

6-1935

Change of Conductivity of Silicic Acid Gels upon Setting

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CHANGE OF CONDUCTIVITY OF SILICIC ACID GELS UPON SETTING

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A thesis, presented to the Department of
Chemistry of Union College, in partial fulfillment of
the requirements for the Degree of Bachelor of Science
in Chemistry, by

Robert Louis Slobod.

Approved by Charles B Hurd

May 18, 1935

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CHANGE OF CONDUCTIVITY OF SILICIC ACID GELS UPON SETTING

Introduction

The investigation of electrical conductivity of gels began in the middle of the last century, the investigators including such notable figures as Arrhenius (1887) and Kohlrausch (1885). The method of investigation followed by them generally involved the use of some modified form of the Wheatstone bridge, and the results they obtained were rather inconclusive, to say the least.

In the course of the investigation that has been conducted at Union College by Prof. Charles B. Hurd and his student assistants, it was soon found that something more accurate than the Wheatstone bridge would have to be used in measuring the electrical conductivity of gels. This becomes evident if we consider that in such studies we encounter the measurement of very small changes in the total resistance, changes of the order of one or two parts in twenty thousand (1 : 20,000). Accordingly, a modification of the Carey Foster bridge was developed for this work.

Apparatus

The apparatus used was substantially the same as developed by R. W. Gurry or as improved by him. (For a detailed description and diagrams of connections see his

thesis "Changes of Conductivity of Silicic Acid Gels upon Setting", submitted to Union College May 19, 1934). It consists principally of an alternating-current Carey Foster bridge involving capacity, and operating on 60 cycles; an a-c. galvanometer; a special type of double-throw reversing switch which gives reproducible results; and an electrolytic cell. The latter is provided with heavy platinum electrodes placed about ten inches apart in order to give a column of length sufficient to provide a resistance of about one hundred ohms.

Since the equivalent conductivity of an electrolytic solution changes about two percent for each degree change in temperature, and since the total change expected is only a fraction of a percent, we see that the temperature control must be very close. A comparatively small thermostat, equipped with a thermo-regulator containing a very large toluene chamber designed to regulate within $.001^{\circ}\text{C.}$, was used. Finally, a Beckmann thermometer was employed to check temperature effects and temperature differences.

Results Obtained at Union College
by Previous Investigators

H. Swanker, who worked on this problem using the Wheatstone bridge method, with an estimated accuracy of .4%, reached the conclusion, previously attained by several other investigators, that the resistance of a gel does not change upon setting.

R. W. Gurry, using the apparatus briefly described above, performed several runs the results of which, although

obscured by temperature effects which he did not have time to take into account, indicated that there were some definite changes in the resistance (or conductivity) of the gel during the time of setting.

Experimental Procedure

In order to obtain some data on the change of resistance upon setting, which would not be the result of too many conflicting physical conditions, we tried to remove, as definitely as possible, the temperature effect. The thermostat and thermo-regulator were adjusted as carefully as possible to give a nearly constant temperature. The heats of reaction of various concentrations were also measured. These heats were used to adjust the temperature of the reactants before mixing, by means of a second thermostat at lower temperature than the first, so that the heat of the reaction would bring the temperature of the silicic acid solution to just 25°C., the temperature of the bath. This procedure was followed throughout the course of the experiments.

A typical run is made as follows: 100 cc of sodium silicate ($N=1.250$) and 60 cc of water are placed in one beaker, and 100 cc of acetic acid ($N=2.000$) with 65 cc of water are placed in another beaker, both of which are placed in a bath at 23.4°C; this is 1.6°C below the temperature of the main thermostat. The temperature of the solutions is followed by the use of a Beckmann thermometer, and when they have reached the temperature of the bath, they are thoroughly mixed and poured into the cell. The time is

recorded, and the readings are taken on the bridge. The two columns of figures refer to the usual double settings which are required when using the type of bridge mentioned above. The notation "on left" and "on right" refer to the direction of the double-throw switch. The readings are taken as soon as possible after mixing of the solutions at the rate of one per minute for the first ten or fifteen minutes, after which readings are taken every five minutes until the gel is well set. In order to follow the course of the run to the best advantage, it is well to place some of the gel mixture in a separate beaker in the bath and use this solution as a means for determining the time of set.

On the pages immediately following are given the data (Table I) and the graph of a typical run of this sort. The procedure outlined above was used for several different concentrations, and since all of the curves followed the same general shape, some showing slightly sharper "breaks" than others, we shall discuss this curve and some of the possible inferences which may be logically derived from this and the following experiments.

This curve of the change in resistance plotted against time, measured in minutes after the mixing of the silicate and acid, can be divided into four sections. In the case of curve 1, the first section represents the initial 15-minute period of the run in which we have an apparently inexplicable large decrease in resistance. This drop in resistance could be explained by an increase in temperature,

