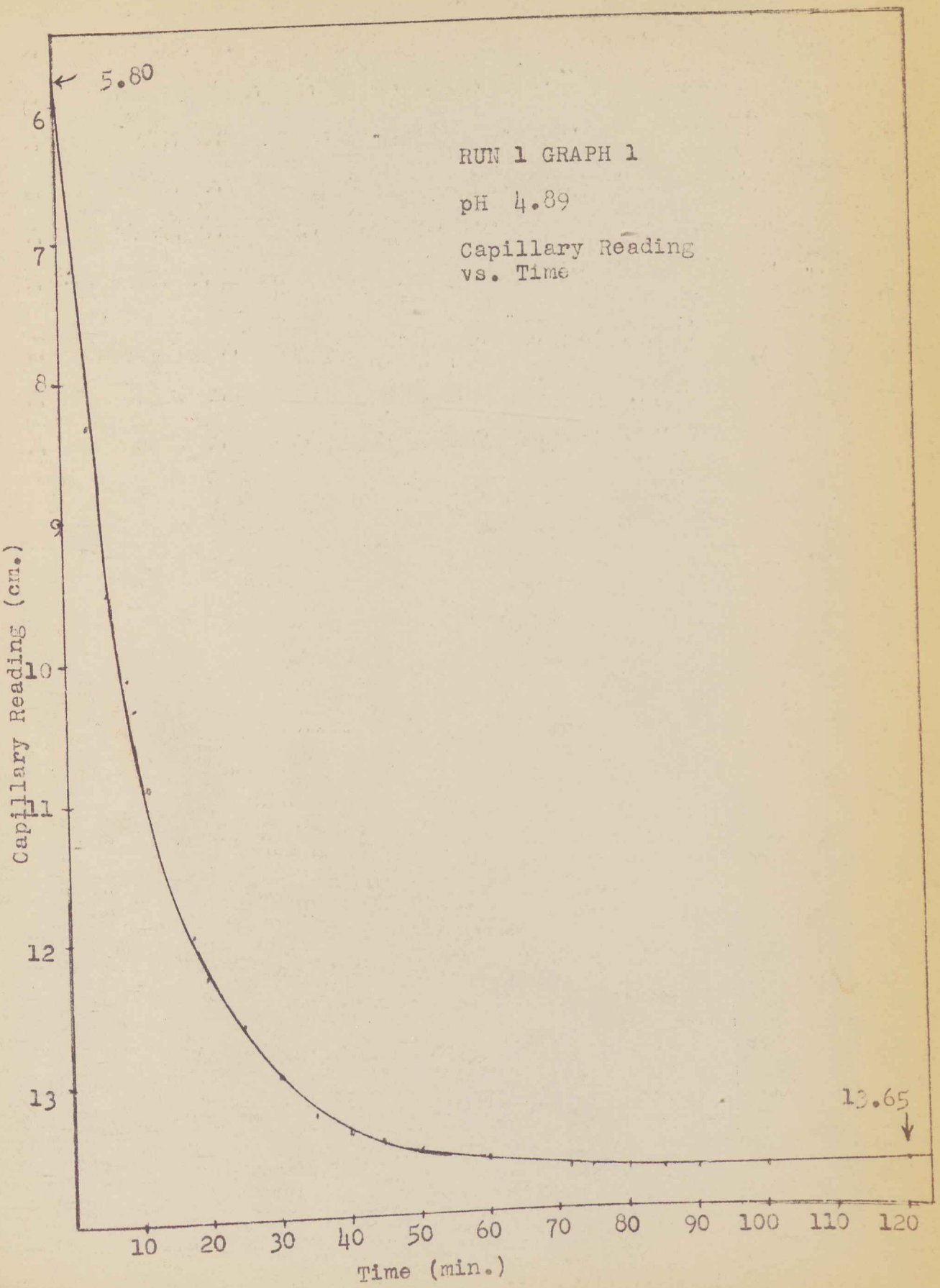
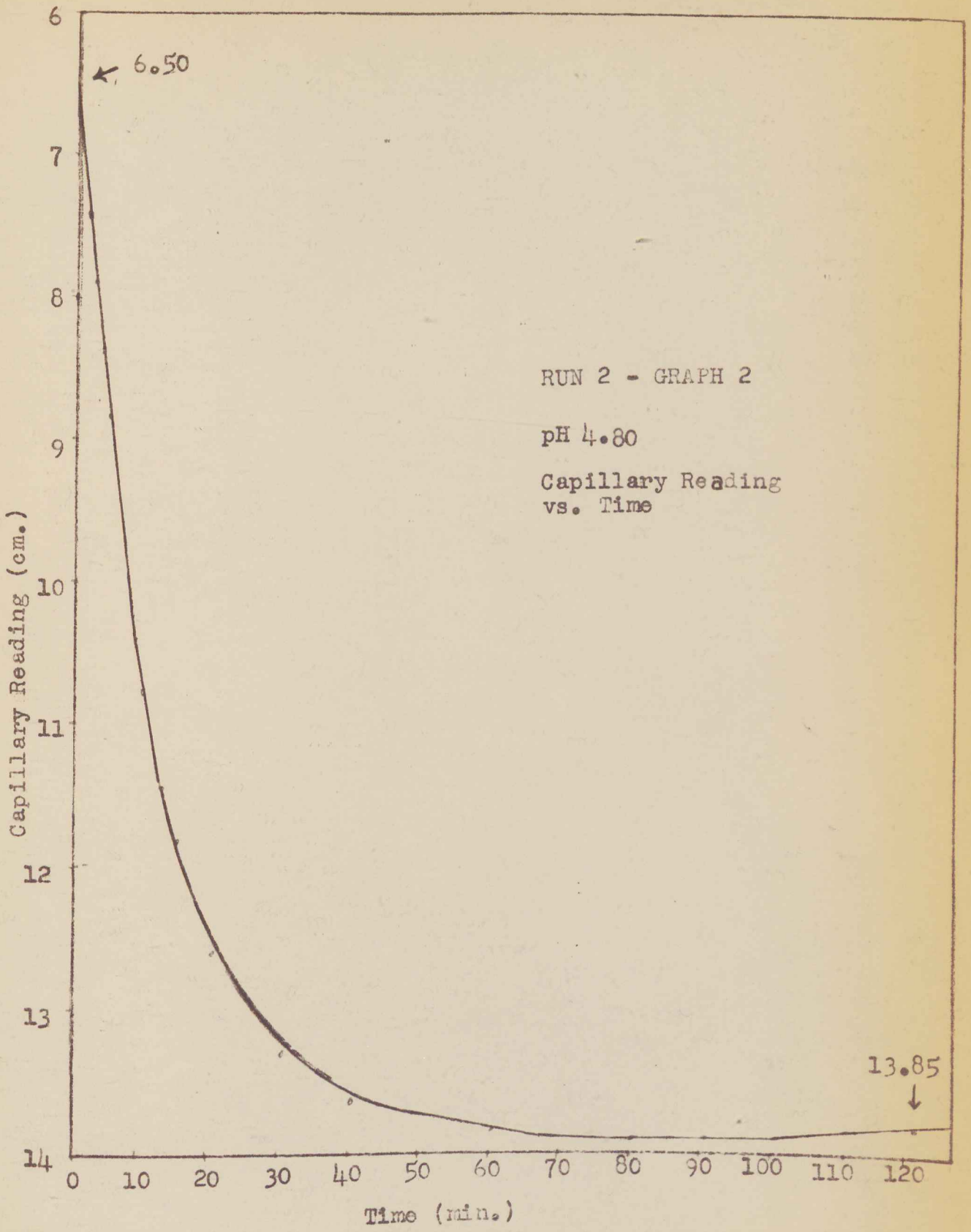
