

CHANGE OF CONDUCTIVITY OF SILICIC ACID GELS UPON SETTING

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## CHANGE OF CONDUCTIVITY OF SILICIC ACID GELS UPON SETTING

### Introduction

The problem of how the electrical conductivity of colloidal sols changes during setting has been a source of much speculation for a long time. Work has been done upon a variety of sols and gels with various and oftentimes conflicting results.

The purpose of this investigation was to find out whether the conductivity of a silicic acid sol changes during setting or not; and, if so, how it varies. It was also hoped that the results might lead definitely to some theory of gelation and gel structure.

### Historical

The interference offered by the colloidal formation to the passage of ions is in every case of much lower order than would be expected from consideration of viscosity. Graham<sup>1</sup>, 1850, found that gelation had no appreciable effect upon electrical conductivity. Arrhenius<sup>2</sup>, in 1887, obtained a similar result with a system composed of gelatin, water, and salt.

Much later, in 1920, Laing and McBain<sup>3</sup> worked on a system composed of soap and water. They also found that, when properly thermostated, the conductivities in the sol and gel were the same for equal soap concentrations. In 1924, Martin Fischer<sup>4</sup> found the conductivity of soap solutions to decrease at and below the temperature of gelation.

Also in 1924, Hatschek and Humphrey<sup>5</sup> carried out an extensive piece of research dealing with a water-gel-salt system

similar to that of Arrhenius. They noted that in this case the conducting ion came from the salt, not the gel forming material. The electrical conductivity of copper sulfate was measured in the presence of agar at such a temperature, 50° C., that both gel and sol were present. Their results, however, contradicted Arrhenius' for this type of system, and showed the conductivity of copper sulfate to be different in the agar gel and the agar sol at the same temperature. In fact, conductivity in the gel was as much as 2% higher than in the sol at the same concentration and temperature, for both direct and alternating current.

Hatschek and Humphrey interpreted their results as showing that the migrating ions traveled only in the liquid phase of the gel. In the gel the viscosity of the liquid phase was less than in the sol due to presence of the solid phase. This would explain the higher conductivity in the gel.

Henry Swanker<sup>6</sup>, in 1932, investigated conductivity of silicic acid gels produced by various concentrations of sodium silicate and acetic acid. His method was to use a capacity-balanced Wheatstone bridge, excited by 1000 cycle current, employing ear phones as a detector. In no case, no matter how firm a gel was used, did he find any change upon setting.

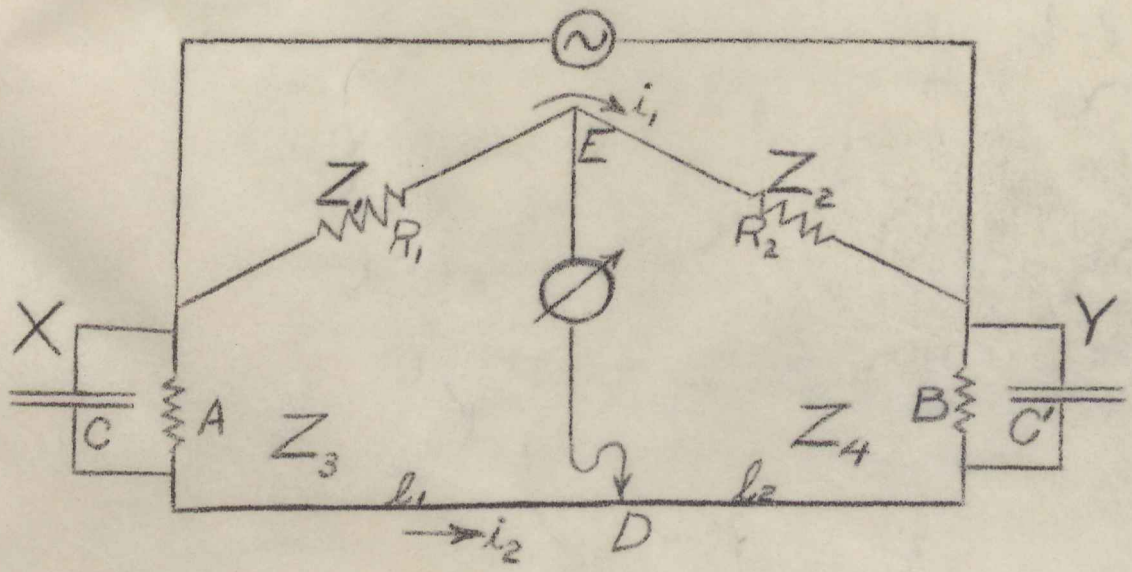
Thus we see that, with two exceptions, no change in conductivity upon gelation was found above experimental error. One exception was Fischer's case, in which he found a decrease in conductivity during gelation. The other was the result of Hatschek and Humphrey, showing higher conductivity in the gel than in the sol.

Theory

In view of the fact that all previous investigators found little or no change in conductivity, and since it seemed incredible that such transformation could take place in a substance without some change, however slight, the first problem was to discover, if possible, some method for measuring very minute variations in resistance.

