

DECOMPOSITION VOLTAGES AND METAL OVERVOLTAGES
IN LIQUID AMMONIA AND IN WATER.

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TABLE OF CONTENTS.

	<u>Page.</u>
INTRODUCTION**-----	1
HISTORICAL.	
THE DIRECT METHOD -----	1
THE INDIRECT METHOD -----	4
THE CONTROVERSY BETWEEN THESE METHODS -----	5
APPARATUS AND METHOD -----	9
DIAGRAM OF CELL -----	10
DIAGRAM OF CIRCUITS EMPLOYED -----	12
EXPERIMENTAL -----	15
DATA. -----	17
SILVER NITRATE -----	19
SILVER NITRITE -----	23
SILVER IODIDE -----	27
NICKEL NITRATE -----	29
CADMIUM NITRATE -----	33
CADMIUM IODIDE -----	37
MERCURIC SALTS -----	39
LEAD NITRATE -----	47
ZINC NITRATE -----	49
ZINC IODIDE -----	53
COPPER NITRATE -----	57
COPPER SULPHATE -----	61
FERRIC NITRATE -----	63
AMMONIUM NITRATE -----	67
OTHER AMMONIUM SALTS -----	69

	<u>Page.</u>
TABLE OF RESULTS -----	75
RESULTS -----	76
DISCUSSION OF RESULTS -----	81
DEFINITION OF "DYNAMIC" DECOMPOSITION	
VOLTAGE -----	87
DEFINITION OF METAL OVERVOLTAGE -----	87
RELATION BETWEEN THE DYNAMIC DECOMPOSITION	
VOLTAGES AND THE METAL OVERVOLTAGES	
IN THE TWO SOLVENTS -----	88
SUMMARY -----	93
BIBLIOGRAPHY -----	96

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INTRODUCTION.

Most ^{of the} measurements of decomposition and overvoltages have been in water solutions. It has been the purpose of this investigation to determine the same in liquid ammonia. Wherever possible check runs were also made in water. The direct method, with modification from the usual method, was employed since this seems to be the only method capable of giving fairly consistent and reproducible results.

HISTORICAL.

The direct method of measuring decomposition and overvoltages was first suggested by Fuchs¹ in 1875. Later it was used by Caspari² in the determination of hydrogen overvoltages on various metals. He found that the hydrogen overvoltage increased with increase in current density. He says that it is but slightly influenced by the physical nature of the surface of the electrodes. His figures, however, do not support this last statement very well.

Dannenberg and Coehn³ measured the overvoltages

¹Pogg. Ann., 156, 158, (1875).

²Z. phys. Chem., 30, 89, (1899).

³Z. phys. Chem., 38, 609, (1901).

of hydrogen on various metals by measuring the voltage of the cathode against a hydrogen electrode. They plotted the potential against the current. The potential at which the break in the resulting curve occurred was taken as the overvoltage. Since the rise in the curve was rather abrupt and nearly vertical, this value is practically identical with the value obtained by extrapolating the upper straight part of the curve down to the line of zero current, as is done in the present work.

In 1901 Bancroft⁴ suggested a simplified form of apparatus for determining decomposition voltages. He says that even though the fall of potential varies with the apparatus used, any one apparatus will give consistent values and its use by the student will be a great help in the study of electrolysis.

Tafel⁵ in working with hydrogen overvoltages found that the values obtained depended on the current density used and that an increase in temperature or concentration decreased the overvoltage.

Bennewitz⁶, in determining hydrogen overvoltages, plotted the logarithms of the current against the voltage and claimed much better results. This has been criticised by various people. When the currents are

⁴J. Phys. Chem., 5, 133, (1901).

⁵Z. phys. Chem., 50, 641, (1905).

⁶Z. phys. Chem., 72, 202, (1910).

small the values of their logarithms change rapidly and one can make almost any value appear as the overvoltage, depending on what logarithm is assumed to represent the overvoltage.

Moeller⁷ has also determined hydrogen overvoltages. (See page 82).

Pring⁸, when working with metals deposited as films on platinum, found that different thicknesses for different metals were necessary in order to give the same hydrogen overvoltages as the pure metals in bulk form. He with Tainton⁹ found that various colloids and different acid strengths had certain effects on the deposition of zinc, seemingly due to changes in overvoltage.

