

6-1941

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THERMAL REVERSIBILITY OF SILICIC ACID GELS

A thesis presented to the Department of Chemistry
of Union College in partial fulfillment of the require-
ments for the degree of Bachelor of Science in Chemistry.

By John H. Spittle

Approved by Charles B. Hurd.

May 29, 1941

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INTRODUCTION

The purpose of this research paper is to find out whether a silicic acid gel may be made which will be reversible with respect to temperature; that is, whether there is a gel which may be liquified by heating or cooling. There doesn't appear to be any literature which supports the idea of reversibility.

Our investigation has been carried out in the basic regions where a reversible gel would most likely be found. The setting of a silicic acid gel in the region above 10.4 pH differs from the setting of a gel of lower pH. Pomotti (1) found that a gel above 10.4 pH forms more slowly at a higher temperature than at a lower temperature, which would suggest the possibility of reversibility.

One would like to find a gel which would behave like gelatin when heated; that is, melt by heating and solidify by cooling. However, it would be a coincidence if this were so. The solidifying of gelatin is a physical change, whereas, the setting of a gel is primarily a chemical change involving the condensation (2) of polysilicic acid molecules.

In this thesis an attempt has been made to find sufficient evidence to answer the question of reversibility.

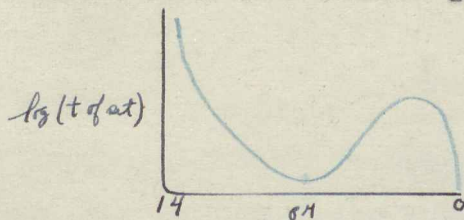
HISTORICAL

Silicic acid gels have been known for over one hundred years. Berzelius (3) mentioned that he prepared soluble silicic acid by the action of ammonium hydroxide upon hydrofluorosilicic acid.

Graham (4) and many others used a simpler method for producing the sol of hydrated silica. They reacted a solution of sodium silicate with an acid.

Today, interest lies more in the conditions under which the gel is formed, in finding out why a gel sets, and in determining the structure of the gel.

Among other things, temperature, pH, and silica concentration influence the setting of a silicic acid gel. In general the higher the temperature the shorter is the time of set (6). Pomotti (1) found that for very basic gels the setting is longer at higher than at lower temperatures. Hurd and Letterton (5) showed that the logarithm of the time of set plotted against the reciprocal of the absolute temperature gave a linear relationship. The higher the silica concentration the more rapidly will a gel be formed. Previous work on acidity has shown that a curve which is formed over the entire pH range is as follows:



Holmes (7) and Hurd and Letterton (5) stated that there was a minimum in the curve.

There are three general theories for the structure of a silicic acid gel: (A) the emulsion theory; (B) the cellular theory; and (C) the fibrillar or micellar theory.

The emulsion theory, explained by Ostwald (8, 9), assumes that the gel consists of a liquid -- liquid system with an emulsiod structure. The theory fails, in the case of silicic acid gels. Hatschek (10) studied the stress-strain curves in connection with the emulsion theory. His conclusions do not favor the emulsion theory.

The cellular theory, which is credited to Bütschli (11), says that the liquid part of the gel is held in the form of small droplets in a cellular structure made up of the solid phase. In other words, an honeycomb-like structure is assumed. This idea explains the elasticity and the ability of a gel to hold a fluid. However, the theory fails because you would expect a change in conductivity (12) as the gel sets. The cell walls should build up a resistance. Actually, no increase in the electrical resistance occurs when the gel mixture sets.

The fibrillar theory, which is usually accredited to Nägeli, is most satisfactory. The gel is considered as a sponge-like framework in which a solid and a liquid phase, each continuous, with the solid forming a fibrous structure and containing the liquid in pores.

This theory is considered from three points of view. The first is the view where the structure is formed by coagulation of the colloid as suggested by Pappada and Sadowsky (14). The

second view assumes that the gel is like a mat of fine crystals which holds water by capillarity. The third view is the polysilicic acid theory. This theory suggests that a silicic acid gel consists of an interlaced fibrillar or brush heap structure consisting of very large polysilicic acid molecules, the spaces being filled with liquid. Condensation (15) takes place where water splits out between two simpler silicic acid molecules to form a more complex structure (16). The polysilicic acid structure is heavily hydrated. Molecular weight determinations support the idea of polymerization. Hurd (2) discusses this theory at length.

EXPERIMENTAL

Preparation of solutions

The sodium silicate solution was made up by adding enough boiled distilled water to 625 cubic centimeters of "E" brand sodium silicate to make 2 liters of solution. The solution was titrated with hydrochloric acid solution using bromophenol blue as indicator. The hydrochloric acid had previously been standardized against a secondary standard of sodium hydroxide. The sodium hydroxide equivalent of the silicate solution was 1.262 N.

The acetic acid solution was made up by using glacial acetic acid and boiled distilled water, 115 cubic centimeters of acetic acid being diluted to 2 liters. Titration with a secondary standard of sodium hydroxide with thymol blue used as indicator gave 1.122 as the normality.

Oxalic acid with two molecules of water of hydration served as the primary standard against which the sodium hydroxide solutions were standardized.

Constant temperature baths

A large glass reservoir packed in excelsior served as a bath, as shown in diagram A. A toluene-mercury thermostat was used in connection with a thyatron unit which controlled an electric knife heater. A motor-stirrer combination kept the water circulating so as to insure uniform temperature. A 110° C. thermometer was used whose boiling and freezing points were checked.