Decrease in Resistance in Ohms

Curve I
Change of Resistance
with Time

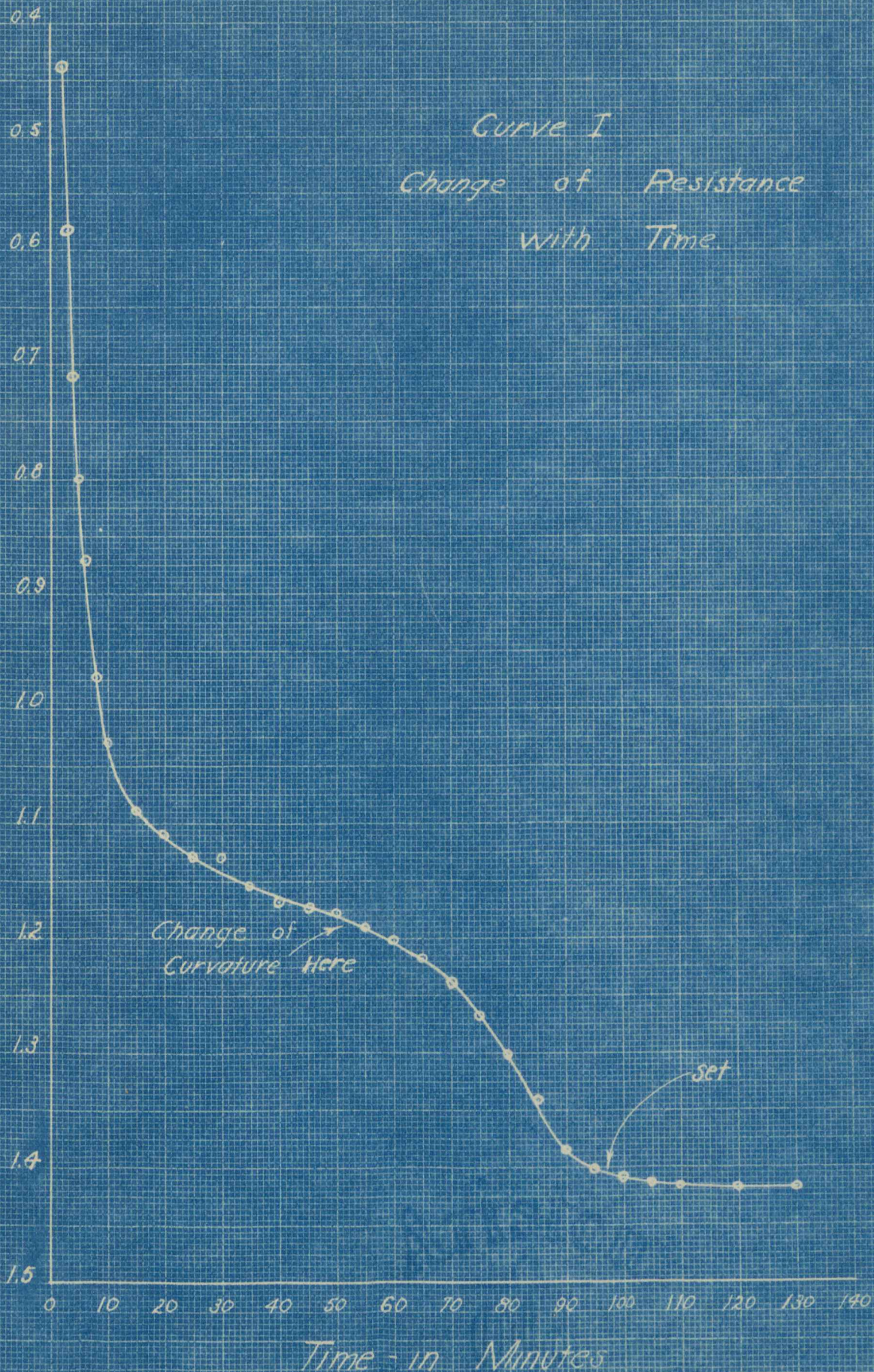


Table No. I

Time	on Left	on Right	Difference	Change from <u>Initial</u> Difference	Decrease in <u>Resistance</u>
0 min.			-43.0 (extrapolated)	.0	0 ohms
1	517.5	482.6	-34.9	8.1	0.259
2	513.8	484.5	-29.3	13.7	0.438
3	512.6	487.8	-24.8	18.2	0.583
4	510.0	489.2	-20.8	22.2	0.711
5	509.0	491.0	-18.0	25.0	0.800
6	507.5	491.7	-15.8	27.2	0.871
8	506.2	493.6	-12.6	30.4	0.973
9	505.3	494.4	-10.9	32.1	1.029
5	504.3	495.3	-9.0	34.0	1.089
0	504.1	495.7	-8.4	34.6	1.109
5	503.7	495.9	-7.8	35.2	1.128
0	503.7	496.0	-7.7	35.3	1.130
5	503.3	496.4	-6.9	36.1	1.154
0	503.1	496.6	-6.5	36.5	1.168
5	503.0	496.7	-6.3	36.7	1.173
0	503.0	496.8	-6.2	36.8	1.178
5	502.8	497.0	-5.8	37.2	1.190
0	502.6	497.2	-5.4	37.6	1.202
5	502.5	497.5	-5.0	38.0	1.217
0	502.1	497.8	-4.3	38.7	1.239
0	501.6	498.2	-3.4	39.6	1.268
5	501.0	498.7	-2.3	40.7	1.302
0	500.4	499.3	-1.1	41.9	1.341
5	499.7	500.0	+0.3	43.3	1.385
0	499.5	500.3	+0.8	43.8	1.402
5	499.4	500.4	+1.0	44.0	1.409
0	499.3	500.5	+1.2	44.2	1.415
0	499.25	500.5	+1.25	44.25	1.417
0	499.25	500.5	+1.25	44.25	1.417
0	499.25	500.5	+1.25	44.25	1.417

Time of set - 97 to 98 minutes.

100 cc of acetic acid #1
 100 cc of sodium silicate #1
 125 cc of water

Temperature of bath-25°C
 Resistance in box-118 ohms
 Temperature difference of
 solutions-1.4°C
 Calculated temperature
 difference-1.7°C

Concentration of Solutions Used

Sodium silicate #1	-	N=1.242
Acetic acid #1	-	N=1.980
Sodium silicate #2	-	N=1.245
Acetic acid #2	-	N=2.043
Tartaric acid #1	-	N=2.078

but extreme care was taken to adjust the temperature of reactants, so that the heat of reaction carried the temperature above 25°C by at least $.1^{\circ}$ or $.2^{\circ}\text{C}$. Since this rapid drop occurred in all runs, of which some had to have the temperature above that of the bath (from the method of mixing), we may safely conclude that this effect is not due to the temperature phenomenon. We may seem to be stressing the temperature effect, but we are justified in doing so, since this effect could have far exceeded the true effect, had we not had careful regulation. Indeed, at each important step of this work the temperature effect was carefully considered.

The large decrease in resistance in the first 10 to 15 minutes, amounting to $.5$ - 1.5 ohms, depending largely on the extrapolation to zero time, is an extraneous factor coming about from possible equilibria which are set up in the cell and at the electrodes, because of the alternating current. We shall give later several experiments that partially explain this change.

The second section of the curve represents the part of the run lasting approximately from the 15th to about the 60th or 65th minute, where the gel seems to be changing in resistance at a comparatively uniform rate. This is a transitory part of the curve located between two sections exhibiting steeper characteristics.