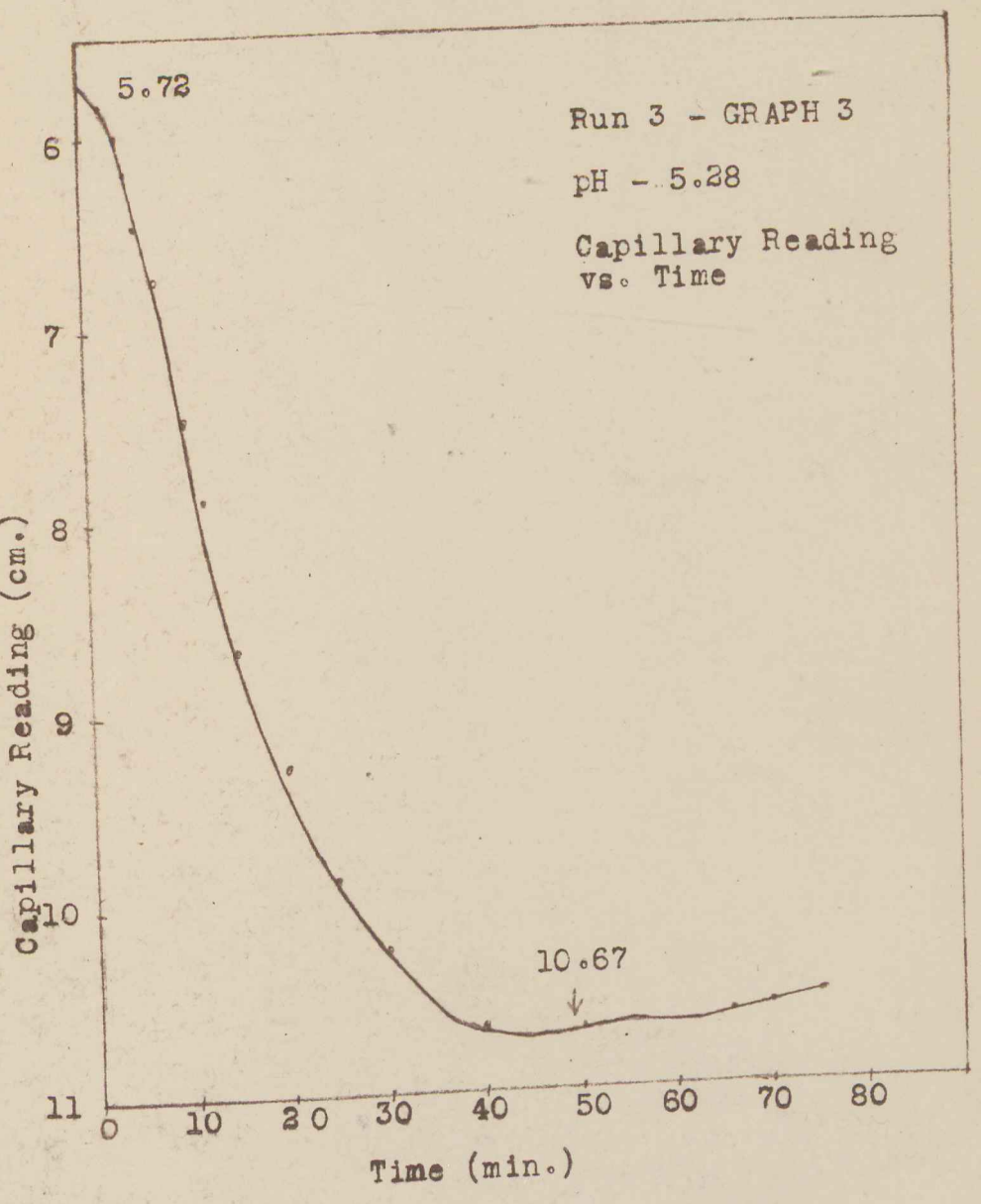
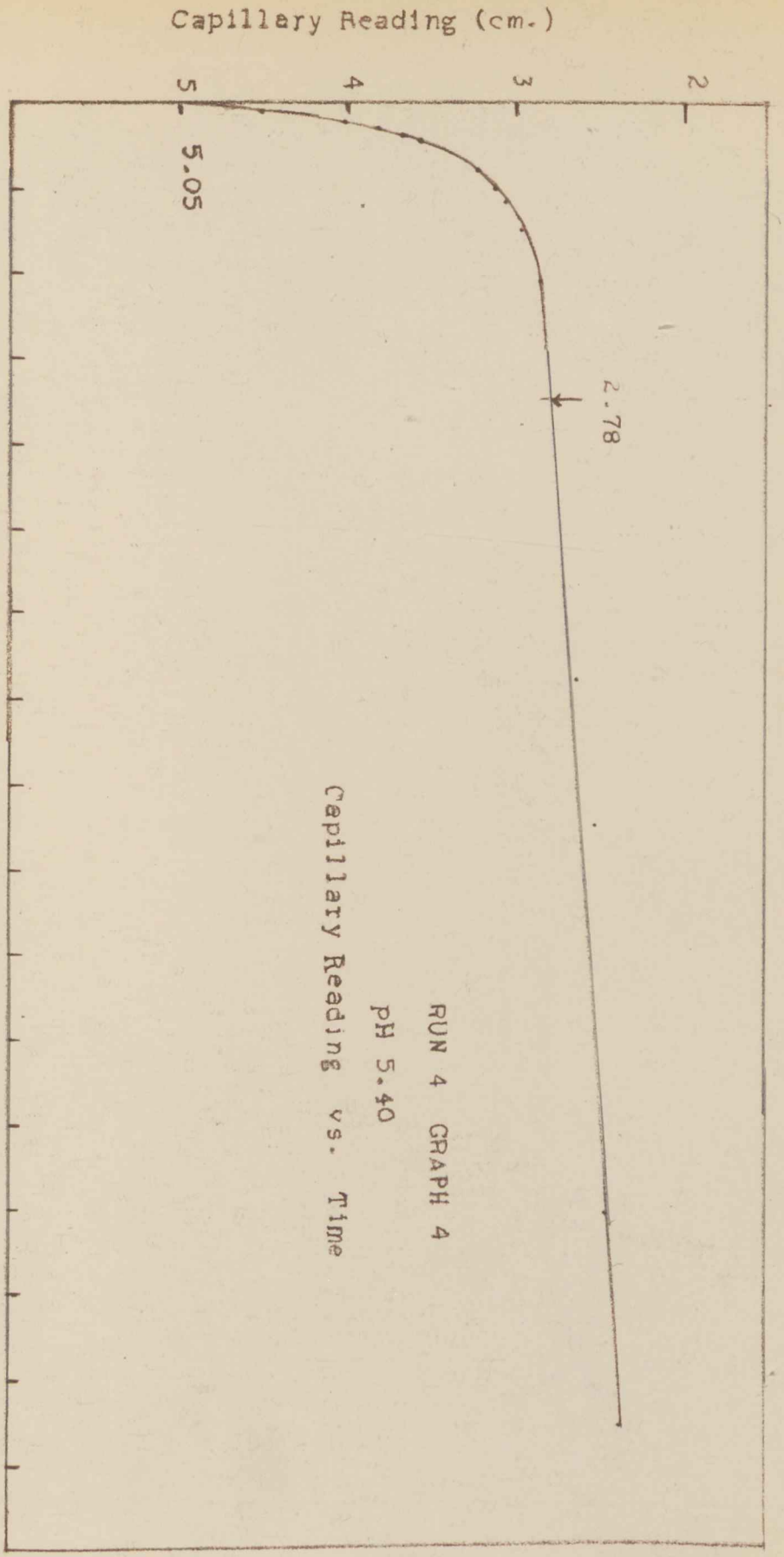