It was known that G. Carey Foster found a very accurate method of determining the difference between two resistances by use of what is known as the Carey Foster bridge, but this applied only to direct current, and balance conditions always involved capacity and frequency for alternating current. Much labor was spent in attempting to find, by application of complex impedances, some bridge which would balance independent of frequency and capacity, and still give results of high accuracy.

Finally acting upon a suggestion of Dr. Wold, the following development was worked out applying Foster's original idea to an alternating current bridge involving capacity.



is constant for the slide wire.

Using complex quantity notation, we divide the network up into four parts as indicated by Zs.

Potential drops through Z<sub>1</sub> and Z<sub>3</sub> are equal, since D and E are at the same potential, as indicated by the zero reading of the detector. Similarly for Z<sub>2</sub> and Z<sub>4</sub>. Since the potential drop equals the product of complex current and impedance:

$$i_1 Z_1 = i_2 Z_3$$

$$\text{and } i_1 Z_2 = i_2 Z_4$$

$$\text{Dividing: } \frac{Z_1}{Z_2} = \frac{Z_3}{Z_4}$$

This is the general balance condition for the bridge.

Now the complex impedance of a resistance is simply R; that of an inductance  $j\omega L$ ; and that of a capacitance  $\frac{1}{j\omega C}$ , where  $\omega$  is equal to the frequency multiplied by  $2\pi$ , and  $j$  is the  $\sqrt{-1}$ . Also, impedances in combination are treated similarly to resistances in direct current theory. That is, the impedance of two quantities in series is the sum of the individual impedances; and the reciprocal of the impedance of two in parallel is the sum of the reciprocals.

$$\text{Thus: } Z_1 = R_1 \text{ and } Z_2 = R_2$$

Let X = impedance of A and C in parallel

$$\text{Then: } \frac{1}{X} = \frac{1}{\frac{1}{j\omega C}} + \frac{1}{A}$$

$$\text{or } X = \frac{A}{j\omega AC + 1}$$

$$Z_3 = X + e^{l_1} = \frac{A}{j\omega AC + 1} + e^{l_1}$$

$$\text{Similarly } Z_4 = Y + e^{l_2} = \frac{B}{j\omega BC + 1} + e^{l_2}$$

$$\text{where } Y = \frac{B}{j\omega BC + 1}$$

From balance condition  $\frac{Z_1}{Z_2} = \frac{Z_3}{Z_4}$

$$\frac{R_1}{R_2} = \frac{X + e l_1}{Y + e l_2} = \frac{\frac{A}{j\omega AC + 1} + e l_1}{\frac{B}{j\omega BC' + 1} + e l_2}$$

Now exchanging systems X and Y, and rebalancing:

$$\frac{R_1}{R_2} = \frac{Y + e l_1'}{X + e l_2'}$$

Equating:  $\frac{X + e l_1}{Y + e l_2} = \frac{Y + e l_1'}{X + e l_2'}$

Adding 1 to both sides:

$$\frac{X + Y + e l_1 + e l_2}{Y + e l_2} = \frac{X + Y + e l_1' + e l_2'}{X + e l_2'}$$

But  $l_1 + l_2 = l_1' + l_2' = L$

Since numerators are equal, denominators must be equal:

$$Y + e l_2 = X + e l_2'$$

$$Y - X = e(l_2' - l_2) = e(l_1 - l_1')$$

Substituting for X and Y:

$$\frac{B}{j\omega BC' + 1} - \frac{A}{j\omega AC + 1} = e(l_1 - l_1')$$

This is the particular balance condition. The ratio arms  $R_1$  and  $R_2$  are not involved; and had we introduced them, we would have found that all contact resistances would have dropped out. We notice that if  $j\omega BC'$  and  $j\omega AC$  were negligible with respect to one, we would have the desired condition:

$$B - A = e(l_1 - l_1')$$

indicating that the difference between the resistances A and B is equal to the wire constant multiplied by the difference in slide setting.

It should also be stated here that for greatest sensitivity of bridge, resistances A, B,  $R_1$ , and  $R_2$  should be approximately equal.

