A STUDY OF THE VELOCITY OF IONS IN SILICA GELS WHEN UNDER THE INFLUENCE OF A POTENTIAL.

A THESIS PRESENTED TO THE DEPARTMENT
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INTRODUCTION

There is speculation among chemists as to the structure of gels. In an effort to get information on this subject, chemists have studied the properties of and reactions in gels. The results have led to conflicting theories. This work measuring the velocity of ions in silica gel has been done in the hope that it may add to the knowledge of the behaviour of gels and furnish a further clue towards the correct structure of silica gels.

HISTORICAL

Since the type of procedure in measuring the velocity of migration of ions in a gel must be much the same as that used in measuring diffusion in gels, a search of the literature was made with the purpose of reviewing the various methods of measurement in order that the method best suited to the apparatus available should be used. Voigtländer (1) and Öholm (2) measured the progress of diffusion of KCl in gelatin gels by subjecting the different layers to chemical analysis. It is needless to say that this method is very cumbersome and time consuming. Herzog and Polotsky (3) in 1914 attempted to measure diffusion in gels by following the diffusion of colloidal dyes thru a gel, but they did not get very consistent results.

Lodge (4) in 1886 used phenolpthalein as an indicator with which to measure the rate of diffusion of OH ions into a gel, but since he was not very much interested in the hydroxyl ion, he made very little mention of the method and consequently his work has been overlooked. W. Stiles (5) and V. Morivek (7) did very thorough work on diffusion into agar and gelatin jellies. Their method was to set a gel with some such substance as silver nitrate in it, and then allowing a chloride to diffuse into the gel, the rate of diffusion being measured by the advance of precipitation. In this manner Stiles showed that temperature greatly affected the progress of the ions.

Friedman (6), however, discredited his results because he claimed that the precipitate blocks diffusion by clogging the pores of the gel, and so he proceeded to measure diffusion by means of the Zeiss Immersion Refractrometer.

A few other methods of measurement have been used, namely, by specific gravity determinations, optical methods such as refractive index or optical rotation, and determination of electrical conductivity. These methods for the most part require special apparatus and are rather cumbersome.

Isgarischew and Pomeranzewa (8) are the only ones found so far who have done any work on the migration of ions in a gel under the influence of a potential. They used Lodge's indicator method for the measurement of ion migration. They used gelatin gels set in tubes with the electrodes at each end. They added NaCl to the gel to make it conducting.

In the following experiment, a modified form of Isgarischews apparatus was used, but no salt was added to the gel to make it conducting because I think the presence of appreciable amounts of salt effects the manner in which the gel will set.

EXPERIMENTAL

Silica gels were set in tubes, each tube containing a different indicator, such as cochineal, methyl red, congo red, phenolpthalein, and methyl orange. Hydrogen and hydroxyl ions were allowed to diffuse into the gels. Of these congo red and methyl orange were the only ones whose indicative properties were unaffected by the gel. Since methyl orange showed the line of demarcation the most clearly and sharply, it was the indicator decided upon as the most suitable.

The progress of the hydroxyl ions could not be measured because the OH dissolved the silica gel.

After experimenting with various concentrations of indicator, I finally decided to use 14 drops to each 30 cc. of gel, since this concentration showed the best line of demarcation under the conditions of this experiment.

An attempt was made to determine the possibility of allowing $K_2 Cr O_4$, $K_4 Fe(CN)_6$, and other colored compounds to diffuse into the gel, and measuring their progress by the advance of color, but the color was either too faint, too uneven, or for some other reason unsatisfactory, so this possibility was discarded.

The next problem was to find suitable electrodes, since platinum discs were unavailable. At first mercury contacts on one side of the gel were tried, but the gel soon dried and cracked. Then contact solutions of HCl were tried, using silver, copper, and other metals for electrodes, but these either dissolved or polarized. Finally a carbon rod was tried and found very satisfactory.

There was some question as to whether the indicator would affect the conductivity of the gel, so several tubes containing various amounts of methyl orange were set in gels along side a gel containing no indicator. Upon applying the same potential across either tube, the same current resulted, thus proving that the methyl orange did not take part in the migration.

