6-1940

A Study of Electromotive Force over a Concentration Gradient

Sherman William Parry
Union College

A STUDY OF ELECTROMOTIVE FORCE OVER A CONCENTRATION GRADIENT

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.

Sherman Parry

Approved by Charles B. Hurd

INTRODUCTION

The problem was entered into to find out whether a gradual change of concentration over a distance of some centimeters would make any change in the electromotive force if substituted for a relatively sharp junction.

EXPERIMENTAL

The first step was a study of two calomel half-cells connected by a salt bridge of 1M potassium nitrate which were allowed to stand for a period of days. During this time the only natural process taking place was diffusion. Half-cells and salt bridge were kept in a thermostat which was operated for only an hour before each potential reading was taken.

A Leeds and Northup Student Potentiometer was used to make the electromotive force observations.

The following data were obtained:

Days	EMF
.003	0.1150
1	0.1158
2	0.1178
7	0.1173
8	0.1167
19	0.1165
11	0.1168
14	0.1172

The thermostat was at 24.8 degrees centigrade.

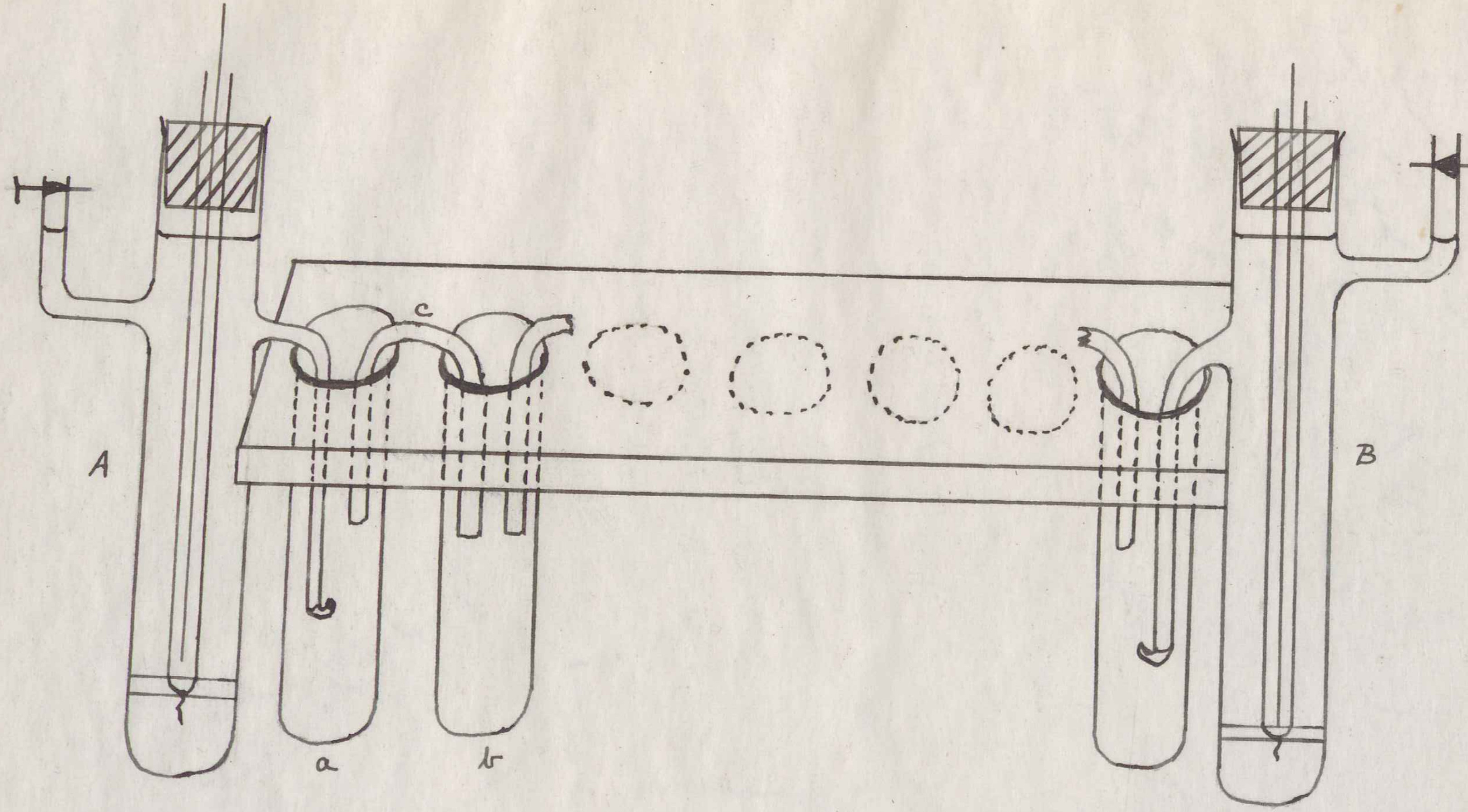
Evidently diffusion did not take place rapidly enough, for there is an absence of any definite trend. Copper sulfate crystals in the bottom of a cylinder will take a year to reach the top. A calculation by the Nernst equation gives 0.1169 volts as the potential of this cell.