The thermostat which gave temperature control accuracy of .05 degrees was set for 25° C. in the bath. Straight beakers of 160 cubic centimeters capacity were supported in the bath by setting them in holes in a bakelite strip. (See diagram B.) The strip of bakelite was laid across the bath. (See diagram C.)

A 40° C. bath was made out of a 2 liter beaker. A bi-metallic thermostat controlling the temperature within .1 degree was used to operate a knife beater. A motor-stirrer combination was used to stir the water. Insulation of cloth was wrapped around the beaker.

A low temperature bath was used at times. This consisted of the 40° bath with the heating unit removed. Ice was supplied to lower the temperature.

pH measurements

pH measurements were made by means of a glass electrode and saturated calomel cell. The glass electrode and calomel cell were made as shown in diagram D.

The glass electrode was made with Corning 015 glass. A piece of glass tubing 25 cm. long and 8 or 9 mm. in diameter was used. The tubing was sealed off about 8 cm. from one end by heating in the reducing flame of an M. I. T. burner. This had to be done quickly and too high a temperature had to be avoided. The end of the glass tube was then heated in a Bunsen flame until the glass got hot enough to color the flame. The tube was then taken from the flame, and blown out quickly to

give a bulb about 3cm. in diameter. Too high a temperature must be avoided or the glass will decompose. If it is necessary to conserve the special ol5 Corning glass, the glass may be sealed on to a tube of ordinary soda glass by means of de Khotinsky's cement. This seal must be above the surface of the liquid in which the electrode is used.

The glass electrode was washed out with 1 normal hydrochloric acid. A pinch of quinhydrone was put in the tube and the glass electrode was filled up to half an inch above the bulb. The solution was saturated by shaking the tube so that the quinhydrone had a chance to thoroughly saturate the solution. A paraffined cork placed in the tube made this operation easy. It is a good idea to have sufficient quinhydrone in the tube in order that a little may be left at the bottom of the bulb.

This glass electrode resembles the Leeds and Northrup 7685 P 1 glass electrode bulb.

Gardiner and Sanders (23) have given a resumé of the theories of glass electrodes. They classified various theories under adsorption theories or distribution theories. The adsorption theory (17, 18, 19) assumes a differential adsorption of ions at a solid liquid boundary which causes a separation of charges and sets up a sort of a condenser. The distribution theory (20, 21, 22) assumes that the "potential determining" ions are considered capable of crossing the glass boundary.

The calomel cell was constructed as shown in diagram D. Special mercury and calomel were used. The cell was constructed

in such a way that the lower part of the cell could be dipped into the solution. In this way the electrode should be at the same temperature as the solution in the beaker. A reservoir of saturate KCl was connected to the cell by a black rubber tube. Pinch clamps were used on the tube to control flowing of KCl solution. Preparation of a calomel half cell is described in Notes on Hydrogen Ion Measurements by Leeds and Northrup (24).

The buffer solutions used was made up of acetic acid (.1N) and .1N sodium hydroxide. The pH of the buffer was obtained by using the glass electrode and checked by the quinhydrone electrode. The mean of the pH of these two methods was used as the pH of the buffer.

No. 7652 potentiometer and No. 2480-C dual galvanometer were used to find the potential of the glass electrode -- saturated KCl calomel electrode. Leeds and Northrup conversion tables (25) were used to convert the millivolt readings into pH readings. Since solutions were very alkaline and contained sodium ions concentrated enough to cause error, an error correction had to be made by consulting correction tables (23) which were made for Leeds and Northrup tables.

Also, Jordan (26), Powney and Jordan (27), and Dole and Wiener (28) gave material which is very useful here.

Gel mixtures

The solutions used were kept constant at 160 cc. Of this 50 cc. consisted of the sodium silicate solution. The amount of the acid solution was varied. The variation of the acid allowed

us to study the gels at different pH values.

Procedure

The water and acid were measured by pipettes and burettes. The water and acid part of the gel mixture were put together in one straight wall beaker. The acid plus the water gave a volume of 110 cc. Next, 50 cc. of sodium silicate solution were pipetted in a straight wall beaker. The temperature of the solutions before mixing was about 1 degree below the temperature at which they set. The rise of temperature on mixing would bring the gel mixture to bath temperature.

The pH of a silicic acid gel was studied as it set at 25°C. The sodium silicate solution was poured quickly into the acid solution and mixed back and forth a few times. Part of this mixture was used to fill three 6" x 5/8 " test tubes half full and the rest was left in the beaker. The beaker was set in the bakelite rack over bath. The test tubes were placed in an upright position in bath.

In the case of gels No. 1 and 2, the glass electrode was left in for the duration of setting. This could not be done with the other gels. Apparently the alkali attacked the glass sufficiently to throw pH measurements off if the electrode were left too long in the solution. Therefore, the electrode was left in the gel only during the time when measurement was made. Right after the pH was determined, the electrode was removed and washed with a stream of distilled water. The electrode was checked in a buffer solution every time a measurement in the gel was made.

In between times, the glass electrode was kept in distilled water. At no time must the glass electrode be allowed to dry out.

After the gel had set by the inverted test tube method as described earlier, one test tube of the gel was heated to 80-100° C. and another test tube was placed in a bath 0-2° C. The gel in the beaker was put in a 40° C. bath and allowed to come to temperature. Then a pH measurement was made. The same gel was next cooled down near 0° C. and pH determined.

The same procedure was followed with all of the gels with the exception of the ice bath treatment in some cases.

RESULTS

None of the gels that were studied were found to be reversible.