As pointed out by Stiles (5) the migration of ions thru a gel is affected by the temperature. In order to assure a constant temperature, an air bath was built, which consisted of a cardboard covered packing box with a hinged door in front. It was heated by a 100 watt electric light bulb which was shielded from the gel so that no heating by radiation should take place. The temperature control was a bi-metallic strip control obtained from Mr. J. H. Payne, of the General Electric Company. This regulator when tested with a 100° thermometer was found capable of keeping the temperature within 1½°C. It was set to operate at 24°C.

Previous workers in diffusion had taken great care to prevent evaporation. In order to find how much evaporation was liable to affect my results, I set gels in two sets of tubes. In one set evaporation was guarded against by covering the HCl with a film of oil. The other was left exposed. I applied 6 volts across each for 24 hours. At the end of that time, no measurable difference could be detected between the distances of migration. So I concluded no elaborate precautions should be taken against evaporation.

In the same manner I tested to see if differences in the level of the HCl would make any difference in the velocity of the ions, The result showed that with a difference of levels of HCl of 2½ inches, no measurable difference took place in 24 hours, showing that small accidental variations in the levels of the HCl solution would not effect the results.

APPARATUS AND MATERIALS

Fig. 1 shows the air bath used.

Fig. 2 and 3 shows the apparatus and circuit.

The tubes containing the gel were 25 cm. long and .065 cm. in diameter. These tubes were inserted thru corks into beakers containing the electrodes and HCl solution as shown. The beakers were 200 cc. beakers. The holes for the corks were drilled thru the glass by means of a die made of brass tubing the diameter of the hole; this acts as a very efficient drill when used with a paste of carborundum and water.

Leaks between the cork and beaker were rather common. Several methods for preventing this were tried, but the most satisfactory was by cementing the joints with rubber cement. This cement sticks very readily to rubber or glass, is easy to apply, dries quickly, and is transparant.

Evaporation was guarded against by placing a piece of cardboard across the top of the beakers.

At first round carbon rods were used as electrodes, but they had to be perfectly centered to give reproducible results, so they were discarded in favor of the flat type shown in Fig. 3. These were turned down on a lathe from carbon rods obtained from the Research Laboratory of the General Electric Company. The wire threaded into the carbon disc was of nickel, shielded from the acid by being encased in glass tubing fastened to the carbon by de Khotinsky cement.

It might be noted that the circuit is so arranged that the milliammeter and voltmeter can be connected at will and independently of each other. The reason for connecting the milliammeter in such a manner that it could be thrown out of the circuit was so that in case a B battery was used as a source of potential, the milliammeter could be thrown out of the circuit so as not to sap the current from the battery and ruin it.

The gels were all made up of equal volumes of .5 M acetic acid and 1.06 E brand water glass. The advantage of this concentration of gel is that it sets immediately and is basic to methyl orange. The gels were set by holding the finger on the tube, filling it with gel, and holding it a minute till it set.

The HCl used was 1.000 ± .002 HCl standardized against NaOH which in turn was standardized against oxalic acid. Enough HCl was made up at one time so that HCl from the same sample was used throughout the experiment, thus eliminating small errors due to slight differences of concentration. In the same manner all data was taken using solutions from the same samples throughout. Even the same pipettes were used continually.

All joints with a possibility of a bad contact were soldered. The same electrodes and tubes were used repeatedly in taking the data included herein. Special care was exercised in placing the electrodes for enough from the gels to prevent gas from the electrodes to form bubbles in the ends of the tubes. For 6 and 12 volts storage batteries were used. Above this voltage the Union College D.C. generator was used.