MacInnes and Adler¹⁰, observed that there were fluctuations in the hydrogen overvoltage with the appearance and the liberation of bubbles from the surface of the electrodes. They expected an increase in overvoltage with decrease in pressure and found this to be the case. Evidently the potential of their hydrogen reference electrode was also greatly influenced by the change in pressure and may account for most of this difference.

⁷Z. phys. Chem., 65, 226, (1909).

⁸Z. Elektrochem., 19, 255, (1913).

⁹J. Chem. Soc., 105, 712, (1914).

¹⁰J. A. C. S., 41, 194, (1919).

Knobel, Caplan and Eiseman¹¹ determined the effect of current density on overvoltage. They believe that "a small glass tip less than one millimeter in diameter pressed against the active electrode while the current is flowing will give correct results". The solution from the reference electrode makes contact with the cathode through this glass tip.

The indirect method for measuring overvoltages was first used by Le Blanc¹². He made very extensive measurements using a tuning fork commutator or a double commutator driven by a motor. He determined the hydrogen overvoltage on many metals. His determinations of decomposition voltages are also outstanding and are among the best values obtainable. He has determined the "static" decomposition voltages of many acids, bases and salts at normal concentration.

Newbery¹³ has again taken up the commutator me-

¹¹Trans. Am. Electrochem. Soc., 43, 55, (1923).

¹²Z. phys. Chem., 5, 469, (1890); 8, 299, (1891); 12, 333, (1893); and Text Book of Electro-Chemistry, Pp. 287 - 320, English translation by Whitney and Brown.

¹³J. Chem. Soc., 105, 2419, (1914); 109, 1051, (1916); 109, 1066, (1916); 109, 1107, (1916); 109, 1359, (1916); 111, 470, (1917); 119, 477, (1921); 121, 7, (1922).

thod and has made a great many determinations on hydrogen overvoltages. He claims that the only overvoltages worth anything are those measured by the commutator method. He says that in the direct method you measure, what he calls, "transfer resistance" in addition to overvoltage and that the only method that gives consistent results is the indirect method with a rapidly rotating commutator. This has called forth a great controversy with Newbery on the one side and several others on the other side.

Holler¹⁴ in 1924 made measurements with an oscillograph operated by a resistance coupled electron-tube amplifier. In this way, he claims, no current is drawn from the electrode under investigation. By this method it is possible to tell just what part of the potential drop is due to resistance. He finds that when there is a gas evolved at an electrode, there is often considerable resistance causing a large part of the potential measured. He suggests the term "boundary resistance" in preference to Newbery's term "transfer resistance" since this calls for no theory as to the exact nature or source of the resistance.

The controversy mentioned above has given great impetus to the study of overvoltage and the results obtained are very valuable. The work of MacInnes and

¹⁴Scientific Papers of the Bureau of Standards, No. 504.

Adler¹⁵, who had used the direct method for the determination of hydrogen overvoltages, was severely criticised by Newbery¹⁶. "Unfortunately, their method of experiment and also certain vital parts of their reasoning are open to most serious objections. It is feared that these objections are of such a nature as to invalidate completely the whole work so far as its original purpose is concerned". He criticises their definition of overvoltage and says that the potential they measured depended not only upon the overvoltage but also upon the potential applied, the resistance of the electrolyte and upon the "transfer resistance".

MacInnes¹⁷ meets this criticism by repeating his definition of overvoltage as "the difference of potential that exists between a reversible hydrogen electrode and an electrode, in the same solution, at which hydrogen, H_2 , is being formed from hydrogen ions." He suggests that the potential obtained with a commutator device be called "counter electromotive force". The difference between this "counter electromotive force" and the overvoltage would then be the "transfer resistance". The controversy then resolves itself as to whether "counter electromotive force" or "overvoltage" is the more important and fundamental.

¹⁵ J. A. C. S., 41, 194, (1919).

¹⁶ J. A. C. S., 42, 2007, (1920).

¹⁷ J. A. C. S., 42, 2233, (1920).

Ferguson and Van Zyl¹⁸ have done a great deal to clear up this controversy. They employed both methods and showed that there is no difference between the direct and the commutator method of measuring, if in the latter method the discharge potential be measured immediately after breaking the charging circuit. Their method consisted in measuring this discharge potential soon after, throughout the whole interval, or only during the latter part of the interval when the charging circuit was broken. They found no consistency in the readings taken in these different ways. They have drawn the following conclusions: "(1) The absolute values obtained by the commutator method are practically meaningless, since they depend upon the mechanical construction and operation of the commutator. (2) There is a decided indication that the commutator and the direct methods would give the same values if the measurements by the commutator method be made at the instant the charging circuit is interrupted."