5.80
RUN 1 GRAPH 1
pH 4.89
Capillary Reading
vs. Time
Capillary Reading (cm.)
6
7
8
9
10
11
12
13
13.65
10
20
30
40
50
60
70
80
90
100
110
120
Time (min.)


6.50
13.85
RUN 2 - GRAPH 2
pH 4.80
Capillary Reading vs. Time
Capillary Reading (cm.)
Time (min.)
6
7
8
9
10
11
12
13
14
0
10
20
30
40
50
60
70
80
90
100
110
120

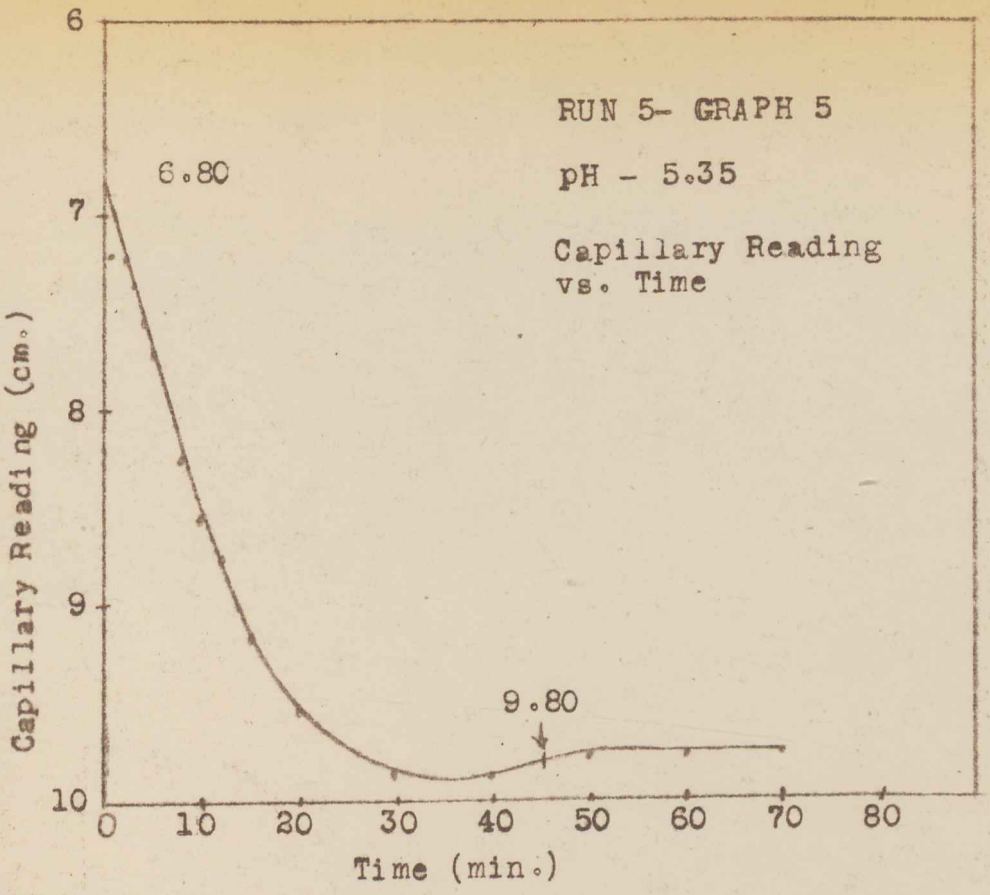

Run 3 - GRAPH 3
pH - 5.28
Capillary Reading vs. Time
5.72
10.67
Capillary Reading (cm.)
Time (min.)
6
7
8
9
10
11
0
10
20
30
40
50
60
70
80