In the third section of the curve (from 65 min. to 98 min.), we find that the absolute value of its slope increases,

the curve again becoming steep and producing a break. In the case of curve 1, this break amounts to slightly less than .2 of an ohm, which break would require a temperature increase of about $.1^{\circ}\text{C}$, had it been produced by a temperature effect; but data were obtained (see graphs below) which show that no such temperature change occurs. Therefore, we must conclude that something of significance is occurring here.

The end of this third part of the curve is marked by a rather abrupt change in slope, which signifies the final setting of the gel. It should be added that it is this part of the curve that corresponds to the time during which the gel mixture changes from a watery solution to a viscous solution undergoing gelation. Then begins the fourth part of the curve, wherein the slope becomes almost zero, showing that after gelation, the resistance changes only slightly with time. The gel continues to decrease in resistance after it has set, and data were obtained which showed that after 24 or even 48 hours, we had a continued decrease, but at a very slow rate, indeed. In the last 22 hours of a 24-hour period the resistance decreases .35 of an ohm.

At this time a few facts should be presented concerning the accuracy of the bridge. The slide-wire resistance was calibrated, its part which was used throughout the experiment showing a resistance of .032 ohms per unit length. The accuracy of individual readings is about .1 of a unit, which means about .0032 ohms. Readings

were consistently reproduced with this accuracy. Any apparent inconsistencies in the value of the results, such as points not falling on smooth curve, can be blamed more on small deviations in the temperature than upon any other factor.

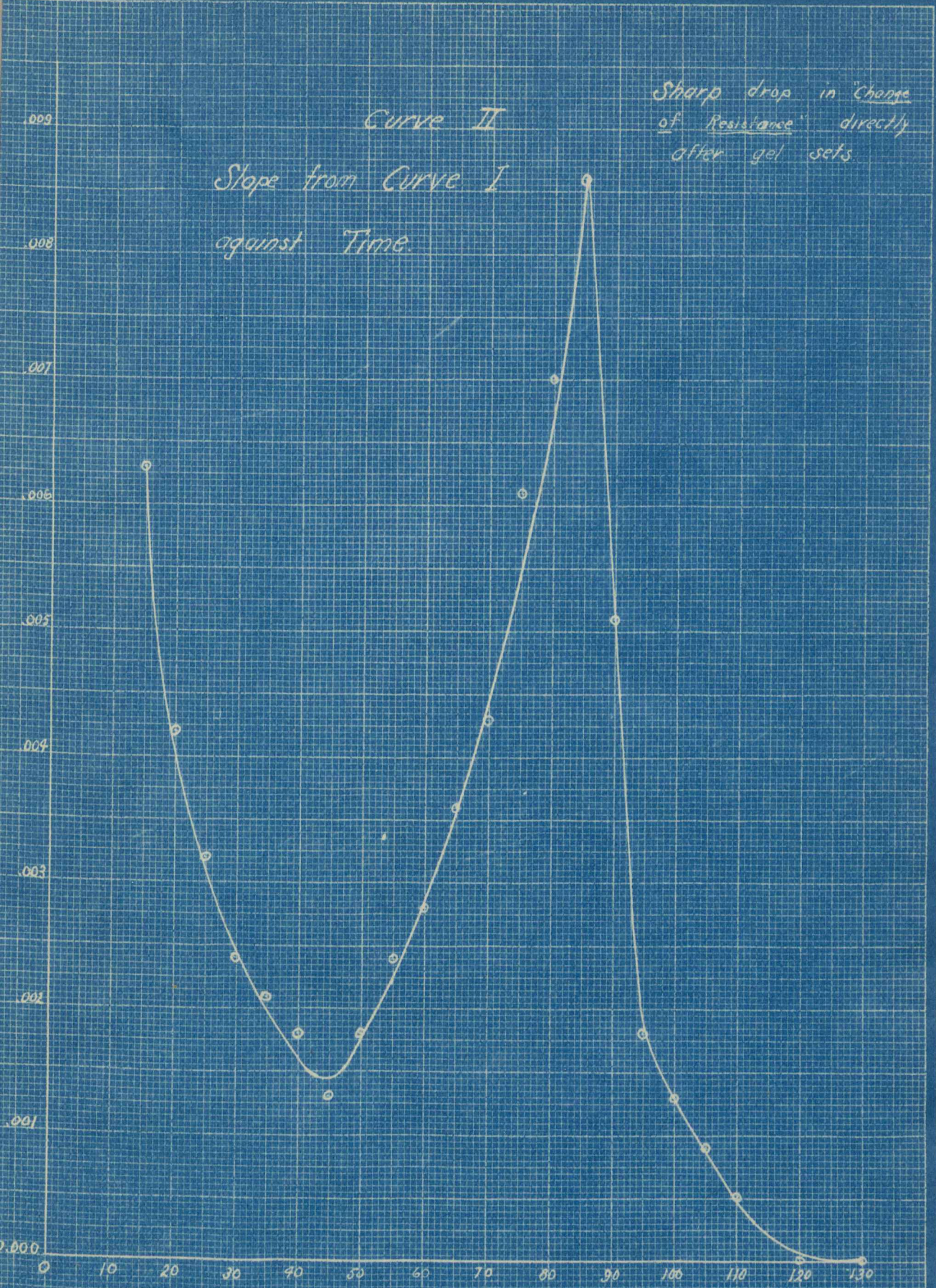
Curve No. 2 shows the negative of the slope plotted against time. While it magnifies the extraneous effect at the start, it shows that the rate of change of the resistance with time reaches a definite sharp maximum during the part of the run represented by the third section of the previous curve; in fact, this peak occurs shortly before the gel sets. The value of the slope then drops off very sharply, and after the gel has set, amounts to practically zero. The curves No. 1 and 2 serve to show that here we have a new possible method of determining the time of set, which comes at the end of the third part of curve 1.