#### Apparatus

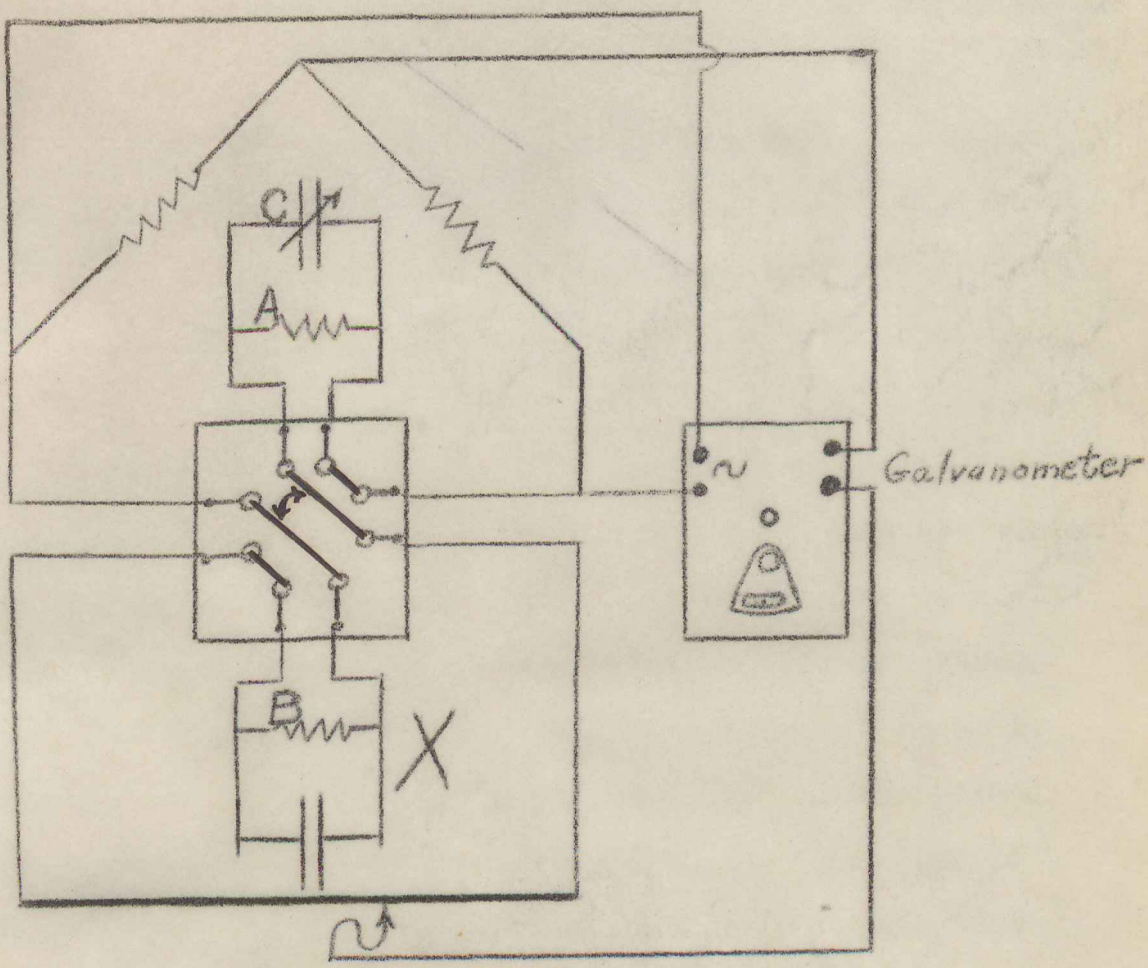
Whether the above mentioned terms actually are negligible or not depends mainly upon frequency and capacity. For this reason, it was decided to try a frequency of 60 cycles, in conjunction with a cell whose electrodes were quite far apart.

A preliminary bridge of the Wheatstone type was set up, with facilities for switching immediately from 1000 cycles with phone detector to 60 cycles with alternating current galvanometer. Capacities at the two frequencies were very easily studied and compared, although data could not be used directly in subsequent work, because at this point a simple dip cell in acid solution was used. At 1000 cycles a large condenser was needed in the opposite arm of the bridge to balance the capacity of the cell; also a relatively small change in this condenser gave a noticeably different balance point on the slide wire. At 60 cycles, however, using the more sensitive detector, the capacity could be varied over a very wide range with no detectable change in balance point. The capacity of this cell, which from dimensions should have been much greater than that of the cell used later, seemed to be about .001 microfarad. This would make the  $\omega AC$  term for 60 cycles and 100 ohms =  $2\pi(60)(100)(.001 \times 10^{-6}) = 3.5 \times 10^{-5}$ , which is quite negligible as compared to one. These considerations were taken as evidence that the capacity effects at the lower frequency were of such a low order, that there was a possibility of using the above discussed bridge to good effect.

In view of this fact, it was decided to proceed in the direction indicated - namely, to set up the new bridge. A very important member which had to be constructed was a set of mercury contact switches for exchanging the two systems as already described. The stipulations on these were that they must give constant resistance, preferably low, and that they must operate easily and quickly. Eight holes were drilled for mercury cups in the form of an octagon in the center of a thick block of bakelite. Each of these was connected to a binding post and by a stirrup to some other cup. These stirrups, which were first made of nickel and later of copper for better contact, were mounted on a small piece of bakelite so that by lifting up, turning through one quarter revolution, and inserting again, the systems were exchanged. With the copper contacts, drum readings could be duplicated to at least one tenth of a division, which corresponds to .0032 ohms.

Power was supplied to the bridge at 15 volts from the galvanometer box which, in turn, was excited by 110 volts. A one to one transformer was introduced between the galvanometer and the line, obviating the grounding of certain points of the apparatus. The slide wire was of the drum type, and capable of very accurate readings. The bridge hook-up was as follows:





Where: X represents the conductivity cell.  
A and B are resistances being compared.

It will be noticed that a variable condenser is introduced, apparently to balance the capacity of the cell. As a check upon the validity of the bridge method, this condenser was varied through wide values to see if readings were influenced. Absolutely no change could be detected, and this condenser may be omitted from the apparatus.