A next attack was the setting up of an artificial concentration gradient across the bridge. This was done with the use of seven test tubes, each successive test tube being connected by a 3mm glass tube bent into a U shape. Each U tube was approximately six centimeters long. At first capillaries were drawn for this purpose but they were found to have a resistance of about 100,000 ohms apiece, and to avoid any resistance effects the 3mm tubes were used which had a resistance of only 12,000 ohms.

The calomel half-cells contained solutions of .8M KCl and .008 M KCl. Them the seven test tubes brought the bridge concentration from .8 M KCl in the first tube down to .008M KCl in the last tube in equal steps. The side arms of the half-cells dipped into the end test tubes each time an electromotive force measurement was taken. In steps, the half-cell was moved from the test tube containing .8M KCl to the following tube containging .668M KCl and so on until both half-cells dipped into the .008M KCl solution in the last test tube. An electromotive force observation was taken at each step. Thus, after the first reading a and c are removed and A is moved over to test tube b and another observation made.

Table I

Bridge Conc.	EMF	Temp. C
.800-.008	0.112512	24.95
.668-.008	0.112512	24.90
.536-.008	0.112512	24.92
.404-.008	0.112512	24.90
.272-.008	0.112512	24.90
.140-.008	0.112512	24.95
.008	0.112512	25.0



BRIDGE WITH CONCENTRATION GRADIENT

A new cell was made up and allowed to stand for three days before an observation of the electromotive force was made.

Table II

Bridge	EMF 2nd day	EMF	EMF 4th day
.8-.668	0.113934	0.113737	0.113931
.8-.536	0.113934	0.113737	0.113931
.8-.404	0.113934	0.113737	0.113931
.8-.272	0.113934	0.113737	0.113931
.8-.140	0.113934	0.113737	0.113931
.8-.008	0.113934	0.113737	0.113931

The temperature range was from 25.0 to 24.0 degrees C.

The data in Table I and Table II were taken on the "Queen" potentiometer which gives accurately five places and an estimation for the sixth place.

Some difficulty was encountered in making up cells which remained constant over a period of days. Fales and Mudge[1] met with the same difficulty and found that by allowing a newly made calomel cell to stand for two days before observations were made a constant electromotive force would be obtained. This was done and reasonably constant values were observed. Other observers[2] experienced this same trouble.

CONCLUSION

It is apparent that no change in the electromotive force has been found. Perhaps an explanation may be found in the transport numbers of the potassium chloride. They do not change appreciably even over a wide concentration range.

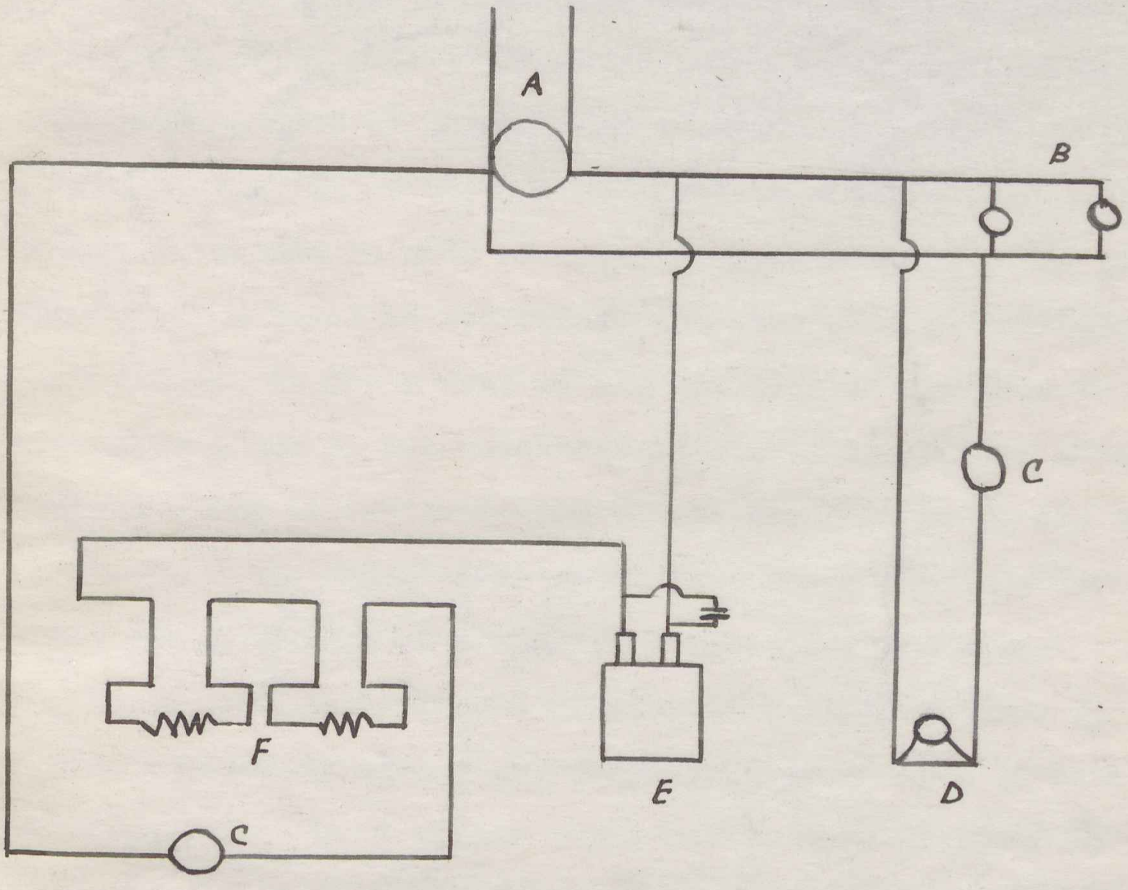
Schatchard[3] says that in considering the Debye-Huckel interionic theory one should expect that both the activities and mobilities should depend slightly upon the concentration gradignt and would scarcely expect to obtain a sufficient gradient in practice to show a measurable effect. He found further that the electromotive force of hydrochloric acid concentration cells increased a few hundredths of a millivolt when the liquid junction was made very thin. This fits in with the opinoin of Dr. Irving Langmuir[4] who believes that a change in electromotive force could be found only over the distance of a hundredth of a millimeter between a very high difference in concentration. In order to obtain this he suggested using a special glass manufactured by the Corning Gààss Company which contains boron oxide and silicon dioxide. When the glass is blown very thin, heat treated, and boron oxide dissolved out, a membrane-like glass is left which can be used for the junction. Then he continued, a situatuin not unlike that found in electrokinetic phenomena is met from which it would probably be impossible to separate out any effects due to the concentration gradient.