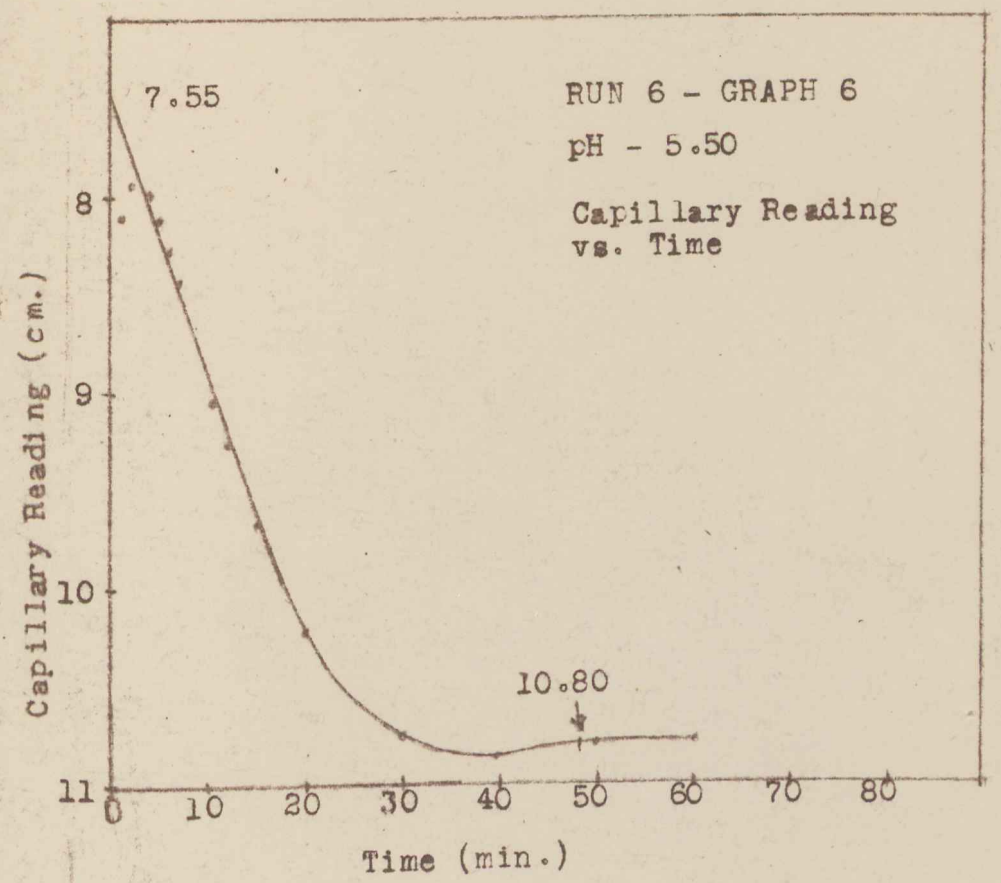


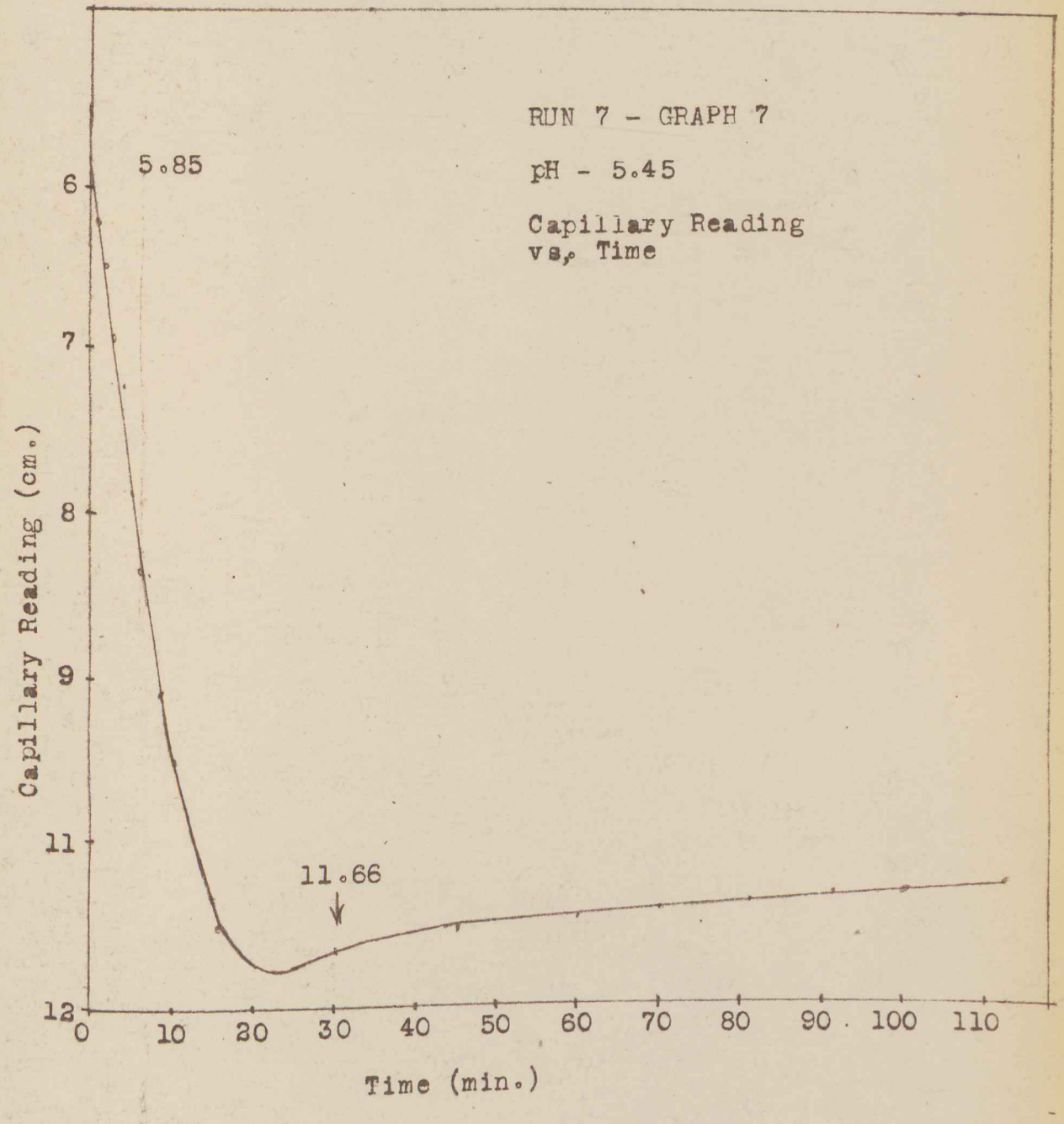
RUN 4 GRAPH 4

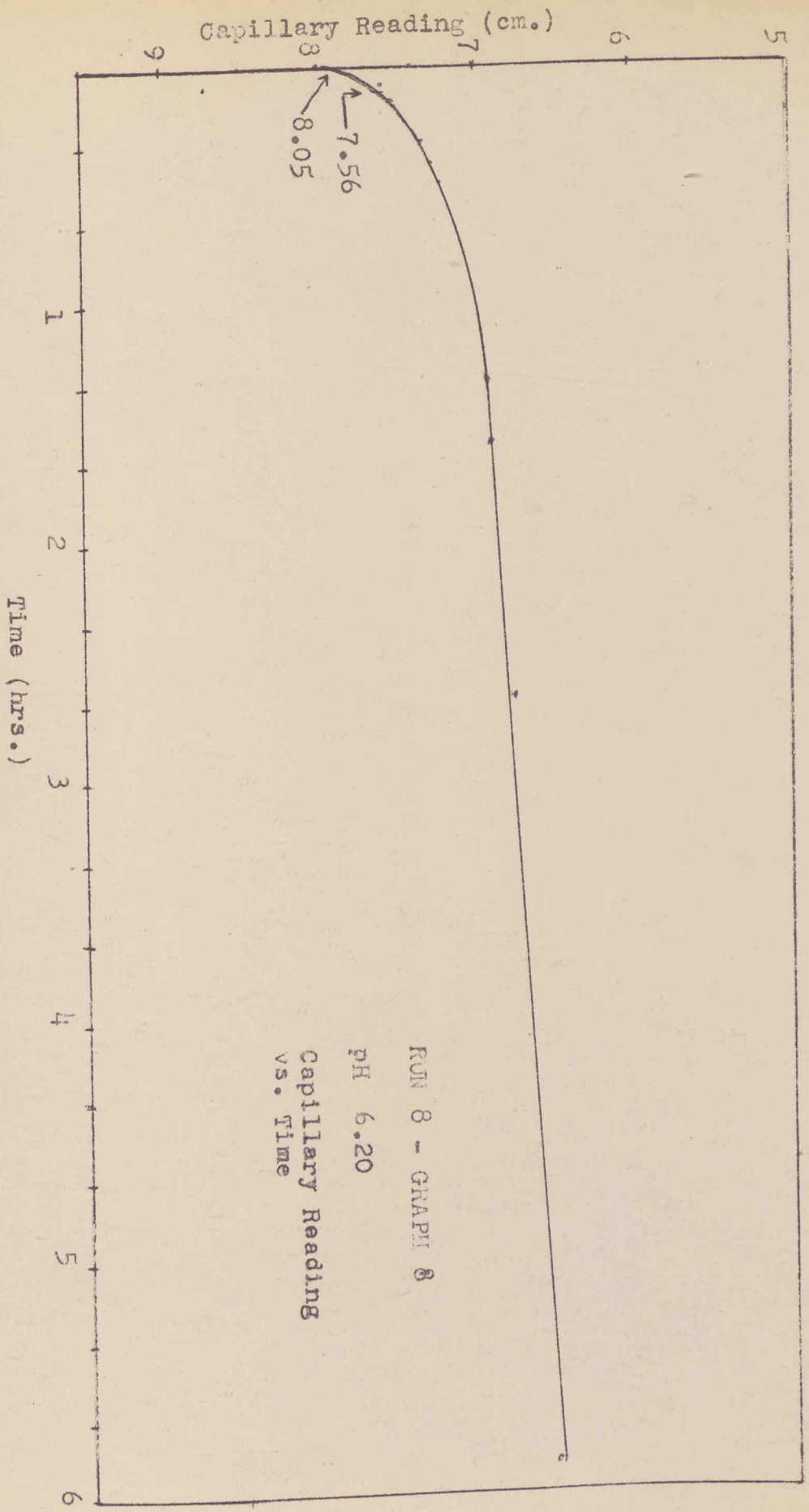
PH 5.40

Capillary Reading vs. Time


RUN 5- GRAPH 5
pH - 5.35
Capillary Reading vs. Time
6.80
9.80
Capillary Reading (cm.)
Time (min.)
6
7
8
9
10
0
10
20
30
40
50
60
70
80


RUN 6 - GRAPH 6
pH - 5.50
Capillary Reading vs. Time
7.55
10.80
Capillary Reading (cm.)
Time (min.)
8
9
10
11
0
10
20
30
40
50
60
70
80