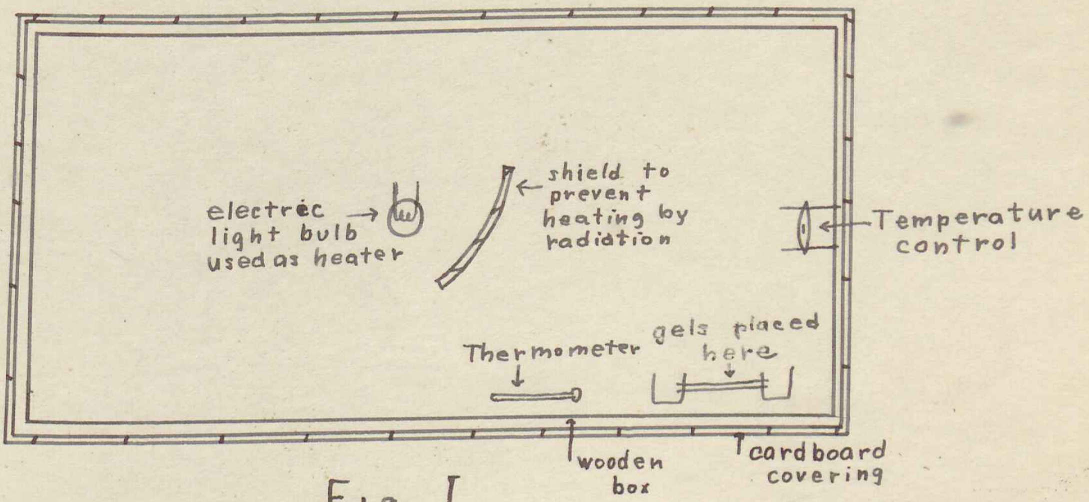

electric light bulb used as heater
shield to prevent heating by radiation
Temperature control
Thermometer
gels placed here
wooden box
cardboard covering

Fig. I

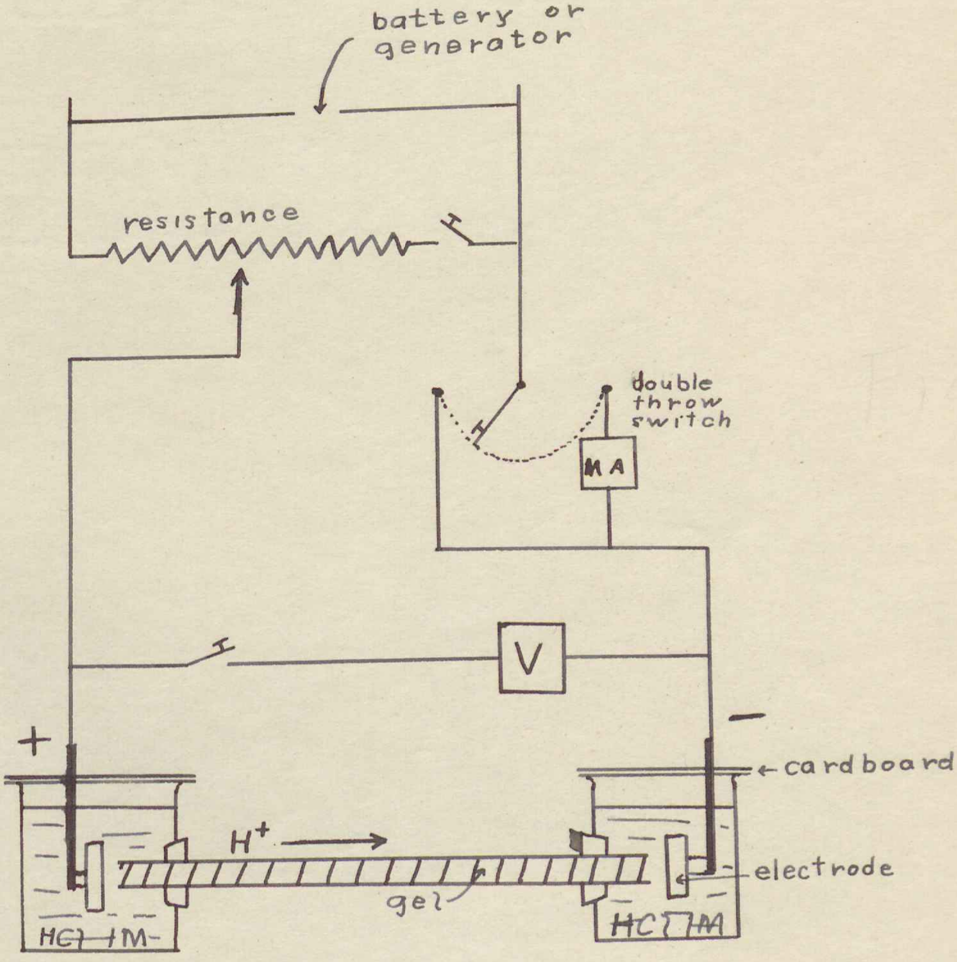

battery or generator
resistance
double throw switch
MA
V
+
−
cardboard
H^+
electrode
gel
HCl 1M
HCl 1M