Since the expected change in resistance was very small, and since the conductivity of solutions changes relatively fast with

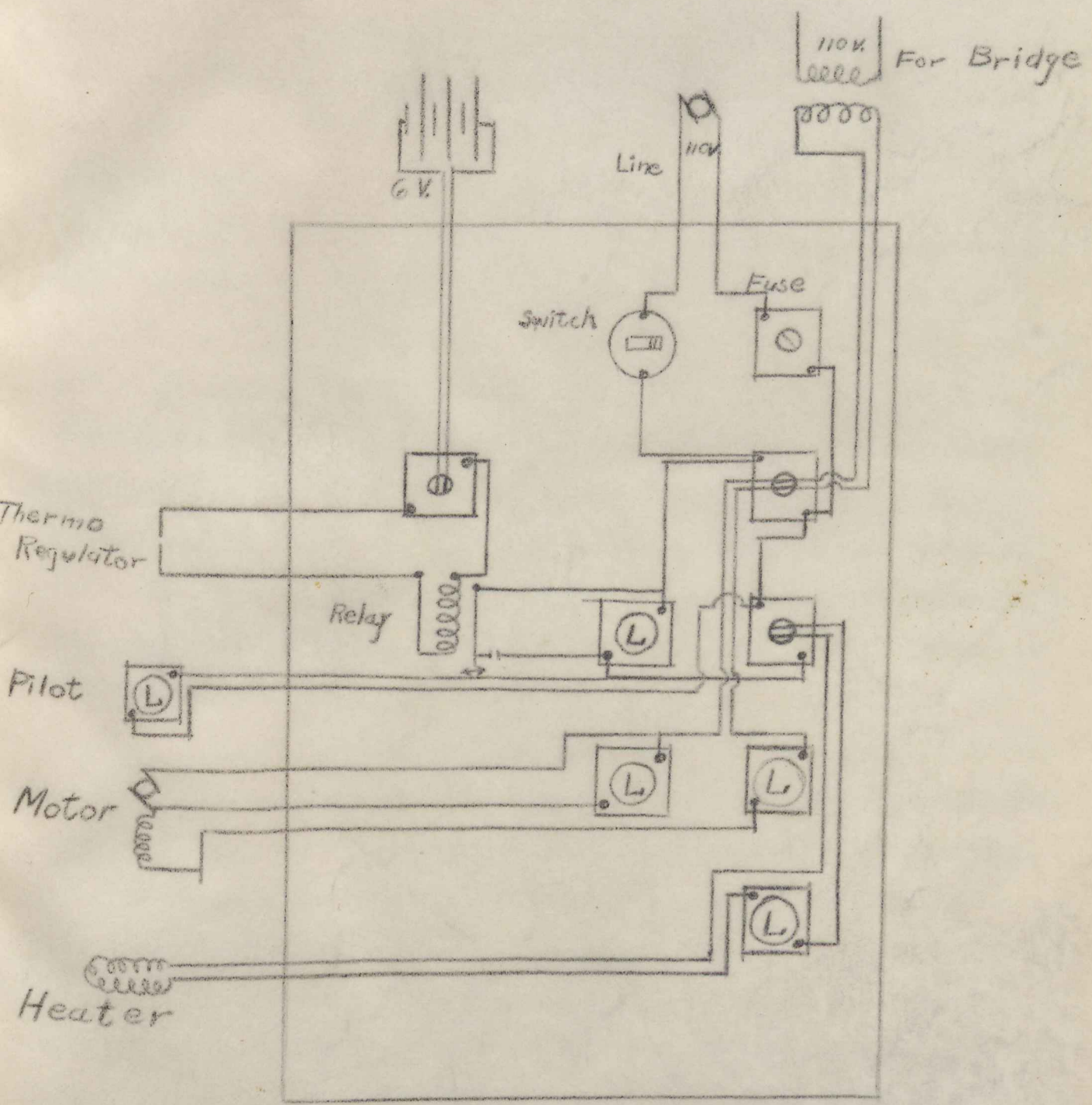
temperature, the need of a very accurately thermostated bath was anticipated in order that changes observed might be great as compared with the experimental error.

The tank was made deep with small exposed surface, so that the heat losses to the atmosphere might be minimized. It also was constructed in a rounded-square form, so that a maximum of working space could be had without impairing the stirring qualities of a round tank.

The thermoregulator was of the toluene-mercury type, and was blown with an especially large toluene chamber so that the contact would operate upon the slightest variation of temperature. A platinum wire, making contact with the mercury in the capillary, caused the 6-volt battery to operate the relay and open the heat circuit.

Resistances in the form of lamps were used in the wiring. In order to decrease the speed of the stirring motor, one lamp was put in parallel with the armature, and another in series with the field. A lamp was introduced across the relay contacts to prevent sparking. The 125-watt heater was found to heat the bath so quickly that a lamp was put in series with it so that it would remain on for a reasonable period of the cycle, thus holding a more even temperature.