The data and graphs show that the pH rose .3 to .4 units during time of setting.

The pH of the gels went down when they were heated from 25° to 40° C. For example, gel No. 5 had a pH of 10.76 at 25°. At 40° its pH was 10.36. This shows that the pH of the gel went down .40 units.

The pH of the gels rose when they were cooled down from 25° to 2° C. Taking gel No. 5, the pH rose .66 units.

It would have been interesting to have let a gel set at 70° C. and then to have lowered it to 5° C. If the gel were of a high enough pH to start with, the rise in pH on cooling might bring about liquification of gel.

The experimental work here only covered gels setting at 25° C. A repetition of this work at other temperature would be interesting.

The error of the pH determinations is about .05 units if care is taken in handling the glass electrode. Alkaline and sodium ion error can be corrected from tables spoken of earlier.

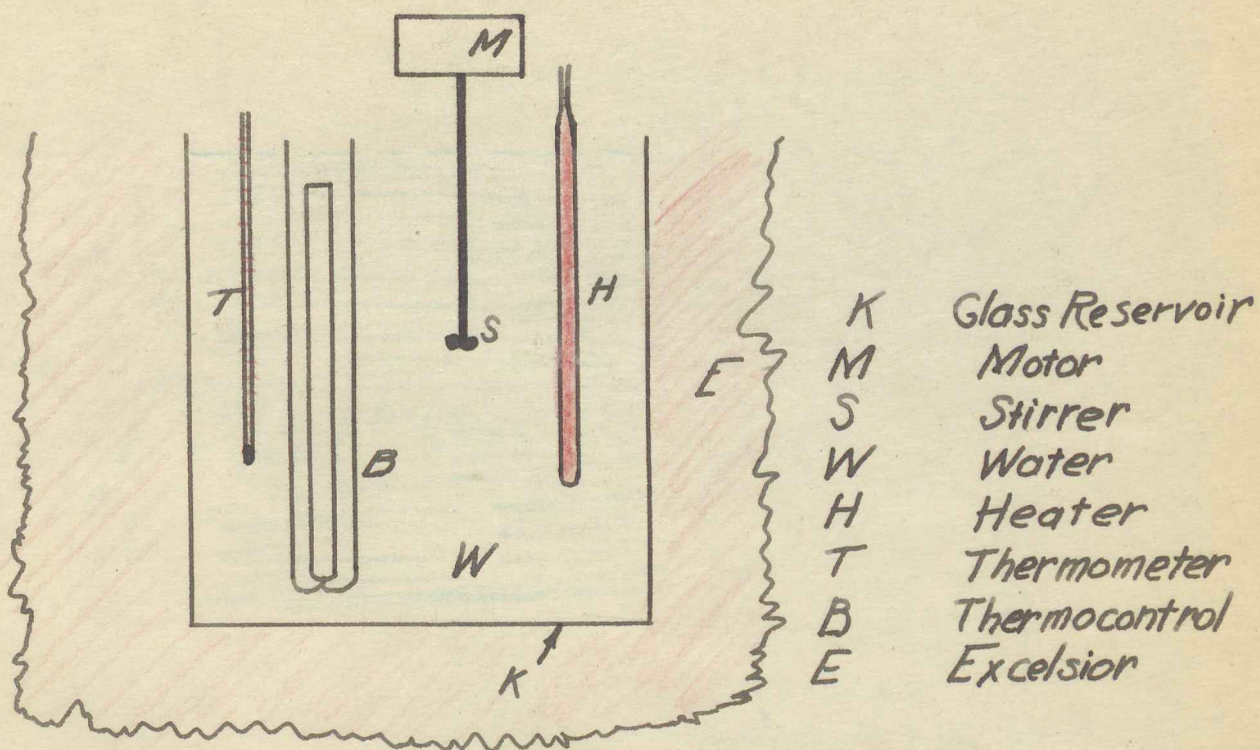


Diagram A

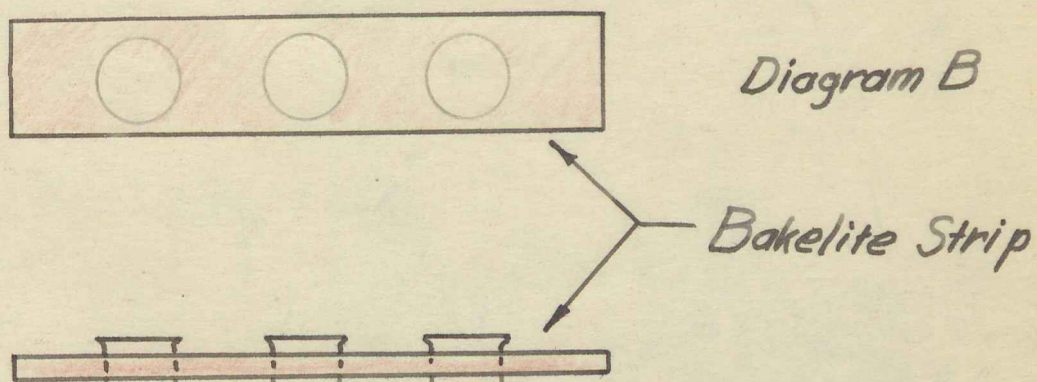


Diagram B

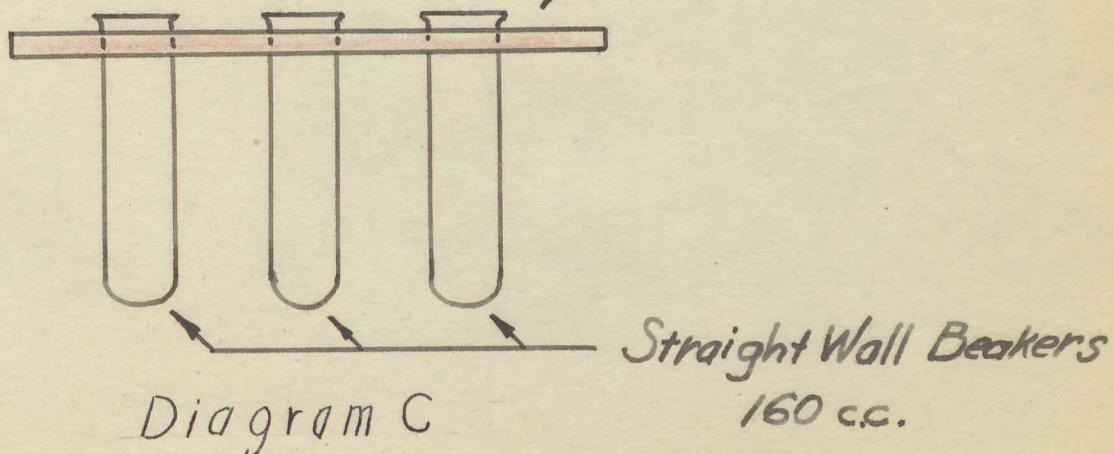
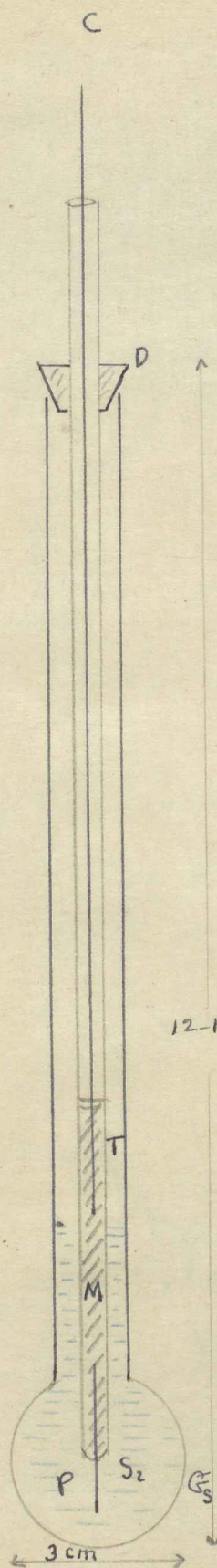
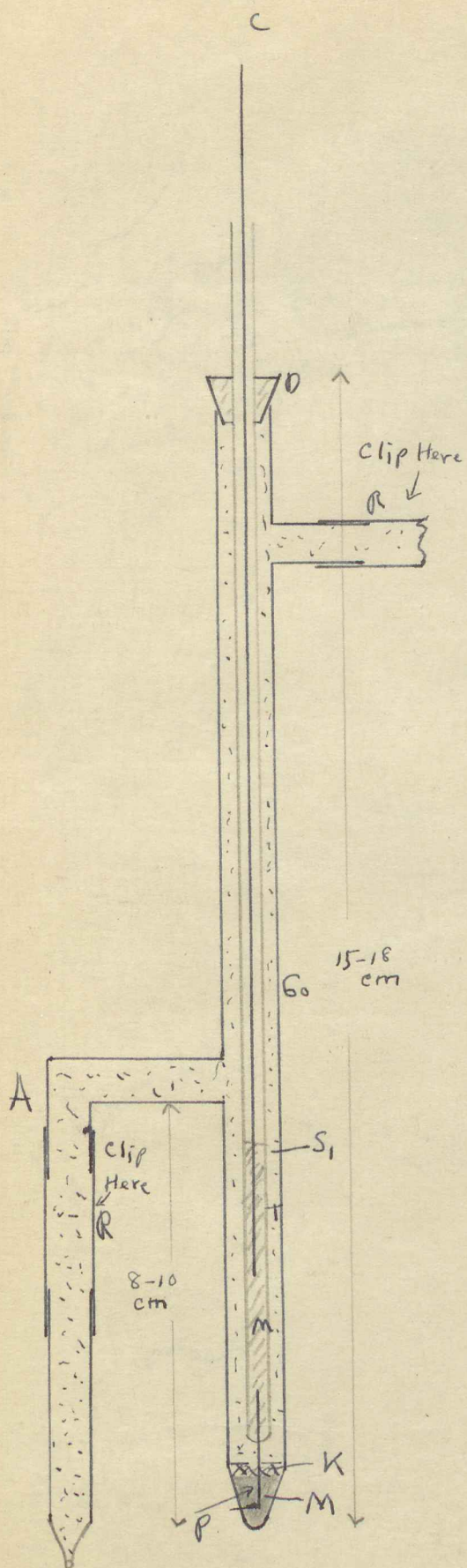