A second phase of the problem was a study of the diffusion of lead acetate in a silicic acid gel. This problem has been studied before by Rothemich,[5] Davies,[6] and Frazier.[7] These men have made an abstract of the literature concerning Liesegang phenomena in their theses.

EXPERIMENTAL

The probing electrode method described in the references above was used to examine the diffusion of lead acetate thru the silicic acid gel.

Lead wire electrodes, cut from sheet lead, were inserted into holes drilled in the walls of tubes A and B in cell I and fastened with de Khotinsky cement. A solution of two



THERMOSTAT CONTROL

A - Power Line
B - Interior Lamps
C - 100 Watt Resistance
D - Fan Motor
E - De Khotinsky Regulator
F - Heaters

parts nitric acid and five parts distilled water made a good rinsing solution for the lead electrodes.

Part C of cell I was filled with a gel containing 40 cc's of silicate solution, 10 cc's of acetic acid (1.8398N), and 10 cc's of .004285M lead acetate solution. Part A contained a solution of 20 cc's of silicate solution, 25 cc's of acetic acid, and 10 cc's of .4285M lead acetate. Into part B was poured a solution of 40 cc's of silicate solution, 10 cc's of acetic acid, and 20 cc's of .004285M lead acetate. The gel in tube C was allowed to set before the other two gel mixtures were added. At the moment of the addition of the gels to the two tubes A and B, potential readings were taken from connections leading to the lead wire electrodes such as A_1 and B_1 and so on up to A_7B_1. This meant that three readings were taken for each wire at A namely, A_1B_1, A_2B_2, and A_1B_3.

Cell II. Another cell similar to cell I was made up and filled completely with a gel consisting of 80 cc's of silicate solution, 20 cc's of acetic acid, and 20 cc's of .004825M lead acetate. It is to be observed that this is the same mixture that was used in part C of cell I. Then upon the gel surface in tube A 10 cc's of a solution of .4825M lead acetate diluted to the volume of the gel mixture in tube A of cell I, and upon the surface of the gel in tube B, 10 cc's of a solution of .004825M lead acetate diluted to the volume of the gel placed in tube B of cell I were allowed to diffuse into the respective tubes. As soon as these solutions were placed in position, potentiometer readings were taken.

Both cells were kept at 25 degrees C in an air thermostat. All electromotive force readings were taken on a Leeds and Northrup type K potentiometer.

CONCLUSION

Liesegang was the first to see the phenomena of rythmic precipitation when he added silver nitrate solution to the top of a gelatine gel containing potassium chromate. Ostwald explained that the silver ions migrated into the gel, met the chromate ions and formed a precipitate of silver chromate. Because the precipitation caused a deficiency of chromate ions, more of them migrated toward the precipitate and met the silver ions which continued to penetrate into the gelatine thereby causing the appearance of bands of silver chromate spaced in an arithmetic progression.