The following is the electrical diagram of the thermostat:



Thermostat Wiring Diagram

As measured by a Beckmann thermometer the thermostat held the temperature to a maximum variation of  $.005^{\circ}$  C. over the working region, and to a variation of about  $.002^{\circ}$  C. for any specific point. The fact that an accuracy of approximately this order was needed is indicated by the following experiment. In the middle of a run the heater was turned off for a short time, whereupon the readings shifted. However, after turning on the heater the readings returned to normal, although no variation in temperature could be detected on a 1100 thermometer during this whole time.

The conductivity cell was of special design in order that the electrodes might be removed for cleaning and still remain in constant relation to each other. The body of the cell was simply a large tube closed at one end, and fitted at the other with a ground stopper. Sealed into this stopper were two tubes carrying the conducting wires and terminating in the platinum electrodes. The electrodes were made in triangular shape so that they might be easily withdrawn from the gel.

#### Experimental

The silicic acid gels were made by mixing sodium silicate and acetic acid of various concentrations. The silicate used was the "E" brand of ratio  $\text{Na}_2\text{O}:3.25\text{SiO}_2$ . The amounts of acid and silicate to be mixed were put in separate beakers, and an amount of water added - approximately half to each beaker - so that the total amount of solution after mixing would be 325 cc. Now the silicate was poured into the acid, and the solution mixed well by pouring back and forth several times. The cell was filled to a certain line, well above the electrodes, with this mixture, and set in the thermostated bath. Contact was made by inserting the

amalgamated copper wires from the electrodes into the mercury cups which were connected to the bridge.

After closing the switches, the comparison resistance was adjusted so as to equal, as nearly as possible, that of the cell. This was done by working for the smallest galvanometer deflection when contact was at the middle of the slide wire. Once adjusted, this resistance was not changed during the run.

A drum reading was taken for one adjustment of the mercury contacts, and again after switching them. The difference in these drum readings multiplied by the wire constant gives the difference in resistance between the cell and the calibrated comparison resistance box. Thus we see if the box resistance remains constant, the difference in resistance at each reading subtracted from the original difference equals the change in resistance of the cell.

The switch exciting the bridge was left closed throughout a run for the following reason. If the switch were opened after a reading, the next reading, taken immediately upon closure of the switch, would be in error to the value obtained if a few minutes were allowed to elapse between closing the switch and the adjustment of the slide. It was found, however, that during a short interval of time after the switch was closed the readings approached a constant value which was the same as that obtained if the switch had remained closed all the time. Therefore the switch was closed throughout the run, and adjustments made in this manner were assumed to give the correct reading. The effect just related was possibly due to the time required for a steady state of equilibrium to establish itself in the cell.

Although the plate holding the contact rods of the mercury switch could be lowered into the cups in four positions, two positions 90° apart were chosen and used throughout the investigation. A mark was made on the plate which would be either toward the left or toward the right, but always on the side of the plate facing the observer. When this mark was on the left the contact was denoted as being "toward the left." Thus by turning the bakelite plate 90° counterclockwise, we shift the contacts from "the left" to "the right." Only these positions were used, in order to obtain the same situations of contacts for each reading.

For the manner in which the apparatus was connected in this work, if successive drum readings with contacts "on the left" decreased, the resistance of the cell was decreasing, or the conductivity increasing. Of course the opposite of this statement is true. Also, it will be seen from the theory that if readings with contacts "on the left" decrease, then readings with contacts "on the right" will increase.

It was found that the cell should not be disturbed during a run. If the electrodes were moved through the solution, even if it had not set, a definite change in resistance would be noticed, due to the accuracy of the system.

In future work the cell should be calibrated with M/50 KCl to determine the cell constant and to express the conductivity as specific conductivity. Also, the cell should be checked before each run to insure constancy of the positions of the electrodes.

#### Results

The constant of the slide wire was determined by finding its resistance at certain points throughout its length, and then

taking an average over the section used in the experiments.

<u>Drum Reading</u>	<u>Resistance</u>	<u>Resistance per turn</u>
0	0.00 ohms	-
100 (1 turn)	3.206	3.206 ohms
200	6.415	3.209
300	9.631	3.216
400	12.855	3.224
500	16.085	3.230
600	19.335	3.250
700	22.575	3.240
800	25.805	3.230
900	29.045	3.240
1000	32.285	3.240

Since the drum readings in the experiments varied from about 475 to 525, the value chosen was 3.230 ohms per turn of drum. And since there are 100 divisions per turn, the assumed wire constant is .03230 ohms per division.

The concentrations of the solutions from which mixtures were made are:

Normality of Silicate - 1.2512 N

Normality of Acetic Acid - 2.0241 N

Temperature of thermostat bath - 25.0° C.

The case given below is an example to show how data was assembled and arranged:

#### Run A

##### Nickel Contacts

Mixture: 100 cc. Silicate; 100 cc. Acetic Acid; 325 cc. Total Solution; .624 N with acetic acid; .385 N with silicate.

Resistance in comparison box - 116 ohms.

Since the cell is higher than this by 1.5 divisions (the extrapolated value at mixing), the actual resistance of the cell at mixing =  $116 + 1.5 (.0323) = 116.0485$  ohms. Any change indicated is with respect to this value. This, of course, is not correct to the last place, since the 116 ohms could not be cali-

brated this accurately, but it shows the method.