Knobel¹⁹ has carried the above even farther by measuring the overvoltage both during charge and during discharge. His commutator was so arranged that he could measure the overvoltage at any desired in-

¹⁸ Trans. Am. Electrochem. Soc., 45,
311, (1924).

¹⁹ J. A. C. S., 46, 2613, (1924).

interval after making or interrupting the charging circuit. His results show that the overvoltage on making rises from zero rather rapidly to a maximum and that on breaking it is at first equal to the potential on charge and then drops asymptotically to zero. This is shown in Figure 1. A represents the interval of charge, B, the interval of discharge, C, the overvoltage during the interval of charge A, and D represents the overvoltage during the interval of discharge B.

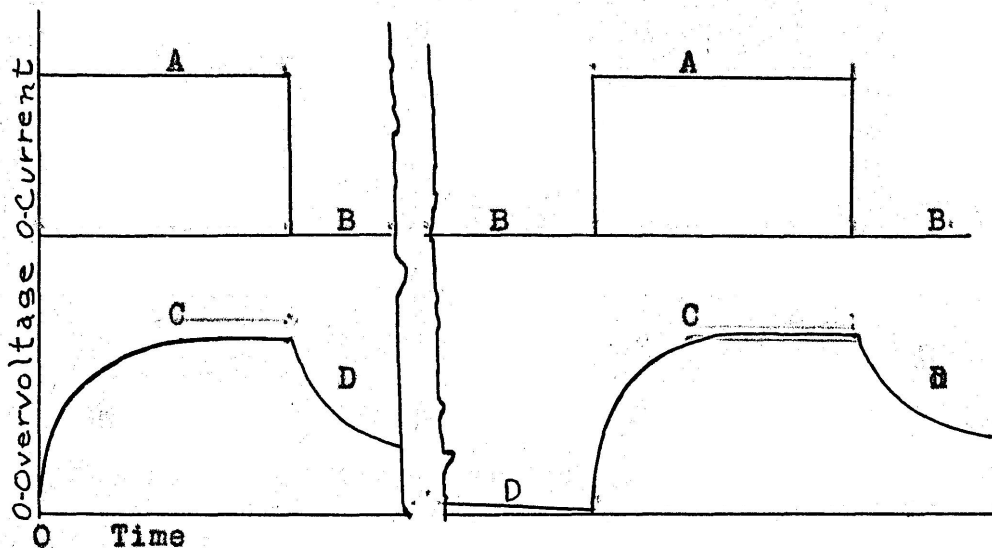


Figure 1.

You will note that the potential measured during charge will be maximum only when the interval is long enough for the overvoltage to build up to its maximum and then remain there for some time. The overvoltage measured on discharge will represent the average of the potential, at first equal to the overvoltage on charge and then decreasing in value. The actual value

obtained will depend upon the construction of the commutator and upon the length of the interval of time used between successive readings. If the charging interval is very short then the overvoltage will not build up to its maximum value. During very short intervals of discharge the measured overvoltages will be very nearly equal to the overvoltage built up during the charging interval. Again, if the intervals are longer then the overvoltage will reach its maximum on charge but these measured during discharge will be considerably lower. Knobel says that "the results indicate, without room for doubt, that the usual commutator method of measuring overvoltage is incorrect."

APPARATUS AND METHOD.

In this investigation the direct method with slight modification from the usual method was employed. It is customary to use stationary electrodes but this permits of great concentration polarization near the electrodes. To avoid this change in concentration the electrodes were rapidly rotated in the present work.