FIG. 2

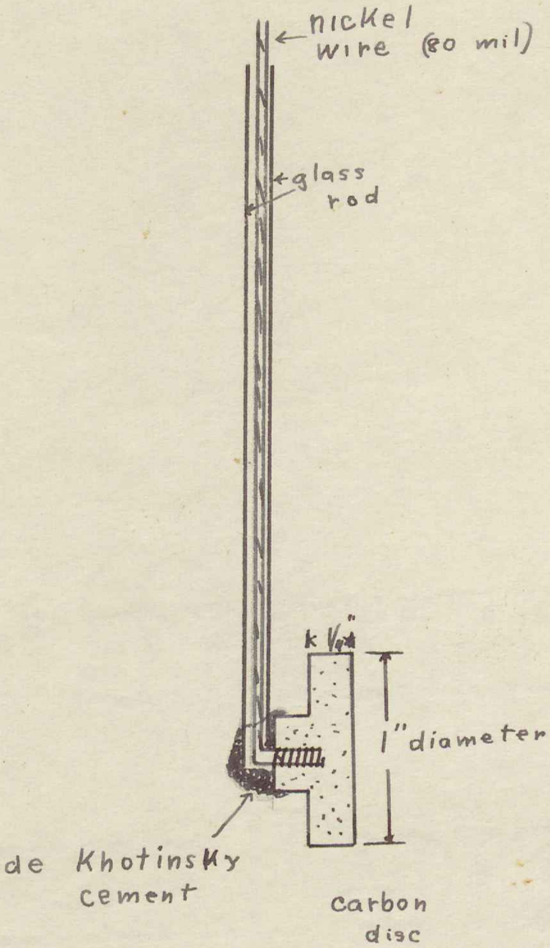

nickel wire (80 mil)
glass rod
k 1/4"
1" diameter
de Khotinsky cement
carbon disc

FIG. 3

EFFECT OF POTENTIAL
ON THE VELOCITY OF H IONS

The apparatus was set up as shown in Fig. 2. A potential was applied, readings being taken at convenient intervals with a pair of calipers. Results are given in Tables 1 and 2. The agreement between different sets of readings can easily be seen for separate runs at 6 volts. Results at 12 volts show approximately as close agreement, but ad the voltage was increased beyond 12 volts the agreement was not so good. Results are shown for 0, 6, 12, 18, 24 and 30 volts in Fig. 4.

The graph suggested the fact that the relative speed of migration increases directly with the voltage, i.e., that with twice as much voltage, the distance traveled in a given time is twice as much. Using the curve for 6 volts as the standard, I drew (in black) the curves that I would expect if this were so. As can be seen, the agreement is almost perfect for 12 volts, but gets poorer as the voltage increases above that value.

I can suggest three reasons for this discrepancy at higher values. First, for 18, 24 and 30 volts the voltage was not constant for the generator was used as the source. A vibration or fluctuation of ± 1 volt took place continually as the generator was running. Second, I believe the gels heat rather rapidly for the higher voltages, and the air bath is not capable of correcting this. A water jacket should have been used, but since constant temperature water was unavailable, the air bath had to suffice. Third, I suspect that the time allowed to elapse between the setting of the gel and the application of the potential has a very decided effect upon the rate of migration of the ions.

CHANGE OF CURRECT DURING MIGRATION

During the progress of the experiment, it was noticed that the current kept decreasing as the hydrogen ions migrated thru the gel, so during the measurements on 24 and 30 volts, a careful record of the fluctuations of the current was taken. The results are shown tabulated in table 3 and Fig. 5.

The graph shows that the current increases for awhile, then decreases rapidly, and seems to approach a limiting value as it flattens out.

As lower voltages are used the maximum current shifts to the right i.e., the maximum current occurs later.

An attempt to explain this decrease in current was made on the grounds of polarization or back potential. The electrodes were dipped in HCl and 50 volts applied. It was found that hydrogen and chlorine formed on the cathode and anode respectively, but the resulting back potential of about 1½ volts was in such a direction that it would have favored an increase and not a decrease in current.