We have previously mentioned that there is a possibility that a temperature effect causes the break in the curve about 30 to 35 minutes before setting. This possibility was investigated as follows: a Beckmann thermometer whose bulb was surrounded by a cylinder made of thin copper foil for the purpose of shielding (preventing radiation with subsequent cooling of bulb), was placed in the gel mixture, and the change of temperature with time was observed. Two types of runs were made: one in which the gel mixture was warmer than the bath, and another in which its temperature was below that of the bath. In the first case the temperature fell off in an exponential-like curve (see the following page) and reached a temperature approximately that of the bath. In the second

Curve II

Slope from Curve I
against Time.

Sharp drop in "Change
of Resistance" directly
after gel sets.



Time in Minutes

Table No. II

Table of the Rate of Change of Resistance against Time, from Curve 1 and Table I

Time	-Slope
10 min.	.0147 ohms/min.
15 "	.0063 " "
20 "	.0042 " "
25 "	.0032 " "
30 "	.0024 " "
35 "	.0021 " "
40 "	.0018 " "
45 "	.0013 " "
50 "	.0018 " "
55 "	.0024 " "
60 "	.0028 " "
65 "	.0036 " "
70 "	.0043 " "
75 "	.0061 " "
80 "	.0070 " "
85 "	.0086 " "
90 "	.0051 " "
95 "	.0018 " "
100 "	.0013 " "
105 "	.0009 " "
110 "	.0005 " "
120 "	.0000 " "
130 "	.0000 " "

Table No. III

Time	Temperature	Time	Temperature
2 min.	4.75	1 min.	3.87
3 "	4.75	2 "	4.000
4 "	4.70	3 "	4.130
5 "	4.656	4 "	4.240
6 "	4.622	5 "	4.302
8 "	4.560	6 "	4.340
10 "	4.518	7 "	4.360
12 "	4.490	8 "	4.371
15 "	4.458	9 "	4.381
20 "	4.421	10 "	4.388
25 "	4.400	11 "	4.397
30 "	4.384	12 "	4.400
35 "	4.379	13 "	4.402
40 "	4.372	15 "	4.402
45 "	4.370	19 "	4.405
50 "	4.370	20 "	4.403
55 "	4.370	25 "	4.400
60 "	4.368	30 "	4.393
65 "	4.366	35 "	4.390
70 "	4.365	40 "	4.385
75 "	4.364	45 "	4.393
80 "	4.362	50 "	4.381
85 "	4.361	55 "	4.380
90 "	4.361	60 "	4.390
95 "	4.361	68 "	4.379
100 "	4.360	70 "	4.379
105 "	4.360	75 "	4.379
110 "	4.360	80 "	4.379
115 "	4.360	85 "	4.379
120 "	4.360	90 "	4.380
		95 "	4.380
		100 "	4.380
		110 "	4.380
		120 "	4.380

(Temperature of Bath - 4.375)

100 cc of sodium silicate #1; 100 cc of acid #1; 125 cc of water.

Temperature difference - 1.55°C
 Temperature of bath on
 Beckmann thermometer - 4.370

Temperature difference - 2.10°C
 Temperature of bath - 4.373

case a peculiar effect was discovered. When the temperature of the gel mixture started below that of the bath, it rose as expected, but instead of stopping at the temperature of the bath, it consistently went slightly but definitely above the temperature of the bath and then cooled off to the temperature of the bath. (See curve III.)

The important result obtained from these curves is the fact that the temperature remains sensibly constant, thus not changing by anything resembling $.1^{\circ}\text{C}$. during the time at which we get the break in the curve. We can, therefore, say that the break in the curve is not a temperature effect.

Similar results in the resistance-temperature curves were found when using tartaric acid with sodium silicate. When however a run was made with gelatine gel, the resistance of which was adjusted to about one hundred ohms by the addition of sodium chloride, we observed only minor fluctuations, but no consistent change could be obtained.

We have stated, in an earlier part of this thesis that the rapid decrease of resistance at the start of the run is a result of several factors, probably involving equilibria effects. Several experiments were performed in order to obtain some information about the latter phenomenon.

The first experiment made was as follows: a gel mixture was placed in the cell, and after about twenty five minutes, when the run is already represented by the second portion of the curve, this mixture was discarded, and a freshly mixed solution was immediately placed in the cell. By this procedure we hoped to find whether any equilibrium between electrodes taken