After much experimenting the cell shown in Figure 2 Page 10 was adopted. a' and b' are the electrodes made of platinum plates, approximately one-half square centimeter in size, sealed by means of platinum wires into glass tubes. The brass rings d and d' are each connected to one of the electrodes. a and b are

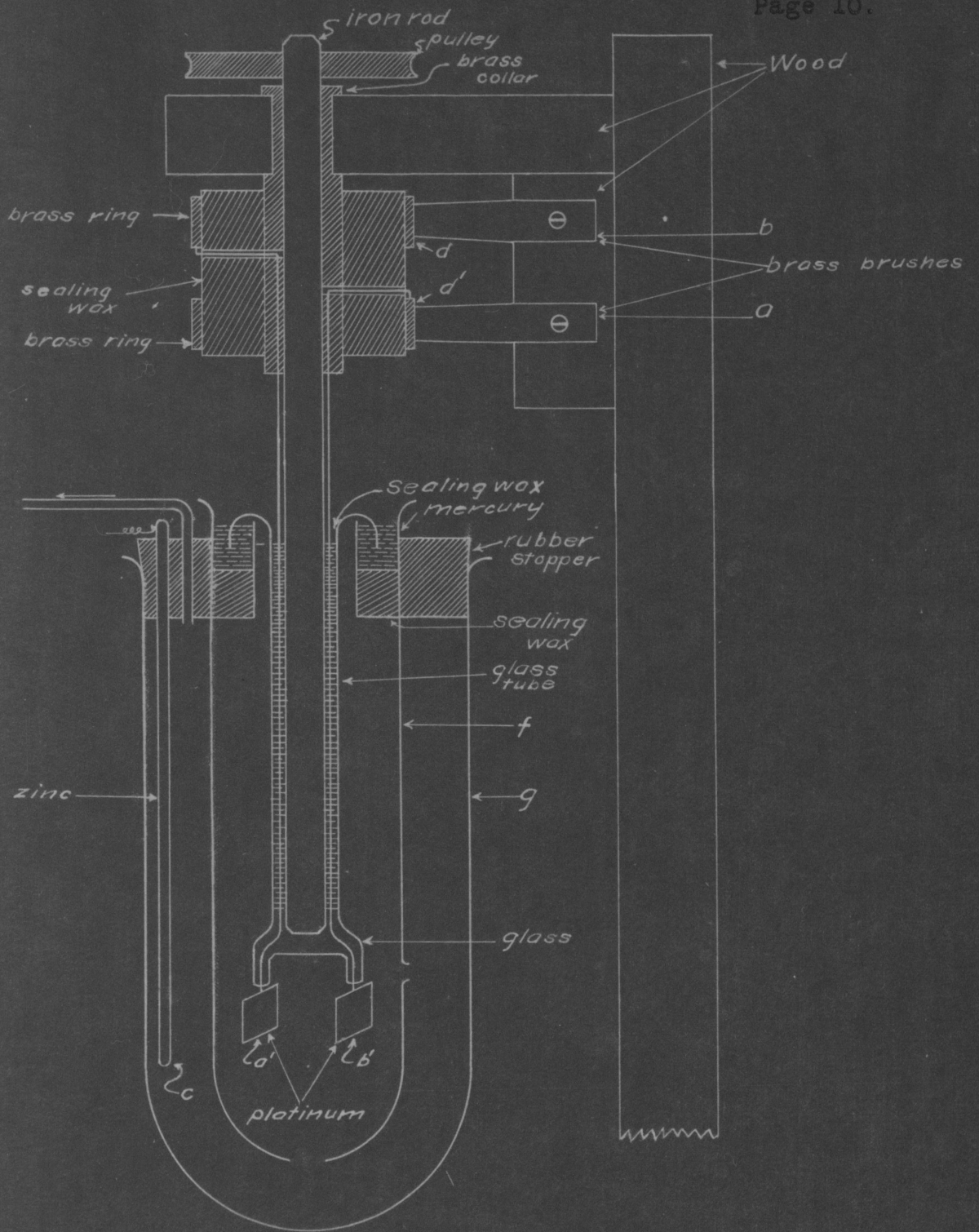


Figure 2.

Diagram of the Cell.

brushes making electrical contact with the rings d and d' and are each connected to a and b respectively of Figure 3 Page 12. The electrodes are mounted on a brass rod which passes through a bearing to a pulley. They may then be caused to rotate at any desired speed by a motor with variable speed. The glass tube f is open at the bottom and has an opening on the side away from the reference electrode c. The reference electrode c is of the same metal as the cation of the salt under investigation and is in direct connection with c of Figure 3 Page 12. The large test tube g contains the solution under investigation. The tube g is immersed in a Dewar flask containing liquid ammonia when working with this solvent. This serves to keep the temperature constant and will be at or slightly below the boiling point of liquid ammonia. When salts in water are investigated, g is immersed in a vessel containing ice and water to keep it at 0° C.