Table A

<u>Time</u>	<u>Drum Readings</u>		<u>Difference</u>	<u>Change from initial difference</u>	<u>Change in R</u>
	<u>on Left</u>	<u>on Right</u>			
0 min.	-	-	1.5 (extrapolated)	0 divisions	0 ohms
4	504.2	501.6	2.6	-1.1	-.035
6	505.4	501.2	4.2	-2.7	-.087
8	505.3	500.6	4.7	-3.2	-.103
14	505.7	500.1	5.6	-4.1	-.132
17	505.7	500.6	5.1	-3.6	-.116
21	506.4	500.7	5.7	-4.2	-.136
27	505.6	500.8	4.8	-3.3	-.107
29	504.9	500.5	4.4	-2.9	-.094
31	504.8	500.6	4.2	-2.7	-.087
34	504.5	500.5	4.0	-2.5	-.081
37	504.5	500.6	3.9	-2.4	-.077
43	504.3	501.4	2.9	-1.4	-.045
49	503.9	501.4	2.5	-1.0	-.032
54	504.0	502.5	1.5	.0	.00
60	503.8	502.3	1.5	.0	.00
64	503.6	501.6	2.0	-.5	.016
69	503.8	501.7	2.1	-.6	.019
74	502.7	503.6	-.9	2.4	.077
79	501.9	504.5	-2.6	4.1	.132
84	501.4	505.3	-3.9	5.4	.174
87	502.1	505.1	-3.0	4.5	.145
88½ Set	501.6	504.8	-3.2	4.7	.151
92	502.8	505.2	-3.0	4.5	.145
99	501.3	505.0	-3.7	5.2	.168
101	501.7	505.1	-3.4	4.9	.158
107	501.0	505.0	-4.0	5.5	.177
114	500.5	504.3	-3.8	5.3	.171
121	502.0	505.9	-3.9	5.4	.174
139	500.3	505.7	-5.4	6.9	.222

The values in the last column seem to vary a great deal from reading to reading, and the question might be asked how anything but a general trend could be indicated by them. Our instruments seem to read to an accuracy which is not warranted by the physical facts in the case. However, although this was a problem for some time, the difficulty was found to be in the unreliable resistance of the nickel contacts. Later, copper was substituted which amalgamated to give perfect contacts, and much steadier readings were obtained.



It will be noted that the resistance of the cell increased during the first six readings before starting its general downward curve. This is because the cell had not yet reached the temperature of the bath. Thus we see it takes about twenty minutes for the cell to assume exactly the temperature of the water surrounding it.

The negative values above indicate that the resistance of the cell was greater at those points than at mixing. Positive values indicate a resistance less than at mixing. Thus, omitting the first temperature effect already considered, we see that the cell resistance decreases from a value  $116.0485 - .136$  at 21 minutes to  $116.0485 - .222$  at 139 minutes, a change of .358 ohms between these times.

#### Run B

##### Nickel Contacts

Mixture: 100 cc. of Silicate; 75 cc. Acetic Acid; 325 cc. Total Solution; .468 N with acetic acid; .385 N with silicate.

Resistance in comparison box - 115 ohms

Resistance of cell at mixing =  $115 - 12 (.0323) = 114.612$  ohms

Total change in resistance .365 ohms, which probably includes the change due to temperature adjustment at the beginning, since we see resistance decreased comparatively quickly there.

Some points obtained in the experiment after time of set are omitted from the table for the sake of brevity.

Table B

<u>Time</u>	<u>Difference in drum readings</u>	<u>Change from initial reading</u>	<u>Change in R</u>
0 min.	12.0 divisions (extrapolated)	0	0
4	17.3	5.3	.171
9	25.9	13.9	.449
15	27.8	15.8	.510
20	30.7	18.7	.604
24	28.0	16.0	.517
26	28.0	16.0	.517
27 Set			
29	29.1	17.1	.553
35	31.5	19.5	.630
42	32.2	20.2	.654
49	34.3	22.3	.720
57	34.3	22.3	.720
68	36.6	24.6	.795
73	38.2	26.2	.845
84	36.7	24.7	.799
104	38.8	26.8	.865

Run C

## Copper Contacts

Mixture: 100 cc. Silicate; 110 cc. Acetic Acid; 325 cc. Total Solution; .686 N with acetic acid; .385 N with silicate.

Resistance in comparison box - 117 ohms

Resistance of cell at mixing =  $117 - 9.5 (.0323) = 116.693$  ohms

The temperature effect is again very noticeable at the beginning of this run, the resistance increasing for about 11 minutes before decreasing.