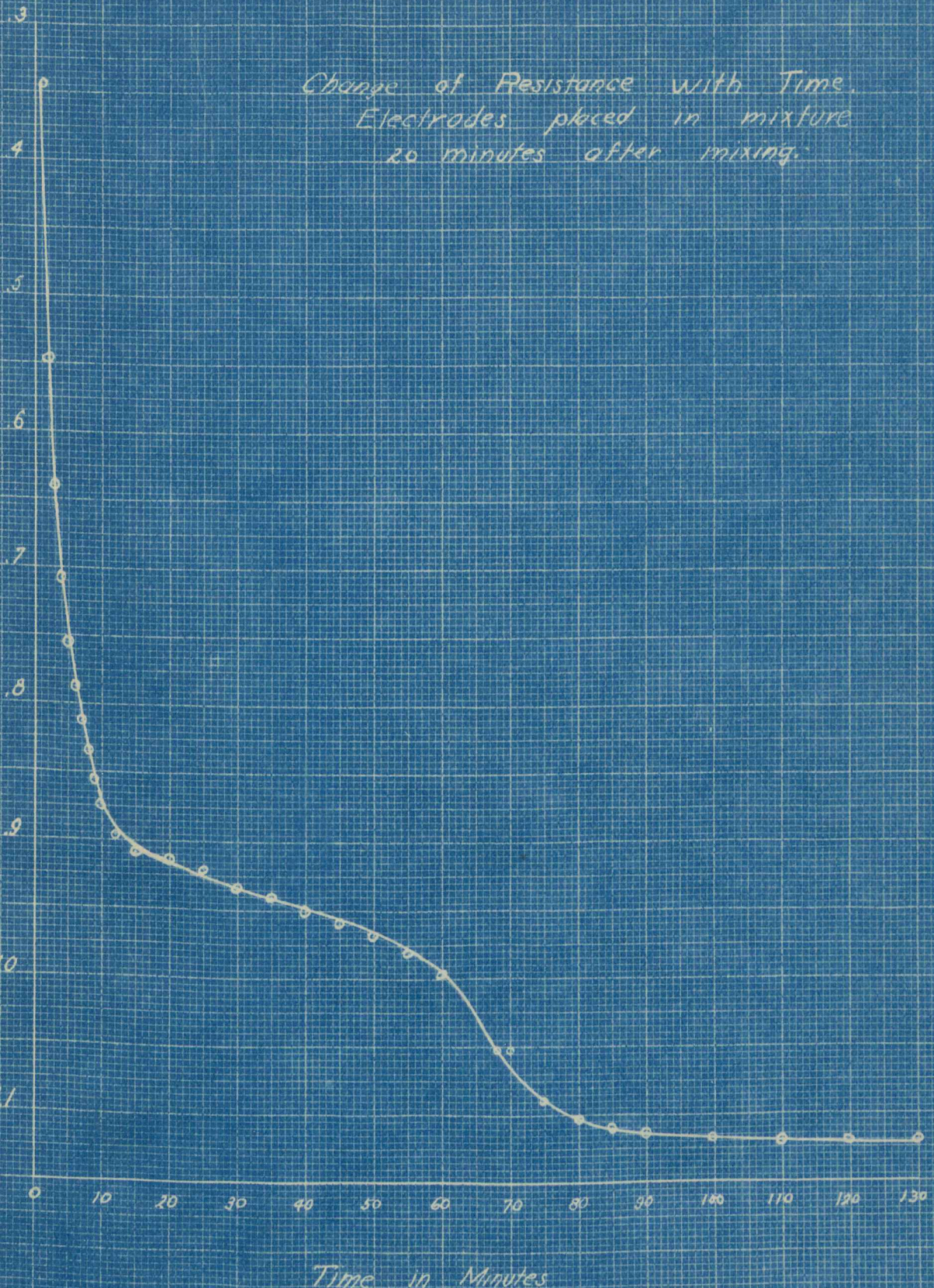
from distilled water and placed in gel mixture, was set up. Since the decrease of resistance against time was only slightly less rapid in this second gel mixture as compared to that in the first, we concluded that nothing very informative could be obtained in this way. But other experiments along this line of thought are possible, and the results of such experiments, as well as the method for obtaining them, are considered below.

From our study of the first curve, we see that the resistance is changing at a nearly constant rate after 15 or 20 minutes. Thus, we assume that if the electrodes are put into this gel mixture 20 minutes after the mixing, the resistance will follow along a curve similar to that part of curve I which is subsequent to the period of 20 minutes. In other words, we imagine that the first part of the curve will simply be left out, and the resistance will change with time as indicated by sections 2, 3 and 4 of curve I. But this is far from the truth.

We get, instead, a curve (see curve IV on next page) consisting of four sections, just as curve I. The resistance drops very rapidly at the start, while actually, from curve I, we know that the resistance is changing slowly at this time (20 minutes after mixing). Thus, we see that the rapid change of resistance at the start is not an intrinsic change in the gel, but is a property of the electrodes and of any other factors which might possibly cause such a change. On the basis of this work and of the work which follows, we conclude that this effect is largely due to an equilibrium which must be set up between the platinized

Curve IV

Change of Resistance with Time.
Electrodes placed in mixture
20 minutes after mixing.



Time in Minutes

where $T=0$ min is 20 min. after gel was mixed.

Time from actual start is $(T+20)$ minutes.

Table No. IV

Time	Difference	Change from Original Difference	Decrease in Resistance
0	-25 (extrapolated)	0	0 ohms
1	-14.2	10.8	.346 "
2	-7.9	12.1	.547 "
3	-5.0	20.0	.640 "
4	-2.9	22.1	.708 "
5	-1.4	23.6	.755 "
6	-.4	24.6	.787 "
7	-.4	25.4	.813 "
8	1.1	26.1	.835 "
9	1.8	26.8	.857 "
10	2.3	27.3	.874 "
12	3.0	28.0	.896 "
15	3.4	28.4	.908 "
20	3.55	28.55	.913 "
25	3.8	28.8	.921 "
30	4.2	29.2	.933 "
35	4.4	29.4	.940 "
40	4.7	29.7	.950 "
45	5.0	30.0	.960 "
50	5.3	30.3	.969 "
55	5.7	30.7	.981 "
60	6.2	31.2	.997 "
68	7.9	32.9	1.052 "
70	7.9	32.9	1.052 "
75	9.0	34.0	1.089 "
80	9.5	34.3	1.103 "
85	9.7	34.7	1.110 "
90	9.8	34.8	1.113 "
95	9.95	34.95	
100	10.3	35.3	
110	10.1	35.1	
120	11.4	36.0	1.120 "
130	10.8	35.8	
140	10.0	35.0	
150	9.8	34.8	
160	9.9	34.9	

100 cc of sodium silicate # 2
 100 cc of acetic acid #2
 125 cc of water

Resistance in box - 118 ohms
 Temperature of bath - 25°C

Electrodes placed in gel 20 minutes after gel was mixed.

This run shows that the initial large change in resistance is not actually a change in the conductance of the gel mixture, but involves the equilibria in electrodes and solutes.

electrodes taken from a distilled water medium and placed in a gel mixture, as well as to an equilibrium which is set up in the gel mixture itself.

To my mind, this experiment conclusively demonstrates that the rapid drop of resistance at the start of each of the individual runs is of no significance as far as telling what is going on in the gel mixture just after mixing.

In order to try to separate the effects of electrode equilibrium from those of gel equilibria, which include several possible unknown factors, the following experiment was performed. The gel mixture was made, and the readings were taken as in the first run. The results obtained are shown in curve V on the following page; it should be identical with the first curve. A comparison of this curve with curve I shows the degree of reproducibility possible. At this point in the experiment a new procedure was followed. The current in the bridge (thus, also the current in the cell) was shut off for 15 minutes. During this time, what we have called the gel equilibria (including several unknowns), may become upset, but the electrode equilibrium should not be appreciably disturbed. One must understand that the current is shut off after the gel has set, which means that the current is off during a time when the change in resistance, on the basis of previous measurements, is practically zero for a period of time as short as 15 minutes.