The arrangement of the apparatus finally used is shown in Figure 3 on Page 12. For the benefit of the reader we give in detail the manipulation of the various switches when making a run. The course of the currents can then be very readily followed. At the start switch No. IV is thrown to the left, the potentiometer is adjusted to the voltage of the standard cell, and then keys K and K' are closed. The galvanom-

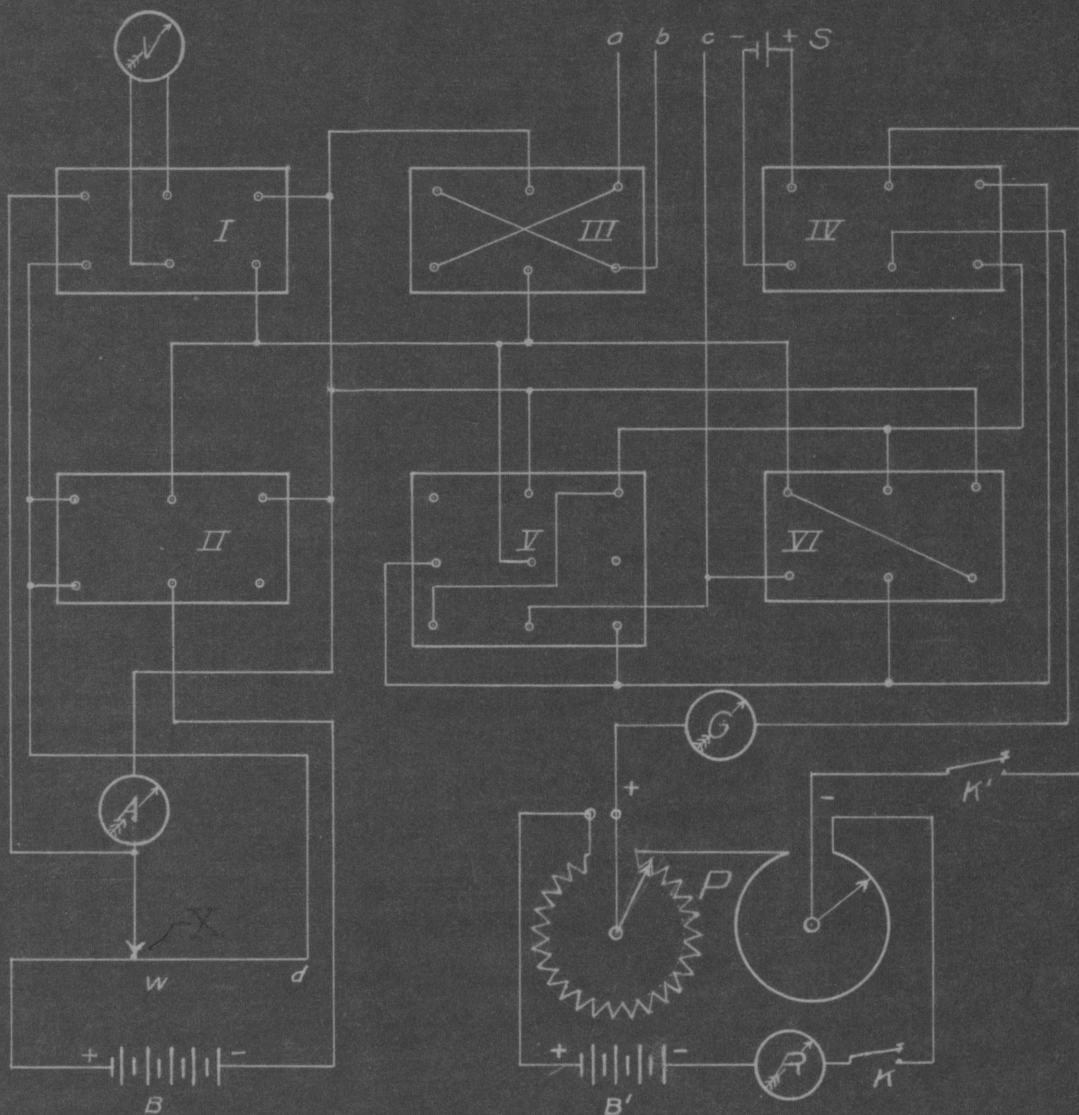


Figure 3. - Diagram of circuits employed. V, a Fritz Kohler voltmeter; A, a Jewell Electrical Instrument Co. milliammeter; G, a Leeds Northrup D'Arsonval galvanometer; R, a variable resistance; P, a Leeds Northrup potentiometer; W, a resistance with sliding contact; I to VI are double throw knife switches; a, b and c are leads to the cell Figure 2; S, a Weston Standard cell; K and K' are contact keys; and B and B' are dry batteries.