In the set up with the silicic acid gel, the lead acetate should migrate because of the difference in concentration which is in the ratio of 100 to 1. This migration was to be measured by the electromotive force method, for in reality, a concentration cell consisting of two different concentrations of lead acetate with lead electrodes is set up.

In order to show this diffusion Dr. Langmuir[4] believes that there should be a maximum change of .03 volts in the potentiometer readings because of the concentration ratio of 100 to 1. The data show no such change from beginning to end of the run. The largest change shown is .013 volts.

It is significant to note from the curves that a distinct maximum occurs within the first twenty-four hours of the run.

Cell I

Tube A	Tube B
Electrode	Electrode
7-10.1 cm. from lip of tube	3- 8.2 cm. from lip
6- 1 cm. from no. 7	2- 3.2 cm. from no. 3
5- 1 cm. from no. 6	1- 4.2 cm. from no. 2
4- 1.1 cm. from no. 5	Gel level at 7.4 cm.
3- .9 cm. from no. 4	below lip of tube B.
2- 1.9 cm. from no. 3	
1- 2.2 cm. from no. 2	

Cell II

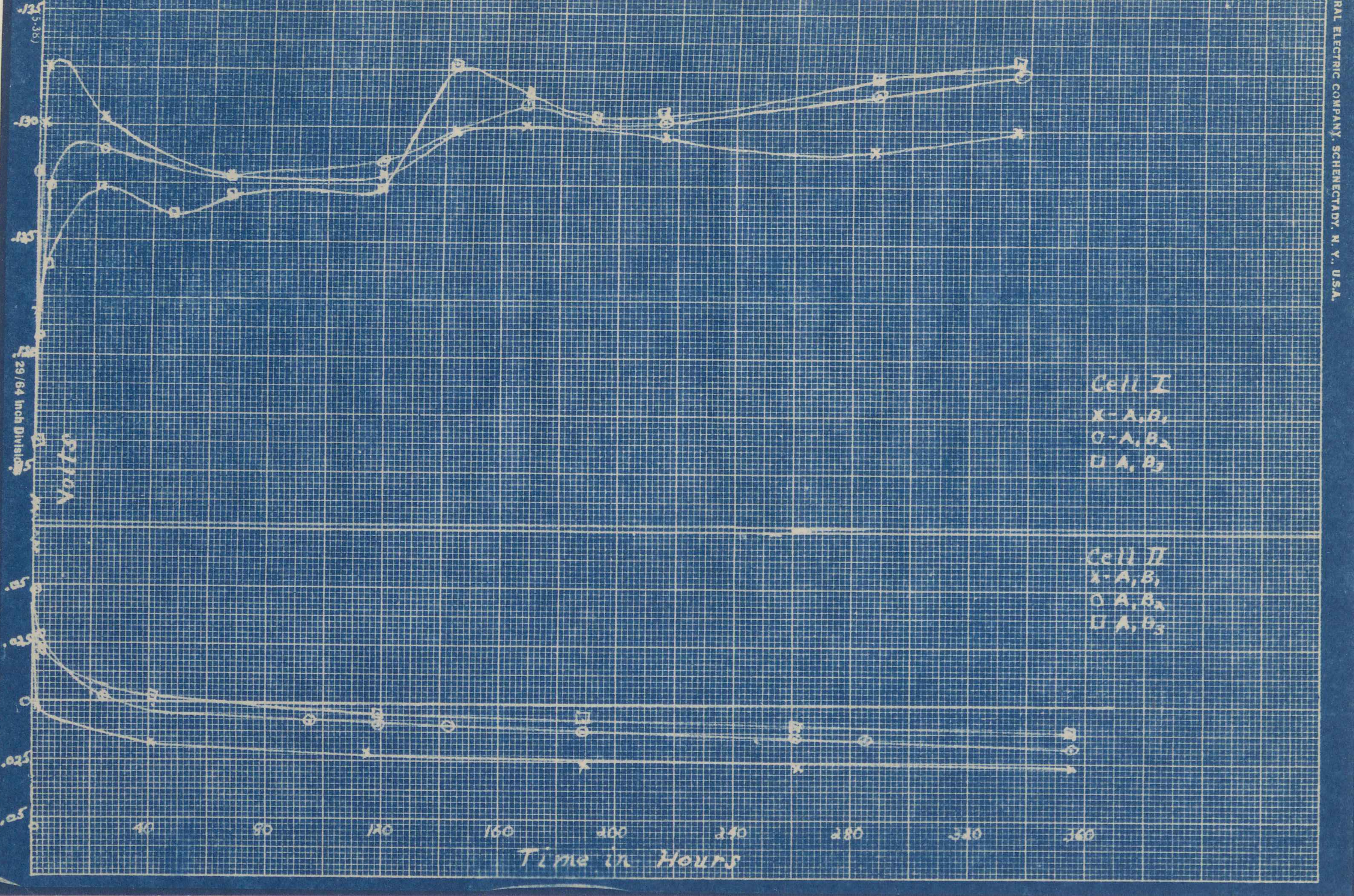
Tube A	Tube B
9- 7.2 cm. from lip of tube	3- 8 cm. from lip
8- .9 cm. from no. 9	2- 3.3 cm. from no. 3
7- 1.1 cm. from no. 8	2- 3.4 cm. from no. 2
6- .8 cm. from no. 7	Gel level at 7.5 cm.
5- 1.1 cm. from no. 6	below lip of tube B.
4- 1 cm. from no. 5	
3- 1.1 cm. from no. 4	
2- 1 cm. from no. 3	
1- 1.9 cm. from no. 2	