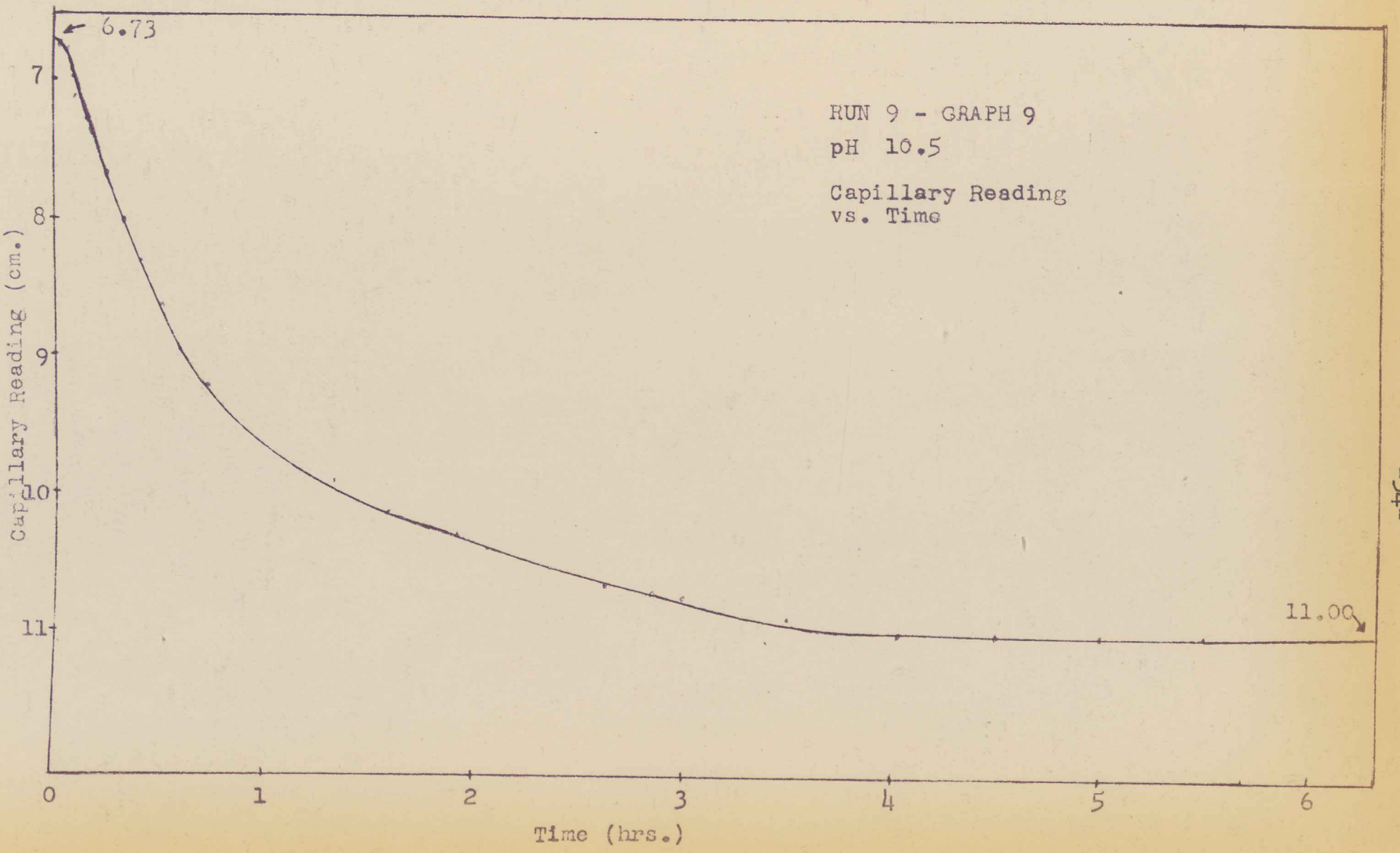

RUN 7 - GRAPH 7
pH - 5.45
Capillary Reading
vs. Time
5.85
11.66
Capillary Reading (cm.)
6
7
8
9
11
12
0
10
20
30
40
50
60
70
80
90
100
110
Time (min.)