Table C

<u>Time</u>	<u>Difference in Drum Readings</u>	<u>Change from Initial Reading</u>	<u>Change in R</u>
0 min.	9.5 (Extrapolated)	0 divisions	0 ohms
8	9.2	-.3	-.010
13	9.2	-.3	-.010
18	10.7	1.2	.039
24	11.9	2.4	.077
28	12.1	2.6	.084
33	12.7	3.2	.103
38	13.0	3.5	.113
43	13.5	4.0	.129
48	13.8	4.3	.139
53	11.7	2.2	.071
63	15.0	5.5	.177
68	14.9	5.4	.174
73	15.8	6.3	.204
78	16.7	7.2	.232
83	17.3	7.8	.252
88	18.1	8.6	.278
93	18.7	9.2	.297
98	19.0	9.5	.307
103	19.3	9.8	.316
108	19.7	10.2	.329
113 Set	19.6	10.1	.326
118	19.8	10.3	.332
124	20.2	10.7	.345
130	20.3	10.8	.349
135	20.4	10.9	.352
145	20.3	10.8	.349
158	21.5	12.0	.388
168	21.4	11.9	.384

Run D

## Copper Contacts

Mixture: 135 cc. Silicate; 135 cc. Acetic Acid; 325 cc. Solution;  
 .841 N with Acetic Acid; .524 N with Silicate;  $P_h = 4.87$

Box Resistance 94 ohms

Actual resistance at mixing 94.000 ohms

Table D

<u>Time</u>	<u>Difference in Drum Readings</u>	<u>Change from Initial Reading</u>	<u>Change in R</u>
0 min.	0 (Extrapolated)	0 divisions	0 ohms
8	9.2	-9.2	-.297
9½	12.2	-12.2	-.394
11	13.6	-13.6	-.439
14	14.8	-14.8	-.478
18½	15.0	-15.0	-.485
24	13.7	-13.7	-.442
28	12.3	-12.3	-.397
33	11.2	-11.2	-.362
40	9.2	-9.2	-.297
42 Set	8.6	-8.6	
45	8.6	-8.6	-.278
50	8.6	-8.6	-.278
56	8.6	-8.6	-.278

Run E

## Copper Contacts

Mixture: 85 cc. of Silicate; 85 cc. of Acetic Acid; 325 cc. of Total Solution; .327 N with Silicate; .530 N with Acetic Acid

Resistance in comparison box - 134 ohms

Extrapolated cell resistance at mixing =  $134 - 8(.0323)$

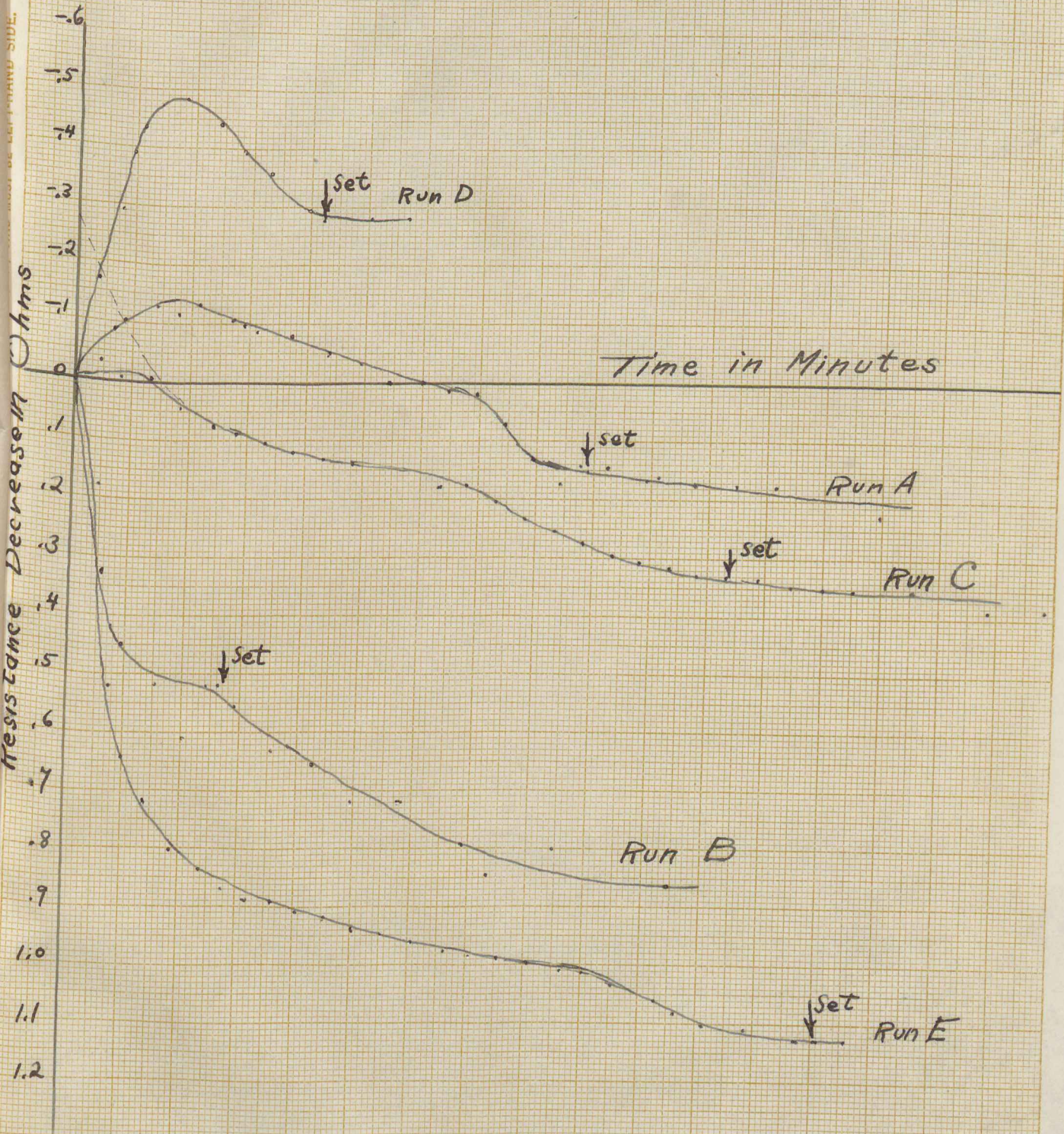
= 133.742 ohms.