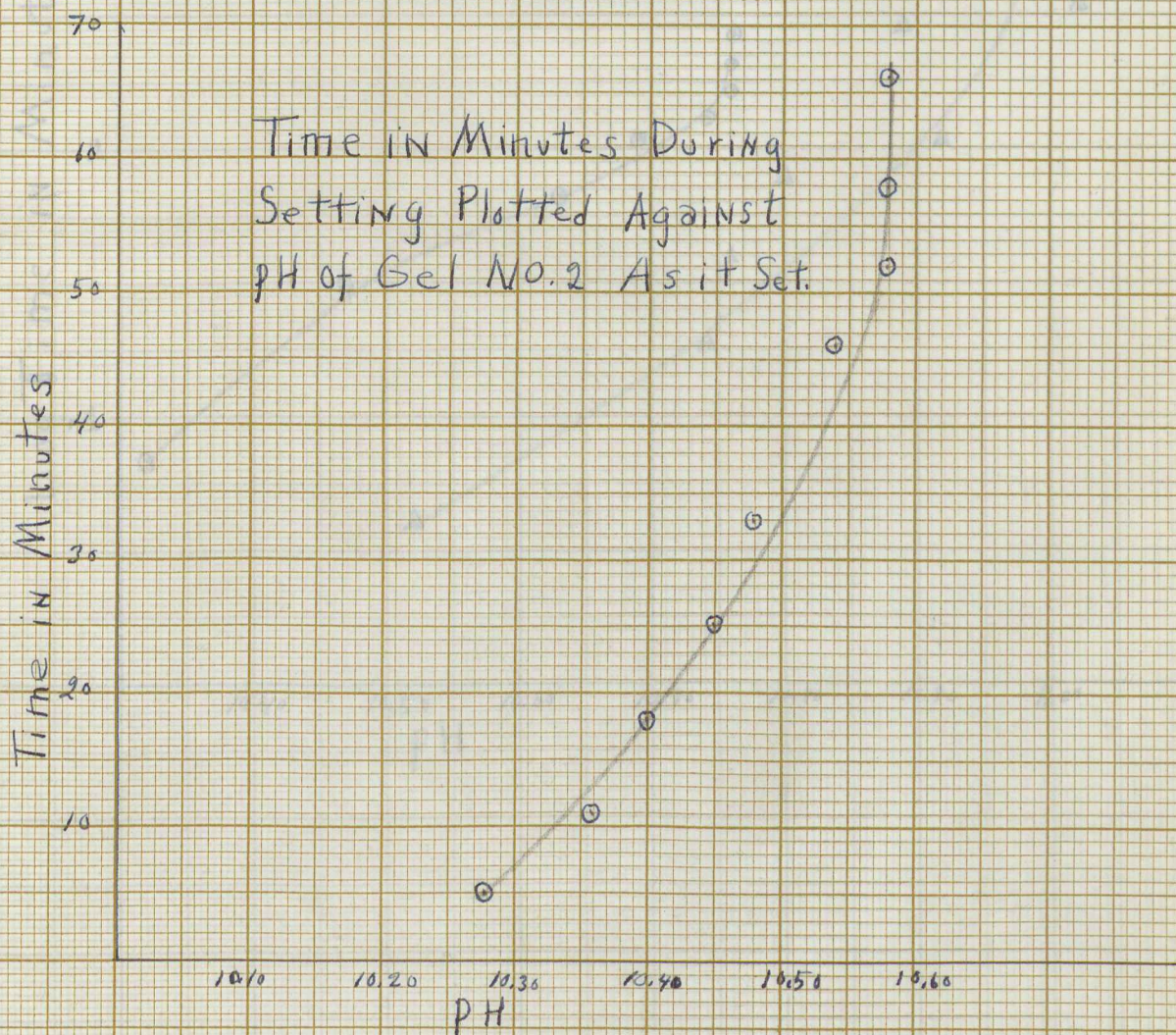
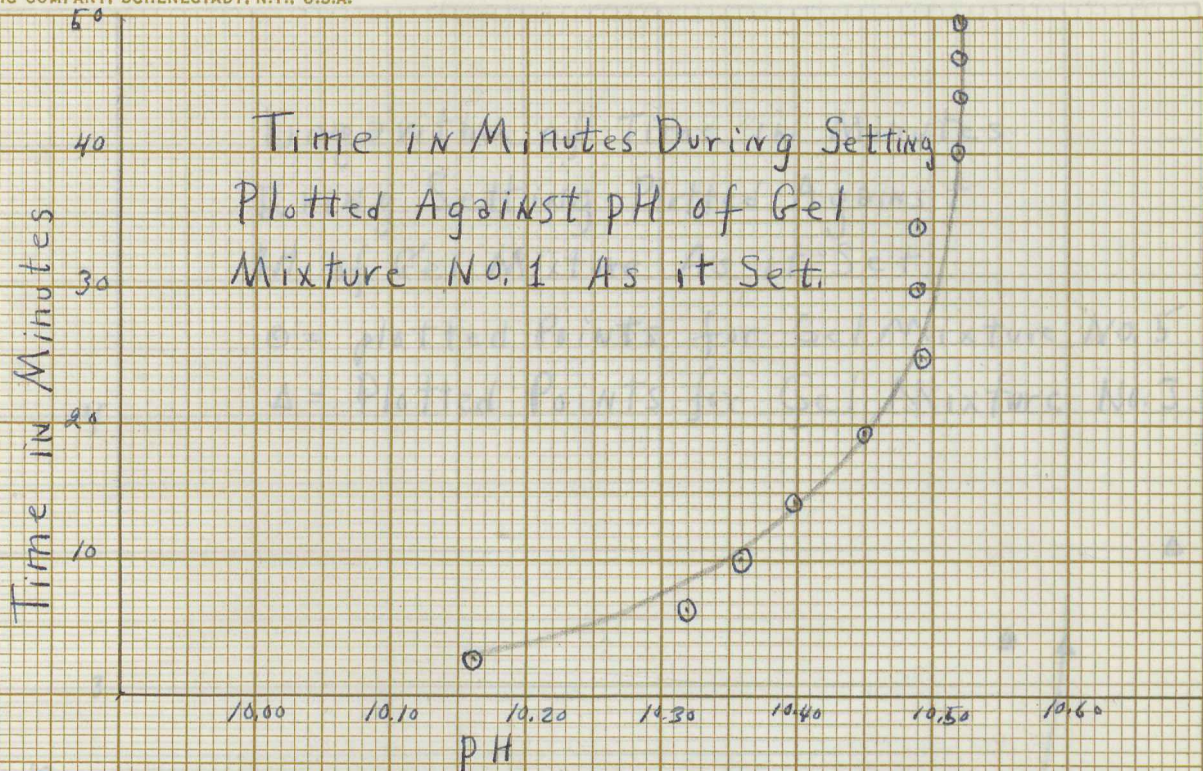
Diagram C