Cell I

Hours	A_1B_1	A_1B_2	A_1B_3
.43	.12105	.12803	.11630
.92	.12548	.12092	.12092
2.12	.12653	.12304	.12404
3.08	.12988	.12555	.12555
3.42	.13236	.12735	.12670
22.08	.13045	.12887	.12732
27.20	.12976	.12865	.12680
46.16	.12827	.12810	.12620
66.91	.12810	.12810	.12672
118.91	.12785	.12862	.12734
142.63	.12852	.12871	.13382
167.85	.12892	.12996	.13167
191.85	.12907	.13040	.13063
215.85	.12840	.13173	.13044
288.11	.12908	.13249	.13173
336.22	.13005	.13020	.13249

Cell II

.06	-.03850	.04848	.02935
1.16	-.00105	.03750	.02710
2.00	-.00415	.02971	.02315
20.58	-.00920	.00350	.00665
24.00	-.01040	.00184	.00465
41.50	-.01531	-.00144	.00209
94.91	-.02175	-.00790	-.00350
119.07	-.02256	-.00883	-.00490
143.19	-.02370	-.00966	-.00581
165.86	-.02480	-.01075	-.00725
189.53	-.02620	-.01156	-.00761
261.59	-.02775	-.01401	-.00930
285.26	-.02775	-.01470	-.01036
309.76	-.02685	-.01595	-.01128
332.36	-.02600	-.01720	-.01135
355.96	-.02520	-.01936	-.01160


Cell I
X - A, B1
O - A, B2
□ A, B3
Cell II
X - A, B1
O A, B2
□ A, B3
Volts
Time in Hours
40
80
120
160
200
240
280
320
360
.130
.025
29/64 Inch Divisions
RAL ELECTRIC COMPANY, SCHENECTADY, N. Y., U.S.A.