Table E

<u>Time</u>	<u>Difference in Drum Readings</u>	<u>Change from Initial Reading</u> 0 divisions	<u>Change in R</u> ohms
0 min.	8.0 (Extrapolated)		
5	18.1	10.1	.326
6 $\frac{1}{2}$	24.1	16.1	.520
9 $\frac{1}{2}$	27.9	19.9	.643
13	30.4	22.4	.723
18	32.8	24.8	.800
23	33.8	25.8	.834
27	34.9	26.9	.869
31	35.4	27.4	.885
35 $\frac{1}{2}$	35.6	27.6	.892
40	36.0	28.0	.905
45	36.3	28.3	.915
50	37.0	29.0	.926
55	37.3	29.3	.946
60	37.8	29.8	.963
65 $\frac{1}{2}$	38.2	30.2	.975
70	38.5	30.5	.985
75	38.6	30.6	.989
80	39.0	31.0	1.000
86	39.3	31.3	1.010
90	39.4	31.4	1.013
95	40.0	32.0	1.033
102	40.8	32.8	1.060
105 $\frac{1}{2}$	41.5	33.5	1.081
110 $\frac{1}{2}$	42.1	34.1	1.100
118	42.4	34.4	1.110
127	42.9	34.9	1.128
130 Set	42.9	34.9	1.128
135	43.1	35.1	1.132

In all of the above cases, the extrapolation performed does not include a correction for temperature change, and does not attempt to give the initial value which would be obtained if the mixture and the bath were at the same temperature at the start.

Although the resistance of the cell sometimes increased and sometimes decreased immediately upon immersion in the bath, this effect is explained entirely in terms of temperature variation. No other explanation need be introduced, especially since the resistance decreased regularly over the rest of the curve.



Graph of Resistance Change

R.W. Barry  
34 ✓

Discussion of Results

From the curves we see that the general effect is one of gradual decrease in resistance, that is, the conductivity increases with the time after mixing. Let us overlook the first irregularities in the curves, which are due to adjustment of the temperature of the cell to that of the bath, and extrapolate back to zero time. Then the general shape of the curve will be as follows:

- A. The resistance decreases sharply at first, as represented by the steep slope, and later seems to level off asymptotically toward a certain resistance for each gel.
- B. The average change in the resistance is about .7% of the total.
- C. Just before setting occurs there is, in most cases, a quicker decrease than in the surrounding portions of the curve.
- D. The gels of higher silicate content set more quickly and undergo a correspondingly more rapid change in conductivity, thus approaching their final state of highest conductivity earlier.
- E. The total conductivity change seems to be more in the cases of gels with lower acid content.

The increase in the conductivity of gels upon setting is accepted as evidence in support of the fibrillar gel structure, and the following mechanism of setting is proposed in explanation.

As the gel sets, the solid matter goes out of solution to form the silicic acid fibers. These form a structure which has a sufficiently open mesh so that ions are not impeded appreciably. However, the conducting medium is made less viscous by the extraction of this solid material, and therefore is capable of more rapid ion migration. If the increase in conductivity due to the decreased

viscosity is greater than the decrease in conductivity due to the gel forming ions extracted from the solution, the net result will be one of increase in conductivity, as observed.

Since a comparatively small amount of solid matter leaves the solution, the viscosity change will be very small, and a small percentage change in conductivity will be the result. This is verified by the small change in resistance obtained in the experiment.

As the gel begins to set, we would expect the fibers to form with increasing rapidity, and to slow up as the structure nears completion. This might explain the more rapid change in conductivity just before setting, and the approaching of an asymptote after setting.

Other theories suggested as possible explanations of the increased conductivity:

Metallic type of conduction on the part of the fibers. As the fibers form, their conductivity adds to the conductivity of the liquid, and the general effect is one of increase in conductivity.

Releasing in solution of certain ions which are not present before setting begins. For instance, a sodium ion might be adsorbed or bound in some manner previous to setting, and be freed in the process of gelation. Thus an ion which previously was not effective, would be allowed to function as a current carrier.

The first theory stated above is probably much closer to the truth than either of the others.



Summary

1. There is a slight increase in the conductivity of silicic acid gels upon setting.
2. The amount of change in conductivity depends upon the concentrations of the components in the gel.
3. The increase in conductivity is explained on the basis of a change in the viscosity of the solution between the gel fibers.

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