The amazing result, however, is that when the switch was again closed after the 15-minute interval, the resistance,

Effect of Equilbria on Resistance.

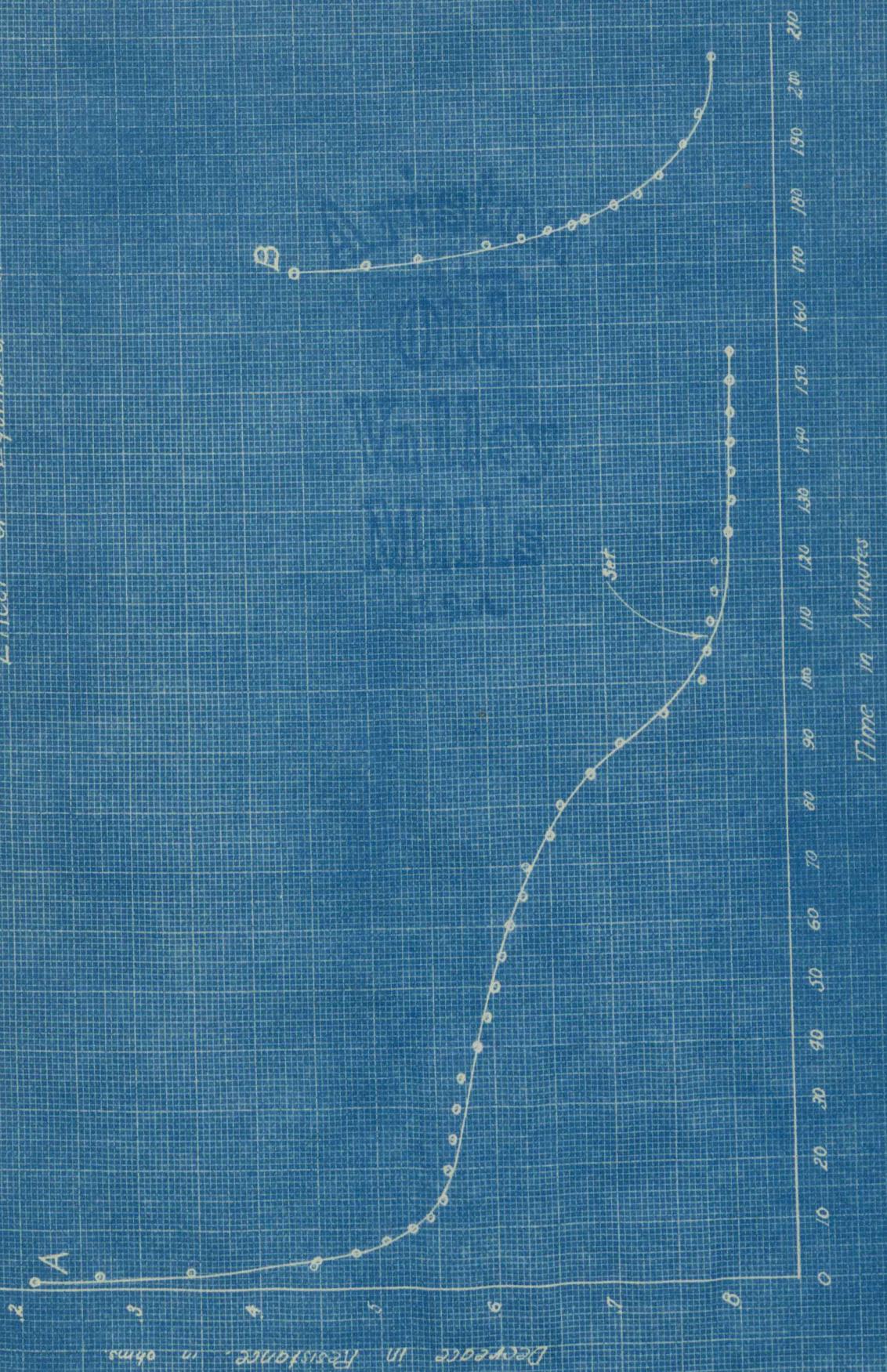


Table No. V - A

Difference	Change from Original Difference	Decrease in Resistance	
n. -15.0 (extrapolated)	0	0	ohms
-8.4	6.6	0.2114	"
-6.7	8.3	0.265	"
-4.3	10.7	0.3425	"
-2.1	13.9	0.445	"
-1.0	14.0	0.448	"
0.0	15.0	0.480	"
0.8	15.8	0.506	"
1.5	16.5	0.528	"
2.0	17.0	0.544	"
2.3	17.3	0.654	"
2.4	17.4	0.556	"
2.6	17.6	0.563	"
2.7	17.7	0.566	"
2.85	17.85	0.571	"
3.3	18.3	0.586	"
3.6	18.6	0.595	"
3.8	18.8	0.602	"
4.0	19.0	0.608	"
4.25	19.25	0.616	"
4.6	19.6	0.627	"
4.7	19.7	0.630	"
5.3	20.3	0.650	"
5.6	20.6	0.660	"
6.45	21.45	0.686	"
7.2	22.2	0.710	"
8.4	23.4	0.749	"
9.4	24.4	0.781	"
9.6	24.5	0.787	"
9.7	24.7	0.790	"
9.8	24.8	0.794	"
9.8	24.8	0.794	"
10.2	25.2	0.806	"
10.4			
10.3			
10.2			
10.4	25.3 (average)	0.810	"(average)
10.3			
10.3			

Time of set - 107 minutes.

100 cc of acetic acid #2
 100 cc of sodium silicate #2
 125 cc of water

Temperature of bath - 25°C
 Temperature difference - 1.5°C
 Resistance in box - 118 ohms

See the following page for Table V - B.

Table No. V - B

Switch was left open for 15 minutes and then closed. The
 e in the following table is measured from the closing of the
 tch, that is, time = 0 min. when switch is closed.

Difference	Change from Original Difference	Decrease in Resistance
-1.1	13.9	0.445
0.8	15.8	0.506
2.2	17.2	0.551
3.6	18.6	0.595
4.0	19.0	0.608
4.9	19.9	0.637
5.6	20.6	0.659
6.2	21.2	0.679
6.6	21.6	0.691
7.4	22.4	0.717
8.0	23.0	0.736
8.6	23.6	0.755
9.2	24.2	0.775
9.6	24.6	0.788
9.5	24.5	0.785
10.0	25.0	0.800

instead of remaining constant or decreasing slightly, increased markedly, as shown on curve V.