Again the current was measured when the potential was first applied and found to be about 105 milliamps. After about 4 hours the current was 103 milliamps. This showed that the fall in the current was not due to increased resistance caused by the accumulation of gas on the electrodes.

Personally, I believe the phenomena of the fall of current is due to the exhaustion of ions in the gel, but

I can offer no explanation for the increase in current at the beginning unless there is some force similar to inertia acting in the gel.

SUMMARY

1. A simple and convenient apparatus for measuring the rate of migration of hydrogen ions is described.

2. The results seem to indicate that the relative rates of migration are proportional to the applied voltages.

3. An unaccountable increase and subsequent decrease in current was noticed as the migration took place.

TABLE 1

6 VOLTS

TIME IN HOURS	DISTANCE TRAVELLED IN MILLIMETERS				AVERAGE
	#1	#2	#3	#4	
5½	19	19	18.5	18.5	18.8
6	21	20	18.8	19	19.7
6½	22	21	20	20	20.8
7	24	23	21	21	22.3
7½	23	23	22	22	22.5
8	24	24	23	23	23.3
8½	25	25	23.5	23	24.1
9½	26	27	25	24	25.5
10	27	27	25	25	26.0
11	28	28	27	28	27.8
12	30	29	29	28.5	29.1
13	31	30	30	30	30.3
14	33	31	32	31	32.3
16	34	34	34	33	33.8
18	37	36	35	34	35.5
19	38	37	37	37	37.3
20	38	37	38	37.5	37.6
22	40	38	41	39	39.5

TABLE 11

For 0 volts figures are average of two runs.
For 12 and 24 " " " " " three "
For 6, 18 and 30 " " " " " four "

TIME IN HOURS	DISTANCE TRAVELLED IN MILLIMETERS FOR FOLLOWING VOLTAGES					
	0	6	12	18	24	30
1	-	-	-	-	-	32.25
1½	-	-	-	-	-	39.75
1¾	-	-	-	-	-	45.5
2	-	-	-	-	37.7	49
2¼	-	-	-	-	39.7	52.3
2½	-	-	27.3	39	43	55.3
2¾	-	-	-	-	45.3	59.5
3	-	-	29.3	41	48.3	62
3¼	-	-	-	-	51	64.5
3½	-	-	31.3	46	53.3	67.8
3¾	-	-	-	-	56	70.3
4	-	-	33.5	-	58.5	72.8
4¼	-	-	-	-	-	75.8
4½	-	-	35	-	-	78.8
5	-	-	-	52	67	-
5¼	-	-	-	-	68.3	-
5½	-	18.8	38.8	55	70.3	-
5¾	-	-	-	-	72.3	-
6	-	19.7	40.6	56	74	90.5
6¼	-	-	-	-	73.3	-

TABLE 11 (cont'd.)

For 0 volts figures are average of two runs.

For 12 and 24 " " " " " three "

For 6, 18 and 30 " " " " " four "

TIME IN HOURS	DISTANCE TRAVELLED IN MILLIMETERS FOR FOLLOWING VOLTAGES					
	0	6	12	18	24	30
6½	-	20.8	41.5	-	77	95.3
7	-	22.3	43	62	-	-
7½	-	22.5	-	-	-	101.5
8	-	23.3	46	65.5	-	-
8½	-	24.1	-	-	98.7	-
9	19	49.4 →	-	-	-	-
9½	-	25.5	-	-	-	-
10	21.8	26.0	52	74	-	-
11	-	27.8	54.5	-	-	-
12	-	29.1	57	82.3	-	-
13	23.5	30.3	-	-	-	-
14	-	32.3	62	-	-	-
15	25.2	-	-	91	-	-
16	-	33.8	66	-	-	-
17	26.8	-	-	-	-	-
18	-	35.5	70	100	-	-
19	27.2	37.3	72	-	-	-
20	-	37.6	-	106	-	-
22	-	39.5	75.5	117	-	-