- C Cooper Wire
- M Mercury
- T 3 mm. Glass Tubing
- P Platinum Wire
- R Rubber Tubing
- K Calomel
- S₁ Saturated KCl Solution
- G₀ 7 mm. Glass Tubing
- G₅ Corning Glass 015
- S₂ 1 N HCl
- A Arm Made With 5 mm. Tubing
- D Paraffined Cork

Note: Clips are used on rubber tubing.

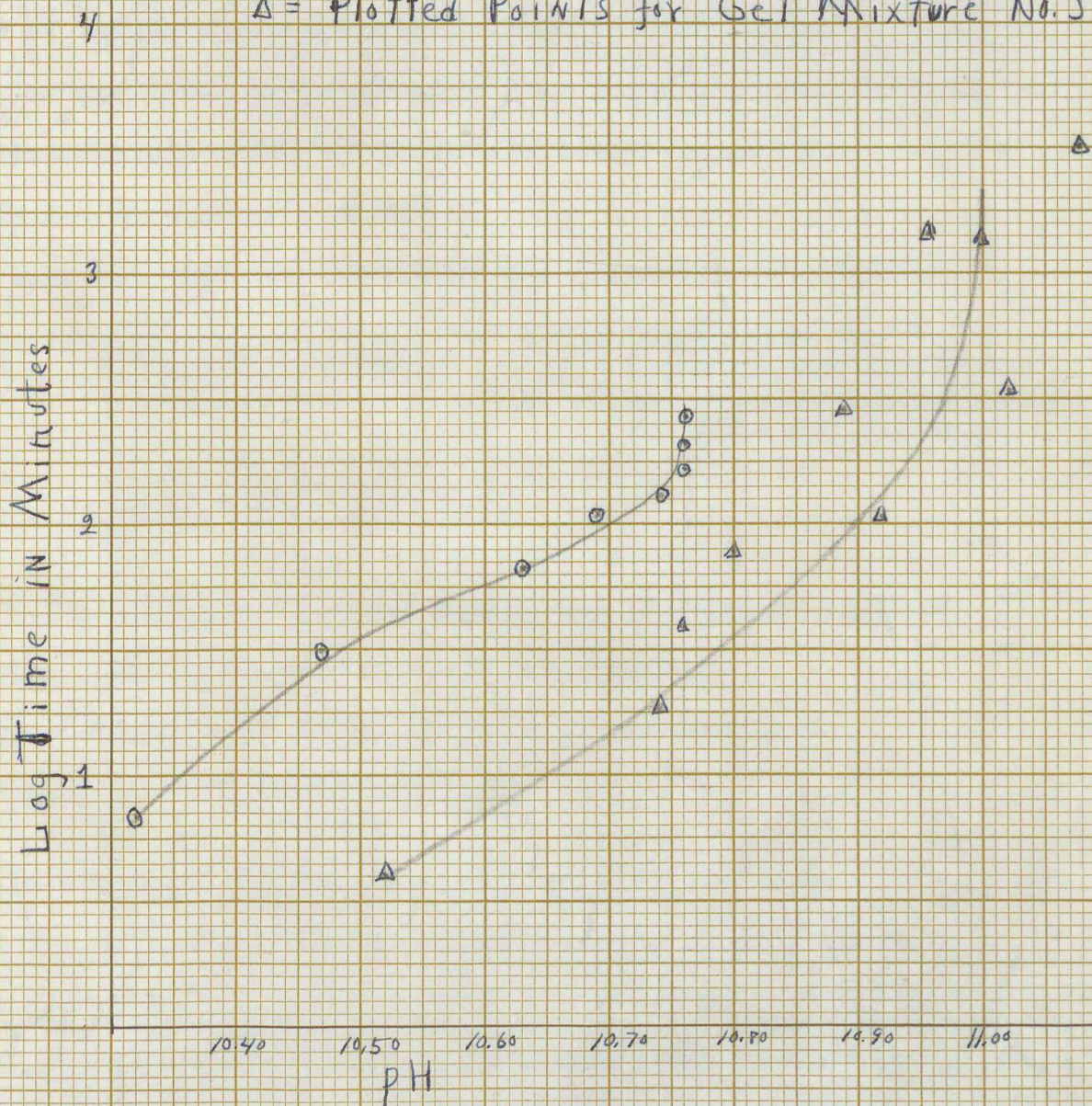
Diagram D



Logarithm of Time in Minutes
During Setting Plotted Against
pH of Gel Mixture As it Set

○ = plotted Points for Gel Mixture No. 5

△ = Plotted Points for Gel Mixture No. 3



DATA AND CALCULATIONS

Buffer solution

Solution contained .05 gram equivalents of sodium hydroxide and .06 gram equivalents of acetic acid per liter.

pH of buffer determined as follows:

Glass electrode and saturated K cl calomel electrode used.