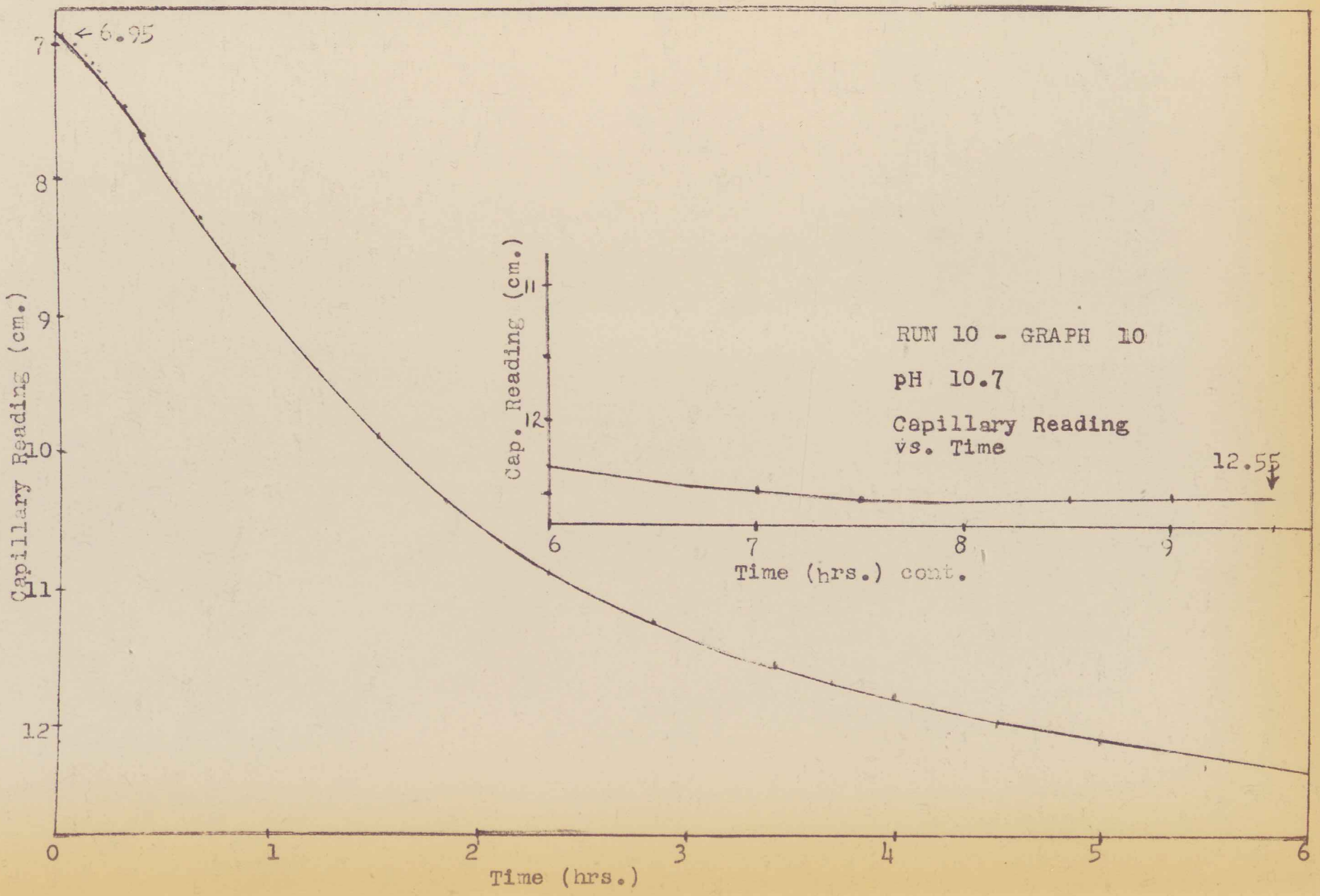


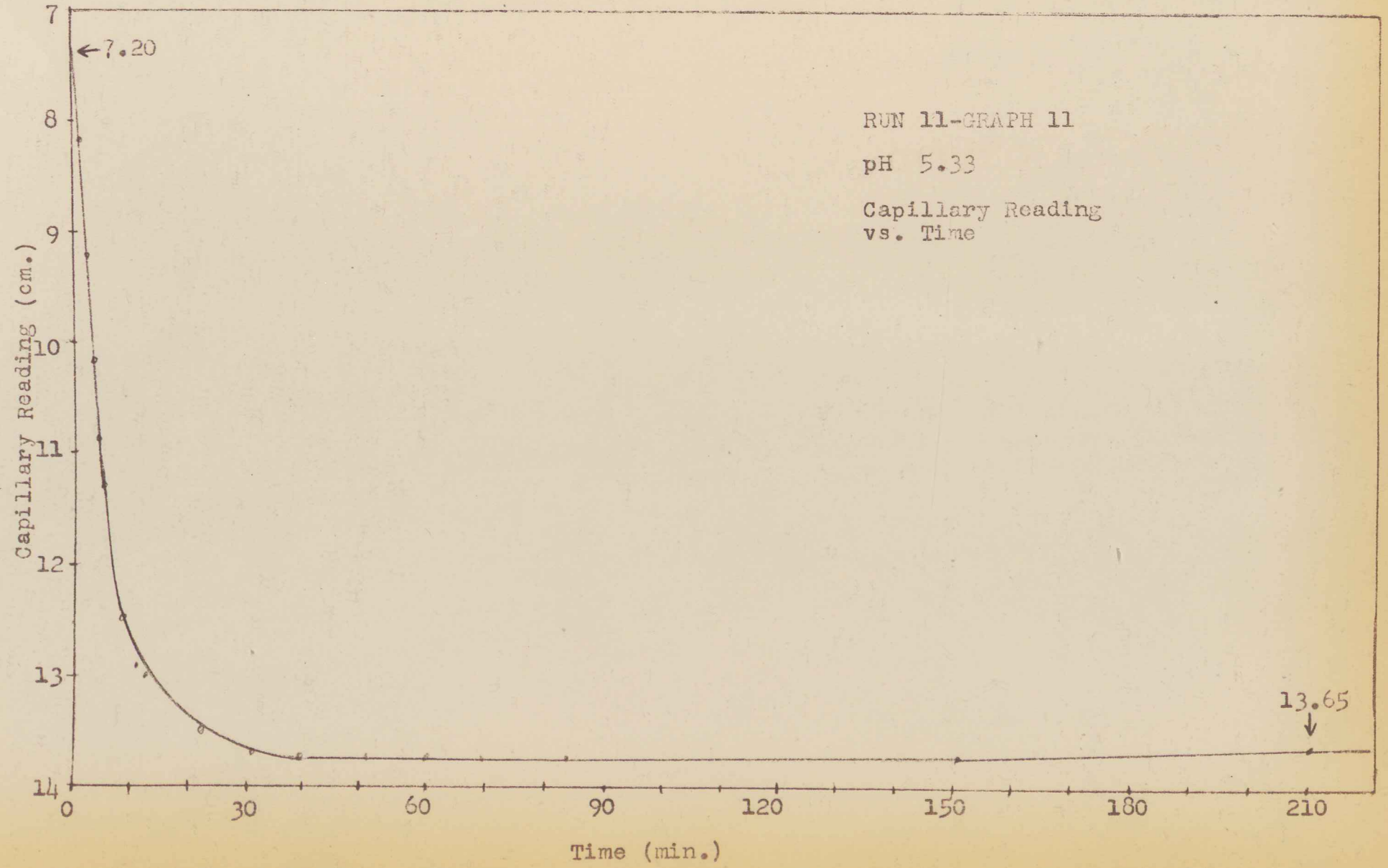
RUN 8 - GRAPH 8

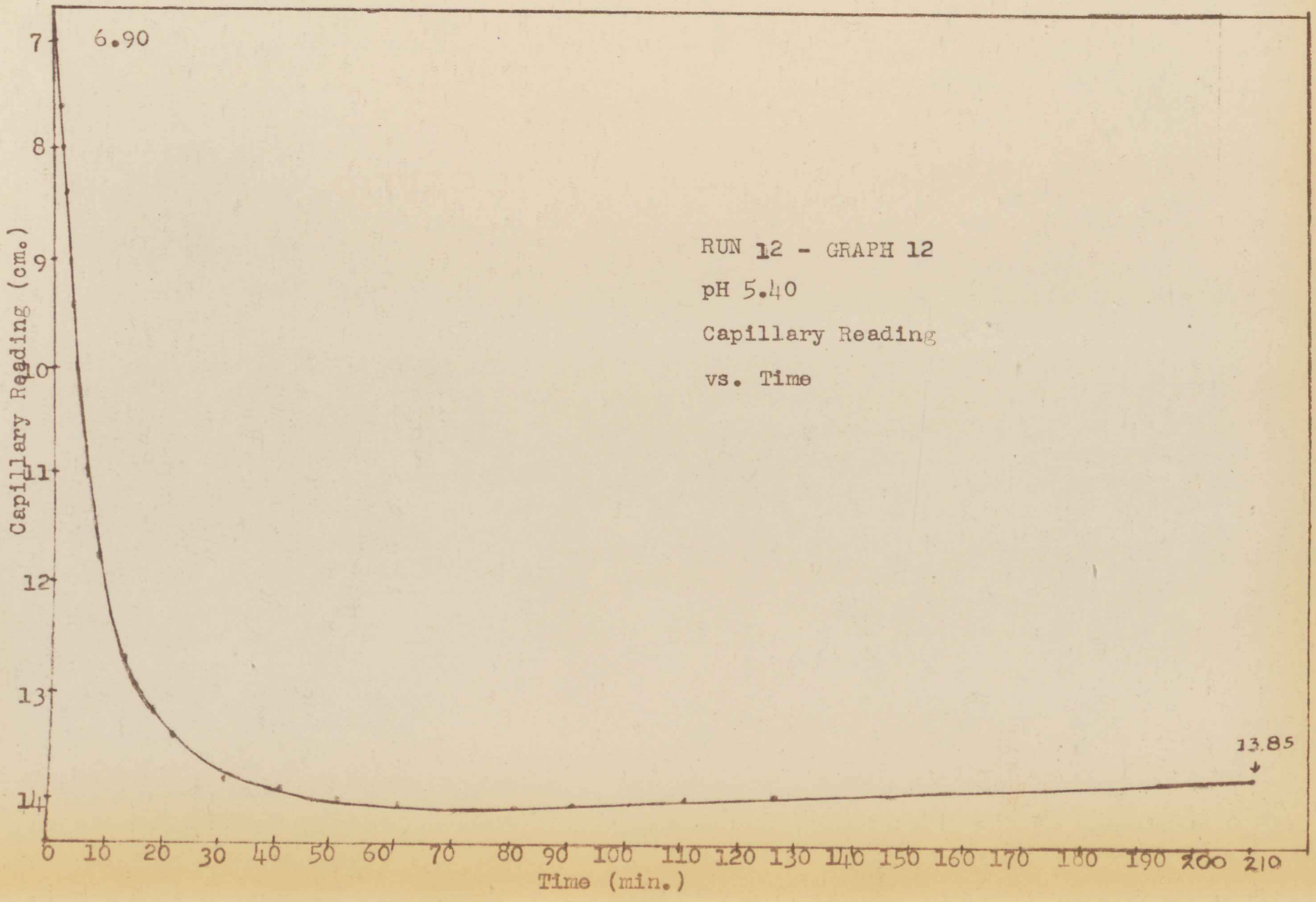
pH 6.20

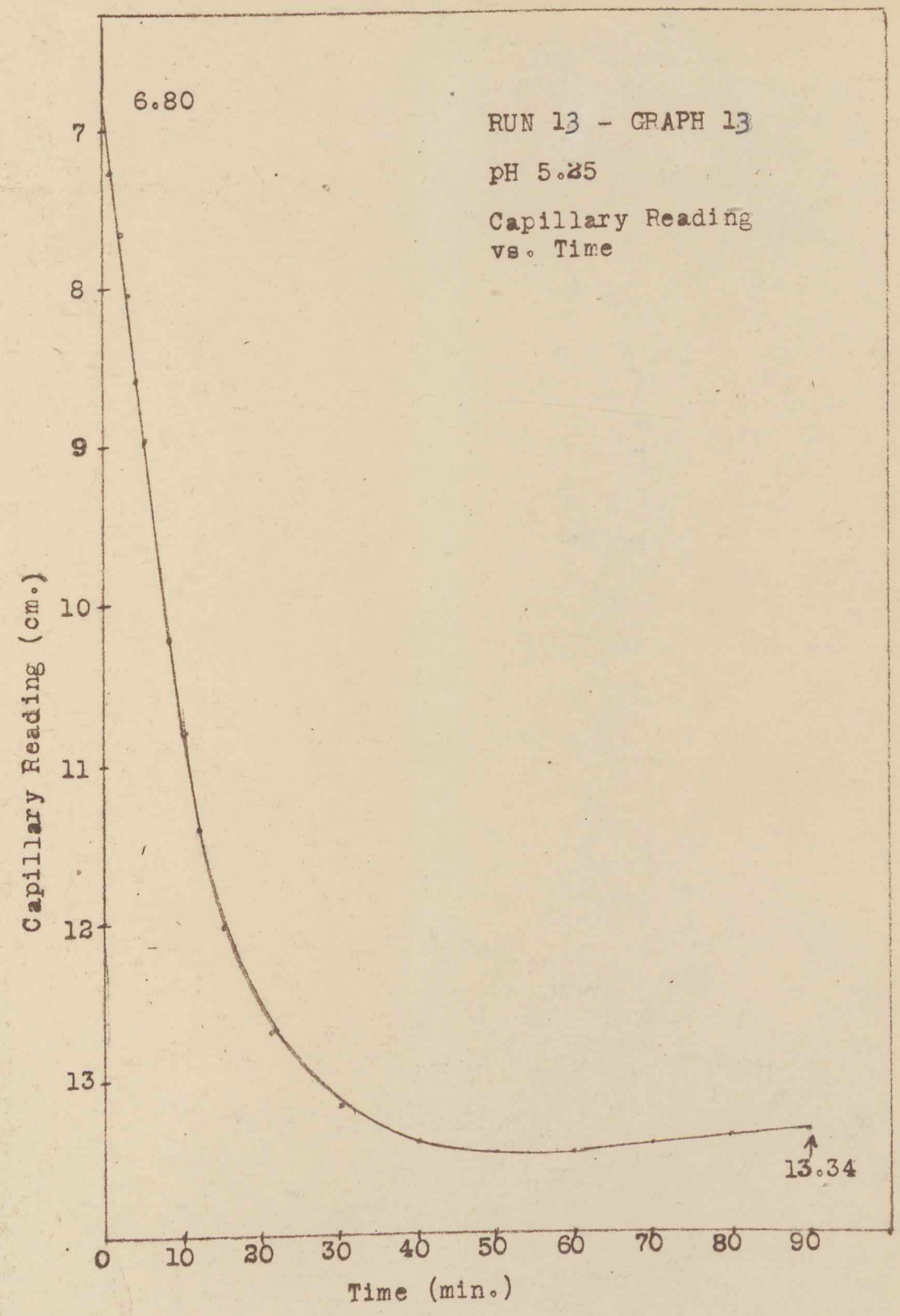