From this curve, and from the manner in which the experiment was conducted, we conclude that this change represents numerically the value of the decrease in resistance which was previously obtained from the establishment of the various equilibria within the gel-mixture by means of the alternating E.M.F. and resulting alternating current.

The part B of the curve V is obtained by simply leaving the current on, and getting the decrease in resistance as the equilibria are again set up. From the fact that this latter curve (B) does not have exactly the same shape, nor the same magnitude as the first part of curve A, which part is based on the extrapolated value of the resistance, we come to the previous conclusion that the effect represented by A, the change of resistance with time at the start of the run, includes an electrode equilibrium, as well as the various equilibria within the gel.

The above experiment suggested a similar, but more intensive and complete one, which yielded very interesting results. The data and curves VI show the relation between time and equilibria in the gel. The results are obtained by using the following method. An ordinary run is made as in curve I, and after gelation, when the resistance is nearly constant, (for best results let the gel remain for 24 or 48 hours before continuing experiment) the actual procedure begins. Open the switch for just one minute. Then close the switch, taking the reading instantly. The deviation of the resistance from the value at equilibrium is about 2 units. (See curve VI). Now keep switch closed (for about 20 minutes) until the bridge is again at

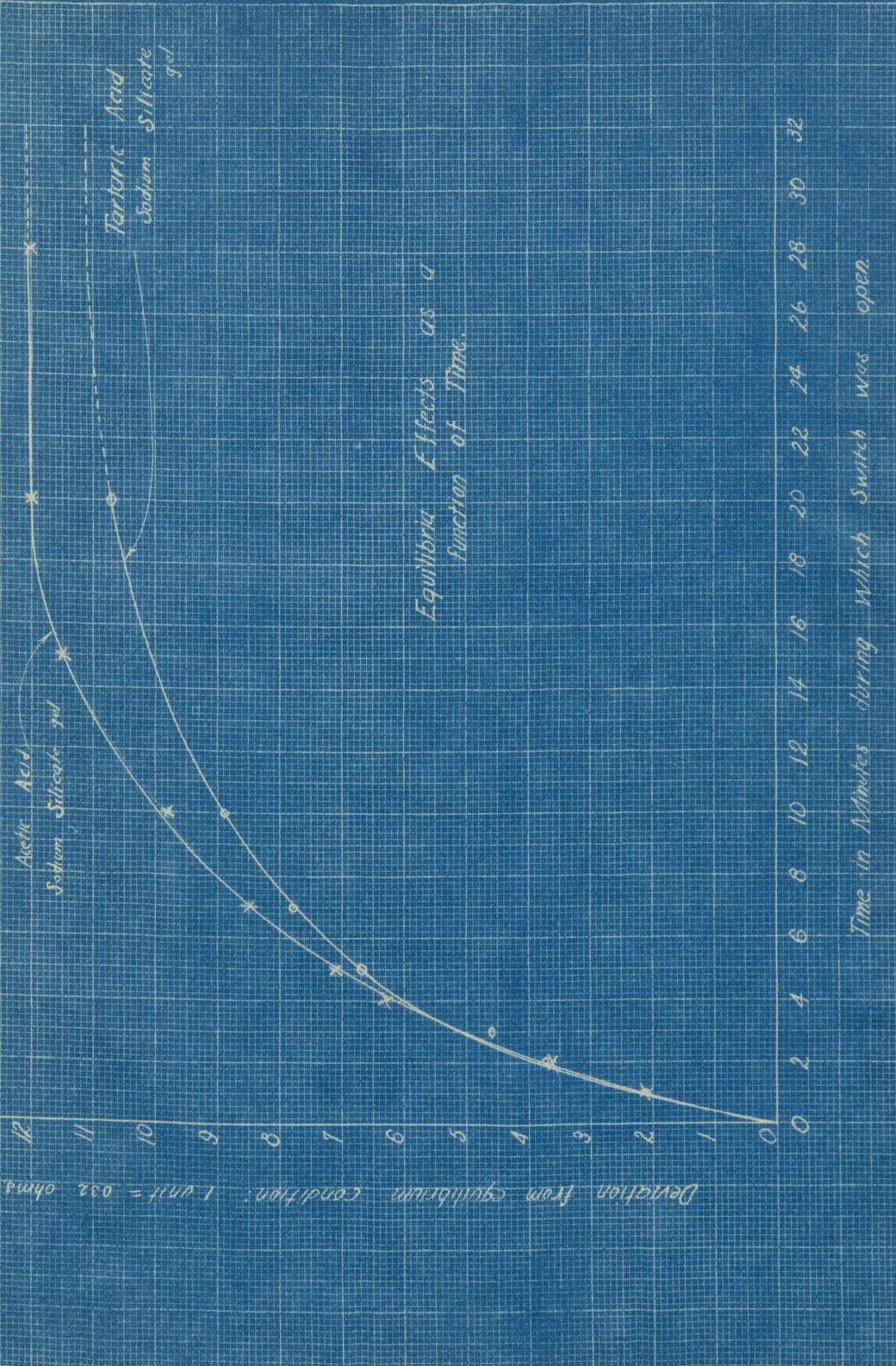


Table No. VI - A

Circuit	on Left	on Right	Difference	Equilibrium Reading	Difference from Equilibrium Value	
.	464.5	534.1	69.6	71.7	$71.7 - 69.6 = 2.1$	units
.	465.5	533.6	68.1	71.7	$71.7 - 68.1 = 3.6$	"
.	466.2	532.8	66.6	71.7	$71.7 - 66.6 = 5.1$	"
.	466.8	532.2	65.4	71.7	$71.7 - 65.4 = 6.3$	"
.	467.0	531.6	64.6	71.7	$71.7 - 64.6 = 7.1$	"
.	467.6	530.8	63.2	71.7	$71.7 - 63.2 = 8.5$	"
.	468.2	530.1	61.9	71.7	$71.7 - 61.9 = 9.8$	"
*	469.4	529.6	60.2	71.7	$71.7 - 60.2 = 11.5$	"
*	466.7	531.9	65.2	77.2	$77.2 - 65.2 = 12.0$	"
*	466.7	531.9	65.2	77.2	$77.2 - 65.2 = 12.0$	"
.	466.5	531.7	65.2	77.2	$77.2 - 65.2 = 12.0$	"
.	469.8	528.9	59.1	71.7	$71.7 - 59.1 = 12.6$	"
.	466.8	531.5	64.7	77.2	$77.2 - 64.7 = 12.5$	"

Data obtained from set gel of the following composition:

of acetic acid #2, 100 cc of sodium silicate #2, and 125 cc of
at 25°C.