Asymmetry potential of glass electrode = .1 mv.

E.M.F. = -144 mv. at 25° C.

E.M.F. = -145 mv. corrected for asymmetry potential.

$$\text{pH} = \frac{V + .4529 + .00002t}{.00019832 T}$$

t = temperature of solution and electrodes
 T = absolute temperature of solution and electrodes
 V = E.M.F.

pH = 5.23

After a period of 4 weeks buffer was checked as follows:

Using glass electrode 5.18 pH was obtained.

Using quinhydrone electrode 5.12 pH was obtained.

Average pH over period was 5.19.

Calculation of Na^+ ion in solution of gel mixture.

50 cc. of 1.262 N sodium silicate was used to make up a 160 cc. solution.

Let N = normality of 160 cc. solution with respect to Na ion.

$$(50) (1.262) = 160 N$$

$$N = .394$$

Upon the basis of this normality was the pH correction applied to Leeds and Northrup tables.

Gel Mixture No. 1:

50 cc. sodium silicate
36 cc. acetic acid
74 cc. distilled water

pH determinations were made as gel set.

In the following table the variables are as follows:

t = time in minutes after mixing of gel solution, when
pH measurements were made.

mv. = E.M.F. corrected for asymmetry potential of +1mv.

$pH_{(1)}$ = E.M.F. at 25° C.

$pH_{(2)}$ = $pH_{(1)}$ values corrected according to correction
chart (23). Error is approximately constant and amounts to
+.1 pH units to be added to $pH_{(1)}$ values.

Table for Gel No. 1 at 25° C

<u>t</u>	<u>mv.</u>	<u>pH₍₁₎</u>	<u>pH₍₂₎</u>
0			
3	138	10.06	10.16
6.5	146	10.22	10.32
10	148	10.26	10.36
14.5	150	10.30	10.40
19.5	152	10.35	10.45
25	154	10.39	10.49
30	154	10.39	10.49
34.5	154	10.39	10.49
40	155	10.42	10.52
44	155	10.42	10.52
45	155	10.42	10.52
50	155	10.42	10.52

Time of set = 45 minutes.

Gel heated to 80°- 100° C for period of two hours gave no
indication of melting.

Electrode system gave -144 mv. in buffer before and after
use in gel.

Electrode system in gel at 40° C gave 175 mv.

pH = 10.20 at 40° C, uncorrected for N_a ion.

Gel No. 2

Gel mixture No. 2:

50 cc. sodium silicate
34 cc. acetic acid solution
76 cc. distilled water

In table No. 2, t, mv., pH₍₁₎, pH₍₂₎, have same meaning as in table No. 1.

Table No. 2 for Gel at 25° C

<u>t</u> <u>in min.</u>	<u>mv.</u>	<u>pH</u> ₍₁₎	<u>pH</u> ₍₂₎
0			
5	144	10.18	10.28
11	148	10.26	10.36
18	150	10.30	10.40
25	152	10.35	10.45
33	153	10.38	10.48
46	156	10.44	10.54
52	158	10.48	10.58
58	158	10.48	10.58
66	158	10.48	10.58

Time of set = 52 minutes.

Gel heated to 90° - 100° C for period of two hours gave no indication of melting.

Electrode system gave 177 mv. in gel at 40° C. pH = 10.24 uncorrected for N_a ion.

Class electrode system checked in buffer before and after use in gel.

Gel No. 3

Gel mixture No. 3:

50 cc. sodium silicate solution
28 cc. acetic acid solution
82 cc. distilled water

In the following table, row headings are as follows:

t = time in minutes after mixing of gel solution when pH measurements were made.

$mv(1)$ = E.M.F. of electrode system in gel solution.

$mv(2)$ = E.M.F. of electrode system in buffer solution.

$mv(3)$ = correction value to be added to mv_1 . The correction is made on basis that, if the glass electrode operated as it should, the mv. reading in buffer at $25^\circ C$ would be -147.

$mv(4)$ = corrected mv_1 values.

$pH(1)$ is as taken from Leeds and Northrup tables.

$pH(2)$ is correction applied to above tables.

$pH(3)$ = pH_1 values as corrected by adding $pH(2)$ to $pH(1)$ values.

Table for Gel mixture No. 3 at $25^\circ C$

<u>t</u> <u>min.</u>	<u>log t</u>	<u>mv₁</u>	<u>mv₂</u>	<u>mv₃</u>	<u>mv₄</u>	<u>pH(1)</u>	<u>pH(2)</u>	<u>pH(3)</u>
0								
4	.602	162	-140	-7	155	10.42	+.1	10.52
19	1.279	169	-143	-4	165	10.62	.1	10.74
39	1.591	170	-143	-4	166	10.66	.1	10.76
77	1.886	173	-142	-5	168	10.70	.1	10.80
111	2.045	175	-144	-3	172	10.80	.12	10.92
295	2.470	176	-142	-5	171	10.77	.12	10.89
249	2.543	180	-142	-5	175	10.87	.15	11.02
1380	3.140	182	-141	-6	174	10.85	.15	11.00
1485	3.172	178	-142	-5	173	10.82	.14	10.96
1725	3.236							
3172	3.501	183	-142	-5	178	10.92	.16	10.96

Time of set = 1725 minutes.