TABLE 111

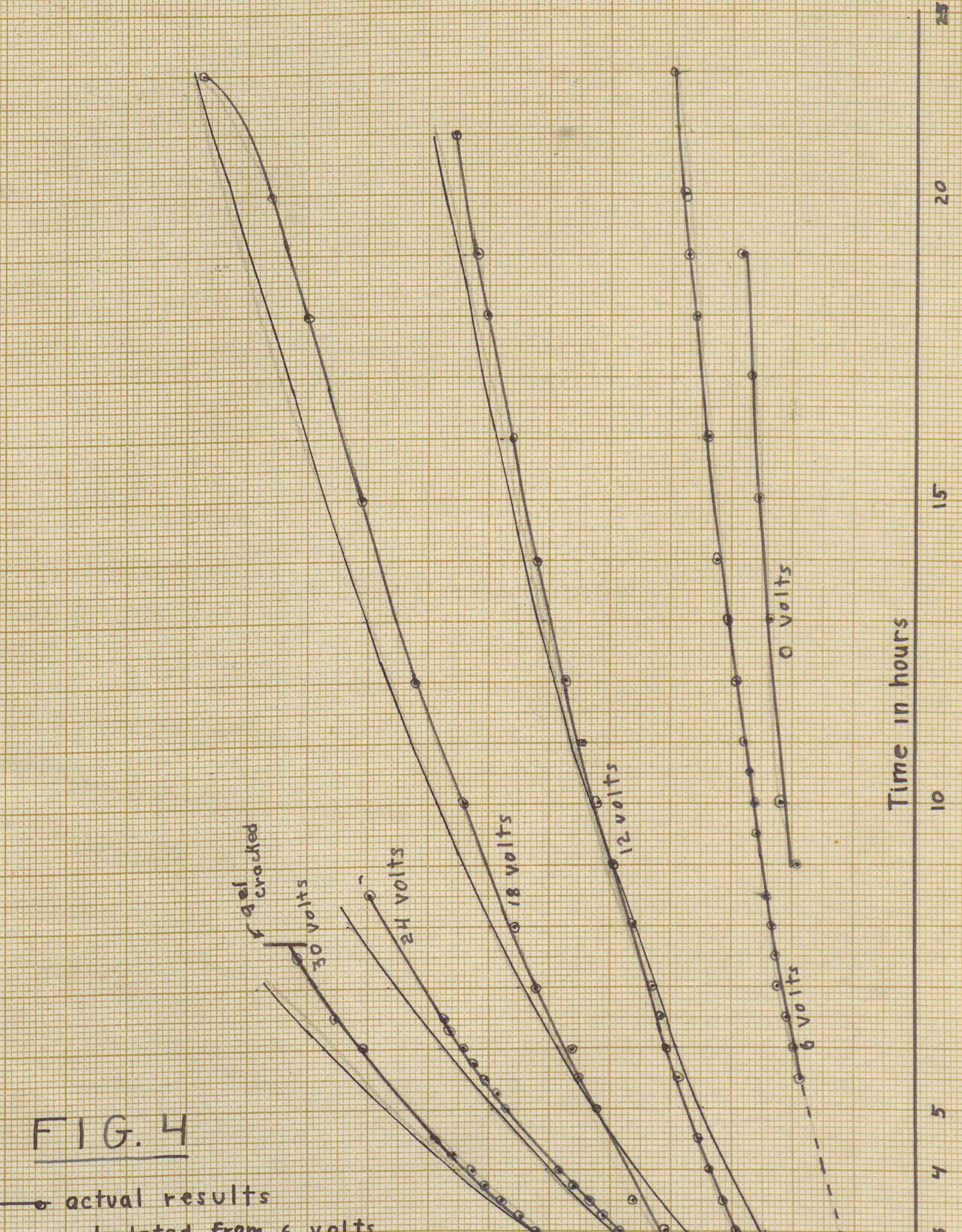
VARIATION OF CURRENT WITH TIME

Column A for 30 volts.

Column B for 24 volts.