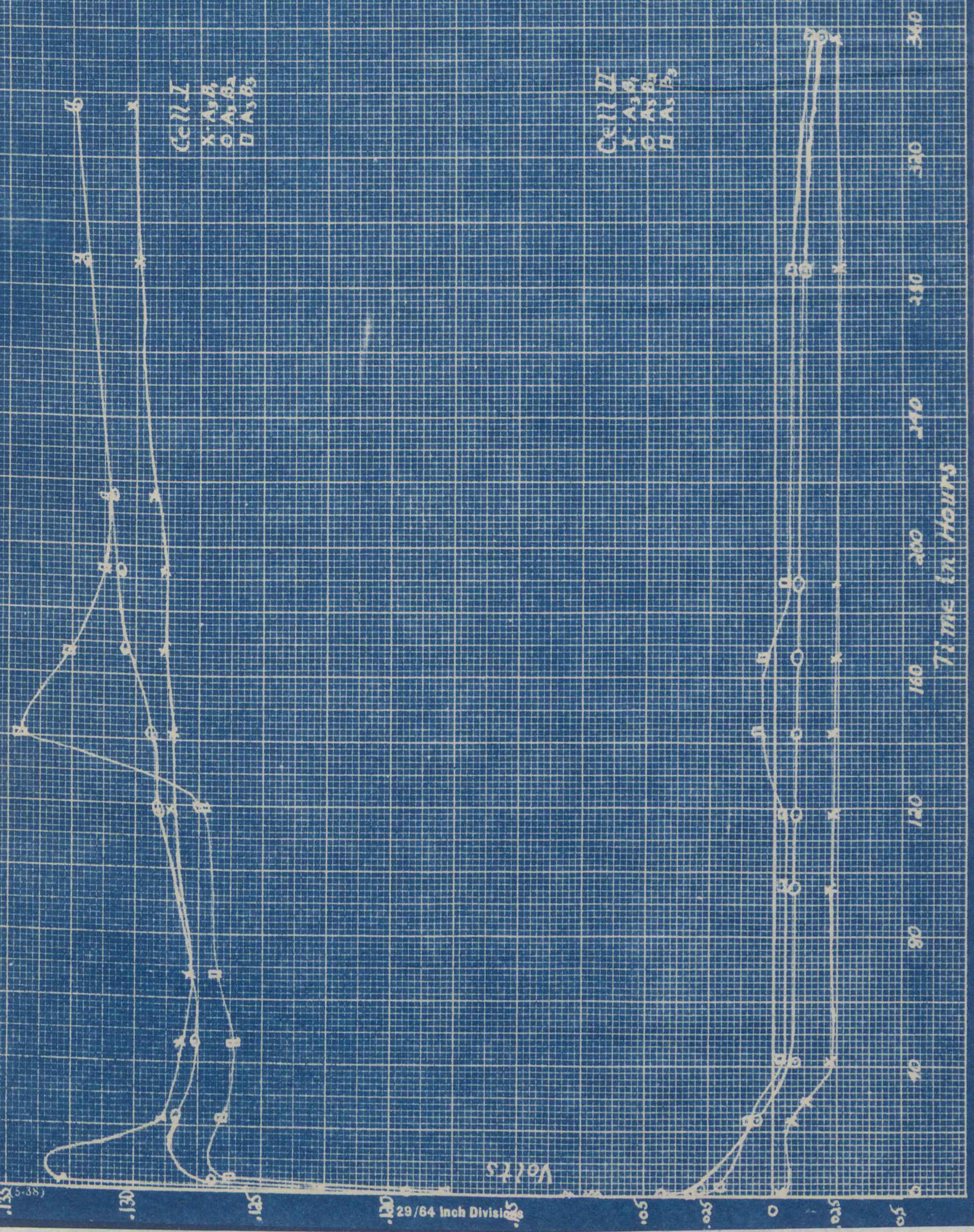
Cell I

Hours	A_3B_1	A_3B_2	A_3B_3
.58	.12274	.11947	.11792
1.05	.12565	.12205	.12188
1.73	.12695	.12335	.12433
2.63	.13010	.12585	.12555
3.33	.13289	.12740	.12645
22.21	.12995	.12844	.12663
27.32	.12986	.12863	.12644
46.25	.12830	.12815	.12611
67.08	.12785	.12785	.12684
119.05	.12840	.12917	.12744
142.82	.12833	.12930	.13456
167.98	.12893	.13038	.13253
192.01	.12885	.13060	.13116
216.01	.12925	.13097	.13097
288.25	.12993	.13203	.13203
336.36	.13021	.13240	.13252
383.92	.13056	.13240	.13275

Cell II

.24	-.00400	.04390	.02656
1.28	-.00351	.03415	.02436
2.15	-.00501	.02798	.02170
20.71	-.00581	.00656	.00921
24.08	-.00623	.00594	.00896
41.18	-.02334	-.00950	-.00570
95.04	-.02240	-.00856	-.00475
119.23	-.02280	-.00849	-.00467
143.33	-.02311	-.00862	-.00500
166.02	-.02356	-.00925	-.00494
189.69	-.02405	-.00952	-.00571
261.73	-.02506	-.01170	-.00723
285.37	-.02513	-.01230	-.00786
311.07	-.02463	-.01375	-.00921
333.45	-.02414	-.01590	-.00990
357.24	-.02404	-.01830	-.01055

AL ELECTRIC COMPANY, SCHENECTADY, N. Y., U.S.A.