Gel heated to $80^\circ - 100^\circ C$ for a period of two hours gave no indication of melting.

Gel cooled to $0^\circ C$ for same period of time also showed no tendency to melt.

Electrode system in gel at 40° C gave 192 mv. after being corrected on basis of electrode system giving -142 mv. in buffer. pH = 10.44., uncorrected for Na ion.

Electrode system in gel at 3° C gave 159 mv. after being corrected.

pH = 11.72 uncorrected for Na ion.

Gel No. 4

Gel mixture No. 4:

50 cc. sodium silicate solution
26 cc. acetic acid solution
84 cc. distilled water

Table headings have same meaning as in table No. 3.

Table No. 4 25° C

<u>t</u>	<u>mv</u> ₁	<u>mv</u> ₂	<u>mv</u> ₃	<u>mv</u> ₄	<u>pH</u> ₁	<u>pH</u> ₂	<u>pH</u> ₃
0							
14	167	-142	-5	162	10.55	.1	10.65
2827	186	-138	-9	177	10.92	.16	11.08
3390	182	-141	-6	176	10.90	.16	11.06

Time of set = 3180 minutes.

Gel heated to 80° - 100° C for a period of 4 hours gave no indication of melting.

Gel at 0° C for 8 hours showed no indication of melting.

Gel at 40° C

mv. = 184 + 1 mv.

pH = 10.38 uncorrected for Na ion.

Gel at 0° C

mv. = 143 + 3 mv.

pH = 11.36 uncorrected for Na ion.

Gel No. 5

Gel Mixture No. 5:

50 cc. sodium silicate solution
33 cc. acetic acid solution
77 cc. distilled water

Table headings have same meaning as in table No. 3.

Table No. 5 25° C

<u>t</u>	<u>log t</u>	<u>mv₁</u>	<u>mv₂</u>	<u>mv₃</u>	<u>mv₄</u>	<u>pH₁</u>	<u>pH₂</u>	<u>pH₃</u>
0								
7	.845	144	-149	2	146	10.22	.1	10.32
31.5	1.50	151	-149	2	153	10.37	.1	10.47
67.5	1.83	157	-150	3	160	10.53	.1	10.63
111	2.05	160	-150	3	163	10.59	.1	10.69
138	2.13	161	-151	4	165	10.64	.1	10.74
172	2.23	162	-151	4	166	10.66	.1	10.76
213	2.33	162	-151	4	166	10.66	.1	10.76
278	2.44	162	-151	4	166	10.66	.1	10.76

Time of set = 276 minutes.

No indication of gel melting either when heated for 2 hours at 80°- 100° C or when cooled to 0° C for 2 hours.

Gel at 40° C

mv = 179 + 1 mv.

corrected mv = 183

pH = 10.36 uncorrected for N_a ion.

Gel at 2° C

mv = 144 + 4 = 148

pH = 11.38 uncorrected for N_a ion.

BIBLIOGRAPHY

1. Pomatti, Thesis, Union College
2. Hurd, C.B., Chemical Reviews, Vol. 22, No. 3, 403 (1938)
3. Berzelius, J., Ann. chim. phys. (2) 14, 363 (1820)
4. Graham, T., Ann. Physik. 190, 187 (1861)
5. Hurd and Letterton, J. Phys. Chem. 36, 604 (1932)
6. Maschke, O., Ann. Physik, 222, 90 (1872)
7. Holmes, H.N., J. Phys. Chem., 22, 510 (1918)
8. Ostwald, W., Kolloid Z - 46, 248 (1928)
9. Ostwald, W. and Fisher, M.H., An Introduction to Theoretical and Applied Colloid Chemistry, p. 102. John Wiley and Sons, New York, 1917.
10. Hatschek, E. Trans. Faraday, Soc. 12, 17 (1916)
11. Butschli, O., Untersuchungen über Strukturen, Leipzig (1898)
12. Hurd, C.B. and Swanker, H.J., J. Am. Chem. Soc. 55, 2607 (1933)
13. Nägeli, K. von, Pflanzen Physiologischen Untersuchungen. Zurich (1858)
14. Pappada, N., and Sadowsky, C. Kolloid -- Z. 6 292 (1910)
15. Jordis, E., Z. anorg. Chem. 44, 200 (1905)
16. Hurd, C.B., Fiedler W., and Raymond, C.L., Journal Phys. Chem. 41, 553 (1937)
17. Schiller, H., Ann. Physik, 74, 105 (1924)
18. Lengyel, B., Z. Physik Chem. 154, 371 (1931)
19. Hangaard, G.Z. physick Chem. 160, 279 (1932)
20. Haber, F., and Klemensiewicz, Z. Ibid. 67, 385 (1909)
21. Cremer, M., Z. Biol. 47, 562 (1906)
22. Dole, M., J. Am. Chem. Soc. 53, 4260 (1931)

BIBLIOGRAPHY (cont.)

23. Gardiner and Sanders, Eng. Chem. Anal. Ed. 9, 274, 8 (1937)
24. Leeds and Northrup Company, Notes on Hydrogen Ion Measurements (Note Book No. 3, 1931)
25. Leeds and Northrup, Standard Conversion Tables, Standard Part, 1074
26. Jordan, D.O., Trans. Faraday Soc. 34, 1305, 10 (1938)
27. Jordan and Powney, J. Soc. Chem. Ind., 56, 133, 7T (1937)
28. Dole and Wiener, Trans., Electrochem. Soc. 72, 21 pp. (preprin. 1937) cf. C. A. 29, 666