HOURS	A	B
0	25.9	20.8
¼	-	23.0
1	30.5	-
1¼	29.5	-
1½	26.5	-
2	-	19.5
2¼	19.5	17.2
3	17.0	15.8
3¼	16.0	15.3
3½	15.6	14.3
3¾	15.3	13.5
4	14.5	13.0
4¼	14.1	-
5	-	11.3
5¼	-	11.0 ~~10.3~~
5½	-	10.~~0~~3
5¾	-	10.0
6	-	9.8
6¼	-	9.3
6½	10.5	9.0
8¼	9.0	-
8¾	-	7.4

FIG. 4


actual results
calculated from 6 volts
Time in hours
Distance in millimeters
0
1
2
3
4
5
10
15
20
25
0
10
20
30
40
50
60
70
80
90
100
110
gel cracked
30 volts
24 volts
18 volts
12 volts
6 volts
0 volts

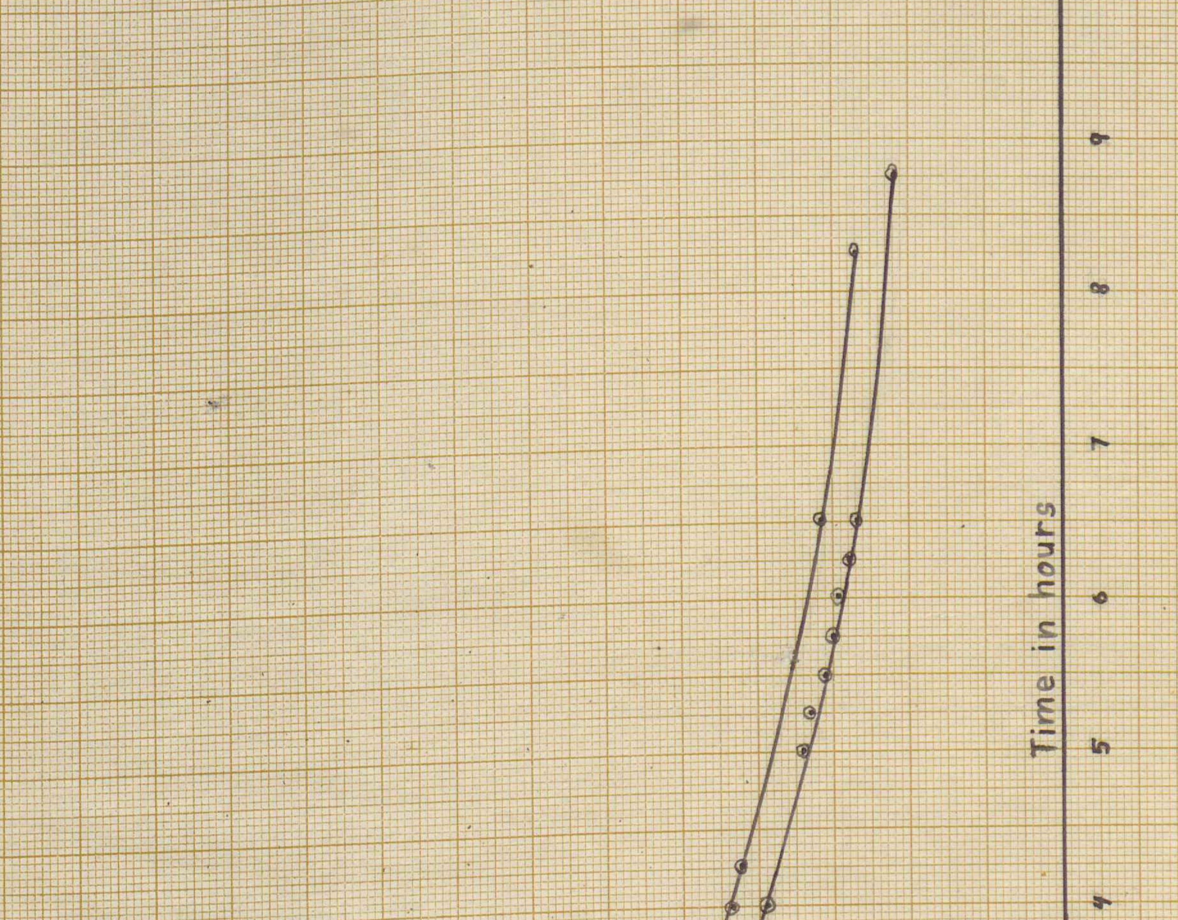

30 volts
24 volts
Current in milliamps
Time in hours
30
20
10
0
0
1
2
3
4
5
6
7
8
9

TABLE 5

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