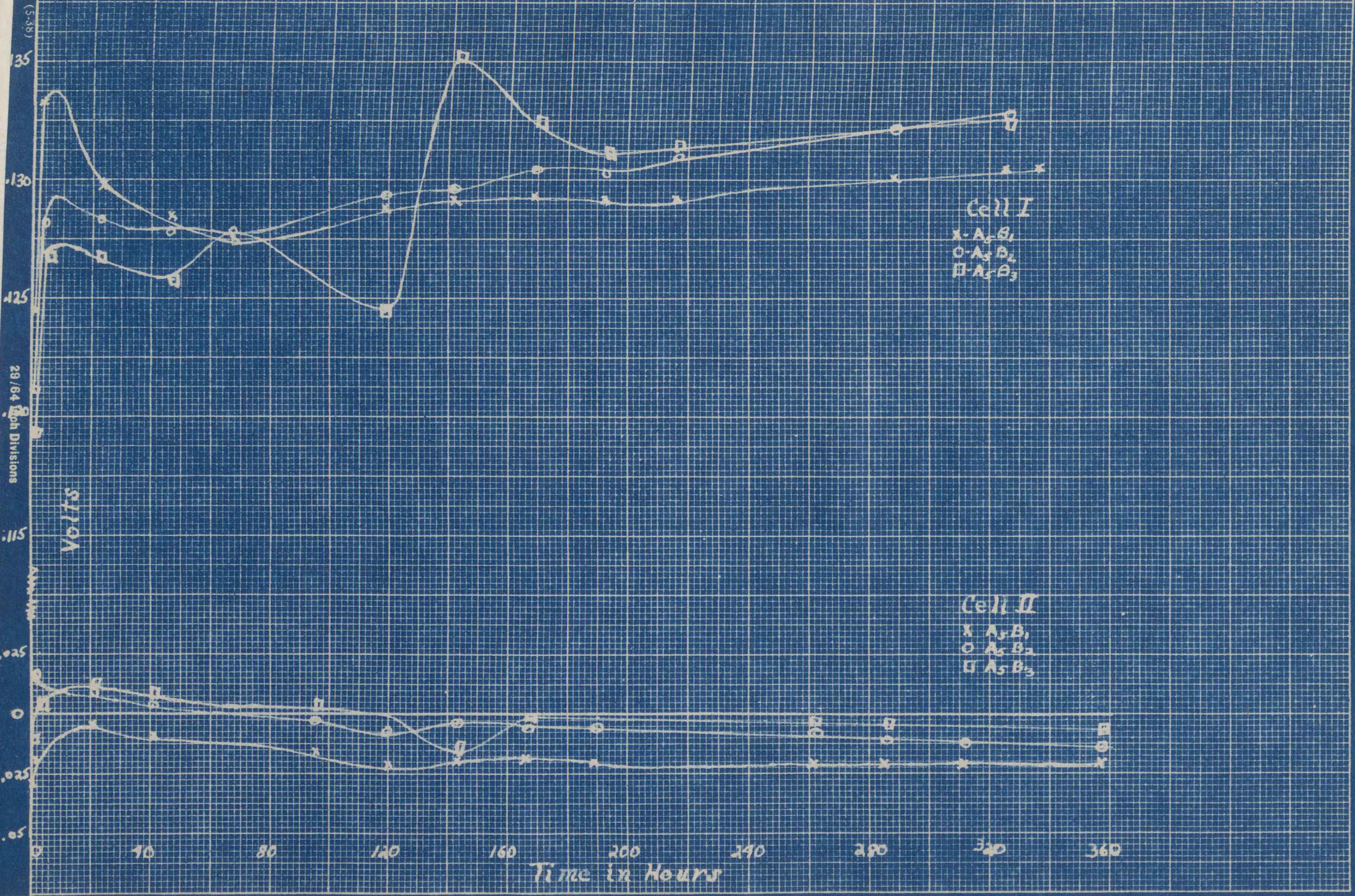


Cell I

Hours	A_5B_1	A_5B_2	A_5B_3
.65	.12447	.12105	.11952
1.15	.12617	.12300	.12256
2.02	.12638	.12605	.12518
2.74	.13047	.12620	.12600
3.41	.13319	.12750	.12690
22.34	.12968	.12839	.12672
27.39	.12967	.12849	.12625
46.38	.12829	.12802	.12582
67.21	.12766	.12766	.12766
119.16	.12860	.12941	.12450
142.91	.12880	.12970	.13541
168.14	.12936	.13053	.13235
192.11	.12916	.13048	.13116
216.12	.12944	.13095	.13124
288.37	.13004	.13218	.13128
336.52	.13036	.13270	.13270

Cell II

.44	-.02805	.01550	-.02806
1.47	-.02443	.01255	.00201
2.26	-.01965	.01345	.00757
20.79	-.00450	.00751	.01025
24.19	-.00742	.00506	.00832
41.31	-.01055	.00371	.00670
95.22	-.01733	-.02420	.00101
119.39	-.02292	-.00843	-.00038
143.46	-.01925	-.00466	-.01806
166.12	-.01915	-.00540	-.00154
189.79	-.02015	-.58000	-.00198
261.84	-.02140	-.00810	-.00344
285.46	-.02175	-.00874	-.00450
311.13	-.02135	-.01030	-.00550
333.73	-.02055	-.01165	-.00591
357.48	-.02030	-.01422	-.00662