Its obtained on different day. Resistance of gel had decreased
previous day.

Table No. VI - B

Tartaric Acid - Sodium Silicate Gel

Open Circuit	Difference	Change from Original Difference
ln.	35.2	$37.3 - 35.2 = 2.1$ units
.	33.6	$37.3 - 33.6 = 3.7$ "
.	32.7	$37.3 - 32.7 = 4.6$ "
.	30.4	$37.1 - 30.4 = 6.7$ "
.	29.4	$37.2 - 29.4 = 7.8$ "
.	28.4	$37.3 - 28.4 = 8.9$ "
.	26.7	$37.4 - 26.7 = 10.7$ "

Data obtained from set gel of composition:

of sodium silicate #2, 100 cc of tartaric acid, and 125 cc of
at 25°C.

equilibrium reading. Then leave switch open for 2 minutes, close and take reading instantly. This procedure is followed for other time intervals, giving the curve VI. The second curve on graph VI shows the similarity of the behavior of tartaric acid-sodium silicate gels. If the switch is left open for about 24 hours, which condition can be considered to represent infinite time (on basis of an arrangement concept, it would represent the totally chaotic arrangement), we find that the deviation from the equilibrium condition is about 12.5 units on the slide wire which corresponds to about $.032 \text{ ohms} \times 12.5 = .4 \text{ ohms}$.

The resulting curve VI seems to belong to the exponential type. The factors which may cause such a change are the heating effect of current in the cell, an orientation of particles or ions, or even a possible orientation of filaments of gel structure to produce a sort of "metallic-like" conduction.

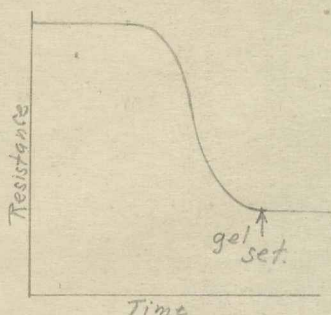
Conclusion and Discussion of Results

After carefully considering all the various factors and allowing for their conflicting action, we can definitely conclude that the resistance of the gel decreases as it sets, which seems to be contrary to what one would logically expect to occur.

A second valid conclusion is that there is a definite break in the curve starting about one-half hour before the gel sets and ending abruptly (leveling out) after setting. This break is actually sharper than indicated, for the first effect of electrode and gel equilibria carries over into this region of the curve and obscures to some extent the true result.

Our belief is that, were it possible to eliminate equilibria effects as previously discussed, the curve would have had the shape indicated in the sketch below.

would be nearly flat at the beginning, then it would become steep during the 30 minute interval before setting, and then it would become a nearly flat curve. This curve, as well as the actual curve



obtained, would indicate the occurrence, during the setting of the gel, of some fundamental change, acting to decrease the resistance. Such a change could be the growth of fibers which might furnish a metallic-like conduction.

On the whole, it is rather difficult to explain this decrease of resistance, for an increase of resistance is what one would reasonably expect. There is a possibility of metallic conduction as suggested above to explain this decrease of resistance. It may also be due to the anomaly of an increased mobility of the ions in the gel. This action, although apparently the reverse of what should occur, would explain the observed effect. The true explanation, we feel, will involve a concrete application of the correct theory of gel structure, which at present, seems to be incomplete.

The equilibria effects which have been studied also deserve some thought. These effects can be divided into two types: the phenomena arising from electrode effects, and those due to certain conditions within the gel itself.

Comparatively little is known about this electrode effect, but we think it safe to say that some change must occur

when a platinized electrode, completely covered and saturated with distilled water, is placed in a totally different medium consisting of water, silicic acid, and sodium acetate, or sodium tartrate. As the water from the electrode dilutes the gel mixture, and as the gel mixture diffuses onto and into the platinized coating on the electrode, we can easily see that we are bound to obtain some significant change in the resistance, as is demonstrated by the very rapid drop in the resistance at the start of a run; this is shown by the various curves included in this thesis.

The second group of equilibria effects are those arising in the gel itself. We have already shown the exponential-like curve which this change seems to follow. What actually causes this change is difficult to tell. It may be caused by a type of orientation in the gel, starting from a chaotic arrangement and finishing as a well ordered system, with an accompanying drop in the value of the resistance. There are probably more concrete and definite explanations possible, which are likely to be presented within the near future. For the present, we can only speculate on the possible changes which are taking place when an alternating current passes through the cell containing a gel.

One procedure which seems to offer promise of yielding some interesting information concerning the question of what goes on in the gel at various times and under various conditions, is the carrying out of several runs on blanks. Such experiments would consist of performing runs, of a nature similar to those described in regard to the gel mixture, on a nonreactive solution such as sodium chloride. One such experiment which was just

sketchily attempted seemed to show that some of the above described effects are present in the salt solution. This observation, however, is not given much weight as it was not carefully performed.

Thus, we see from our study that a supposedly straightforward phenomenon has grown into a much more complicated problem, involving several intricately connected phenomena of varying complexity. In spite of all complications, however, we can reach one definite conclusion. The resistance of a gel-mixture decreases as the gel sets, and shows a definite, rather sharp break, in the period of time of about one-half hour immediately preceding the setting. It then shows a definite flattening of the resistance-time curve after setting.

Acknowledgment

The author wishes to acknowledge his indebtedness to Professor C. B. Hurd whose suggestions and advice have been invaluable.

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