Capillary Reading
vs. Time

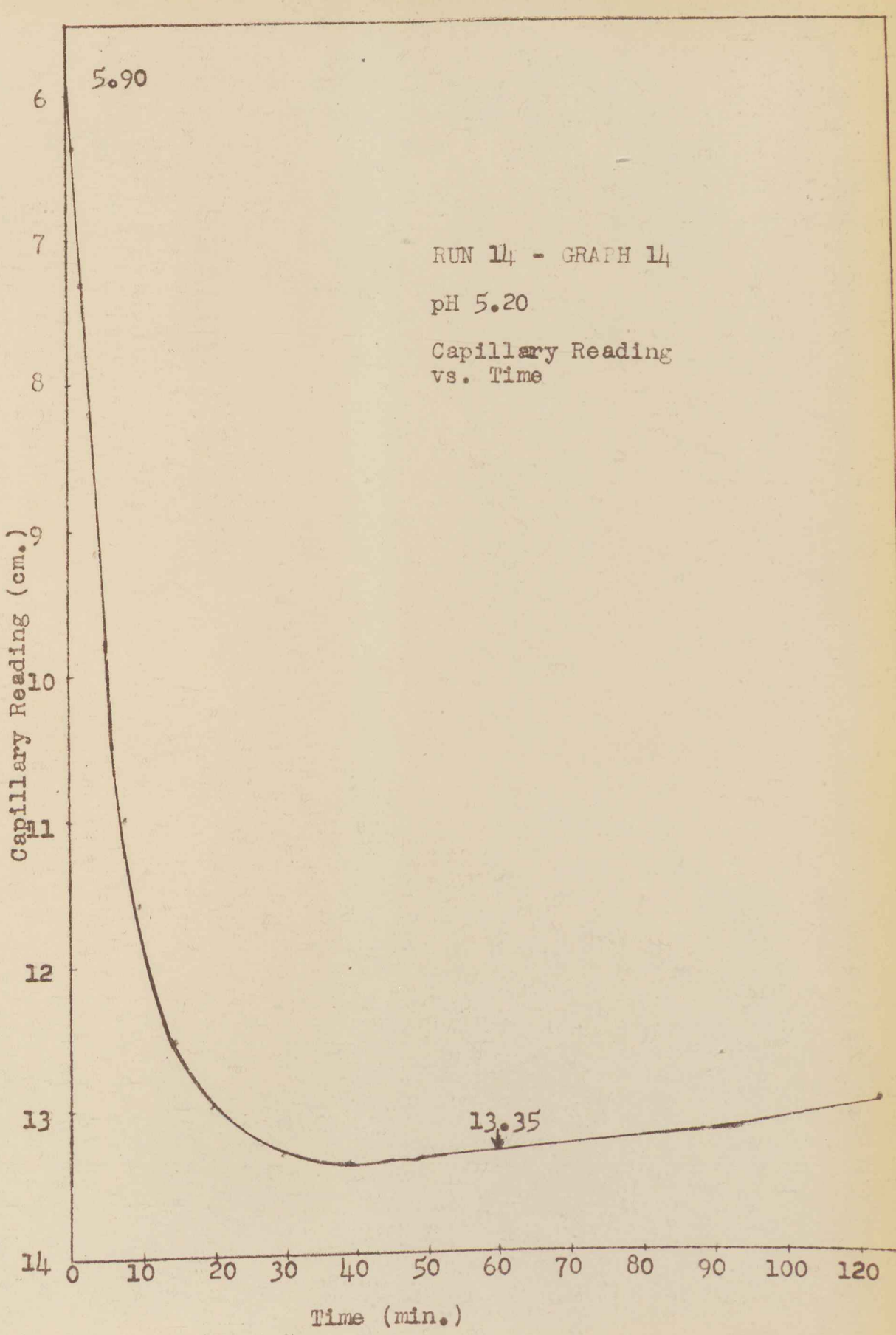

6.73
7
8
9
10
11
11.00
Capillary Reading (cm.)
0
1
2
3
4
5
6
Time (hrs.)
RUN 9 - GRAPH 9
pH 10.5
Capillary Reading
vs. Time