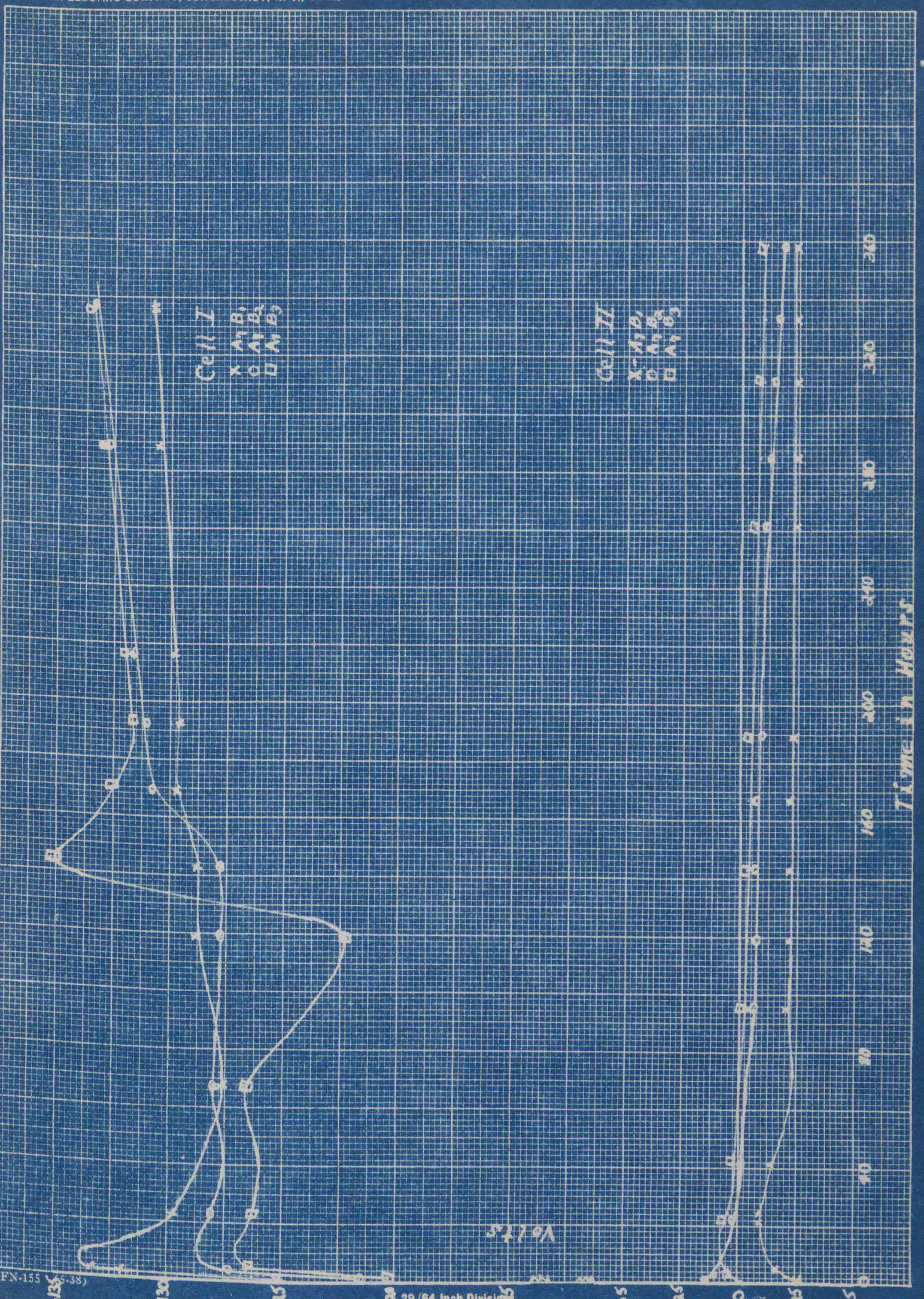
Cell I
X - As B1
O - As B2
□ - As B3
Cell II
X As B1
O As B2
□ As B3
Volts
.135
.130
.125
.115
.025
0
.025
.05
0
40
80
120
160
200
240
280
320
360
Time in Hours

Cell I

Hours	A_7B_1	A_7B_2	A_7B_3
.74	.12505	.12155	.12026
1.23	.12630	.12355	.12285
2.23	.12835	.12581	.12515
2.99	.13205	.12705	.12650
3.48	.13342	.12730	.12660
22.46	.12974	.12810	.12627
27.51	.12954	.12803	.12533
46.45	.12834	.12773	.12565
67.32	.12766	.12755	.12686
119.29	.12890	.12937	.12295
143.05	.12892	.12963	.13530
169.22	.12970	.13090	.13265
192.23	.12965	.13115	.13168
216.22	.12993	.13165	.13165
288.48	.13065	.13282	.13280
336.60	.13088	.13336	.13336

Cell II

.67	-.02675	.01381	-.00110
1.74	-.01580	.01185	.00232
2.40	-.02124	.01008	.00490
20.94	-.01015	.00195	.00509
24.30	-.01067	.00110	.00448
41.45	-.01439	-.00075	.00226
95.36	-.02042	-.00654	-.00305
119.56	-.02070	-.00670	-.00315
143.59	-.02124	-.00700	-.00320
166.23	-.02144	-.00688	-.00335
189.88	-.02256	-.00776	-.00375
261.97	-.02445	-.01087	-.00650
285.51	-.02550	-.01226	-.00806
311.26	-.02498	-.01385	-.00891
333.81	-.02417	-.01578	-.00966
357.76	-.02390	-.01846	-.01045


Cell I
X A1 B1
O A1 B2
□ A1 B3
Cell II
X- A1 B1
O A1 B2
□ A1 B3
Time in Hours
Volts
29/64 Inch Division

BIBLIOGRAPHY

1. Fales and Mudge- J. Am. Chem. Soc., 2434(1920)

2. Lewis, Brighton, and Sebastion-J. Am. Chem. Soc., 39, 2245(1917)

3. Scatchard and Buehrer- J. Am. Chem. Soc., 53, 574(1931)

4. Langmuir, I.- Consultation

5. Rothemich, E.- Master's Thesis (1932)

6. Davies, R.- Thesis (1933)

7. Fraser, W.- Thesis (1934)