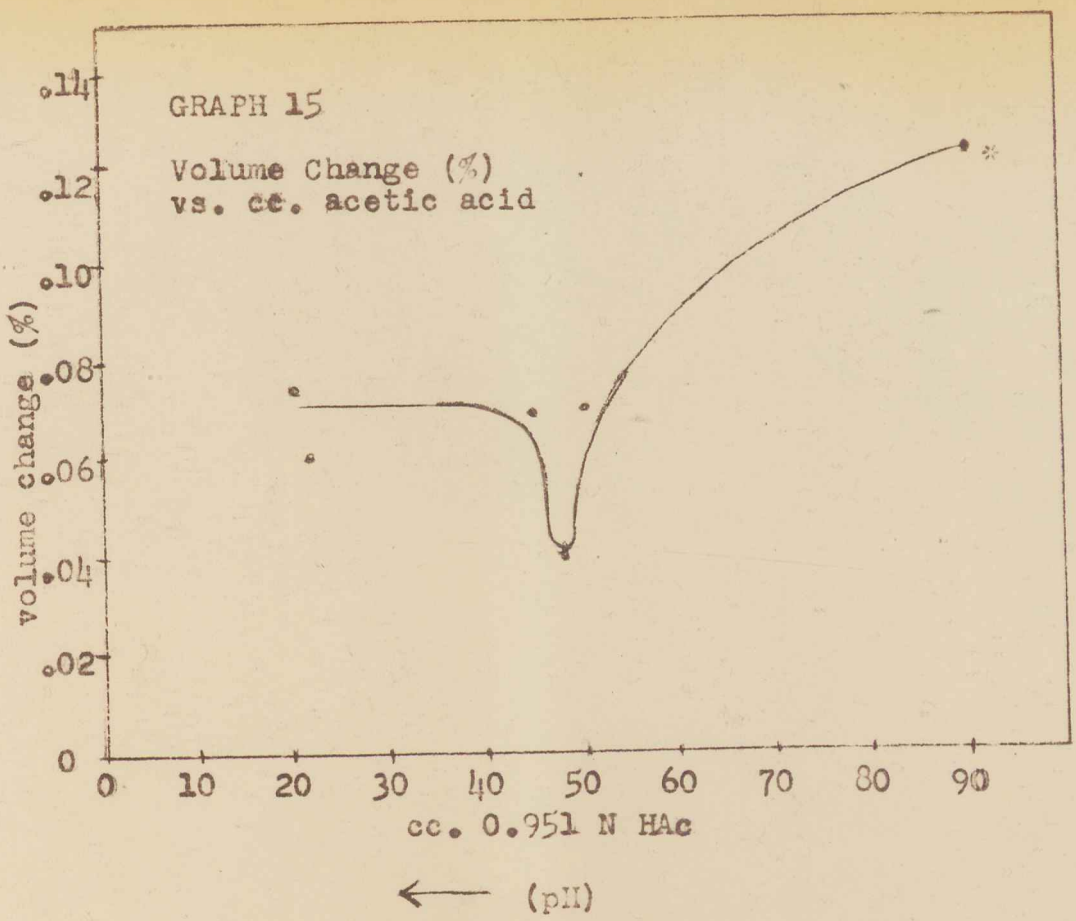

← 6.95
Capillary Reading (cm.)
7
8
9
10
11
12
0
1
2
3
4
5
6
Time (hrs.)
Cap. Reading (cm.)
11
12
6
7
8
9
Time (hrs.) cont.
12.55
RUN 10 - GRAPH 10
pH 10.7
Capillary Reading
vs. Time

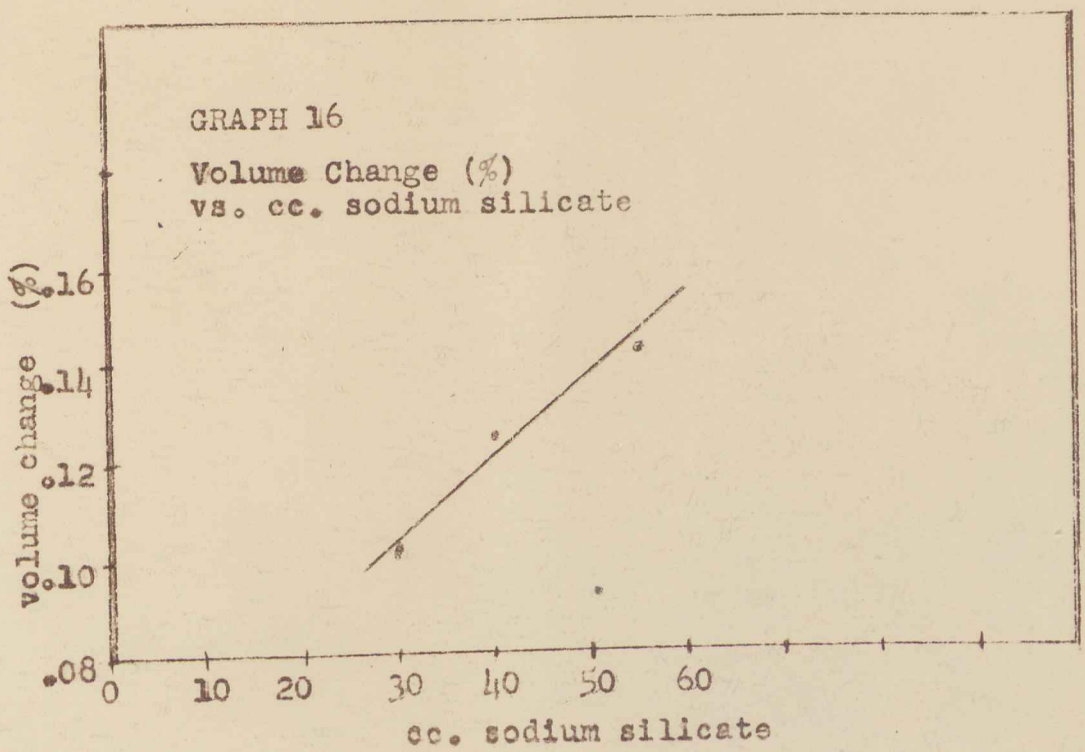

RUN 11-GRAPH 11
pH 5.33
Capillary Reading
vs. Time
←7.20
13.65
Capillary Reading (cm.)
Time (min.)
7
8
9
10
11
12
13
14
0
30
60
90
120
150
180
210


6.90
RUN 12 - GRAPH 12
pH 5.40
Capillary Reading
vs. Time
13.85
Capillary Reading (cm.)
7
8
9
10
11
12
13
14
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210
Time (min.)


6.80
RUN 13 - GRAPH 13
pH 5.25
Capillary Reading
vs. Time
7
8
9
10
11
12
13
Capillary Reading (cm.)
13.34
0
10
20
30
40
50
60
70
80
90
Time (min.)


5.90
RUN 14 - GRAPH 14
pH 5.20
Capillary Reading
vs. Time
13.35
Capillary Reading (cm.)
6
7
8
9
10
11
12
13
14
0
10
20
30
40
50
60
70
80
90
100
120
Time (min.)





* 30 cc. 2.84 N H Ac = 89.6 cc. 0.951 N HAc