meter needle is displaced either to the right or to the left. The variable resistance R is then adjusted until there is no throw in the galvanometer. This makes the potentiometer direct reading. It will remain in perfect adjustment for hours at a time, much longer than is required for a run.

Having the solution in place, as described above, we now throw switch No. 3 either to the right or to the left, depending whether we the one or the other of the electrodes to be the cathode. The slide X is placed to the right and No. I and No. II are thrown to the left. The ammeter and the voltmeter are now connected and the cell is on charge. The potential applied is equal to the drop in potential between X and d. At the start the ammeter reads zero and as the voltage is increased, by sliding X to the left, will rise somewhat only to fall to zero or nearly so again. The slide X is moved to the left until the desired voltage is obtained, governed by the readings of the voltmeter and the ammeter, since as long as the current remains zero there would be no use in making any readings. Switches No. IV and No. VI are now thrown to the right and the keys K and K' are closed. The potentiometer is adjusted for zero throw in the galvanometer which then reads the potential applied to the two electrodes. This^{is} recorded as the voltage applied.

The metal overvoltage is next determined. Switches

No. I, No. II, No. III and No. IV are left as before and, if the potential of the reference electrode is more negative than the cathode, switch No. VI is thrown to the left, (if the reference electrode more positive then switch No. VI is left open and No. V is thrown to the left), keys K and K' are closed and the potentiometer adjusted for zero throw on the galvanometer. This potential is then recorded as the cathode overvoltage.

To have a check on the readings, switch No. V is thrown to the right, No. VI being open, keys K and K' are closed and the potentiometer is again adjusted. This gives us the potential between the reference electrode and the anode. These readings are not recorded in the data since this anode-reference electrode potential is equal to the difference between the voltage applied and the cathode overvoltage.

The ammeter is now read and its value recorded.

The slide X is now moved farther to the left, guided by the readings of the voltmeter and the ammeter, and a second series of readings made as above. This is continued until either one or the other of the instruments has reached its limit or the current has become erratic for some reason or other.

At the end of a run switch No. I is thrown to the right and then switch No. II is opened. The voltmeter now gives the voltage impressed by the cell. The

potentiometer is set to a value near that shown by the voltmeter. Switch No. II is thrown to the left, No. I is open and No. VI thrown to the right. Now switch No. II is quickly opened and immediately the keys K and K' are closed. This throws the galvanometer needle either to the left or to the right depending on the relative voltages of the cell and the potentiometer. After a few trials a value on the potentiometer can be found so that the galvanometer needle will be thrown one way for an instant and then swing to the other side. This represents the maximum voltage that the cell is able to impress under the conditions. This we have called the E. M. F. of the cell in the data.

When after a run the switches were all opened and switch No. IV thrown to the left, the potentiometer set to the standard cell and keys K and K' closed then there was always perfect adjustment of the potentiometer.

EXPERIMENTAL.

Pure dry liquid ammonia was obtained by condensing the vapors of ammonia drawn from a cylinder containing metallic sodium. About fifty cubic centimeters were condensed at a time, this amount being sufficient for a run.

The salts used were of the best c.p. salts obtainable. They were dried in a vacuum over phosphorous pentoxide. Copper nitrate could not be dried in

this way. It was dissolved in liquid ammonia and then by fractional crystallization copper nitrate with ammonia of crystallization was obtained. This was then further dried as above and was completely dehydrated as shown by the ordinary tests. Ferric nitrate was not completely dehydrated.

Enough salt, to make an approximately N/10 solution was weighed, put into the test tube g (Figure 2 page 10) and dry the dry liquid ammonia was introduced. It was then placed into position, immersed in liquid ammonia contained in a Dewar flask, and a run was ready to begin. The same process was followed when an investigation was to be carried out in water, except that the test tube g was immersed in a beaker containing ice and water.

After a complete run the current was plotted against the voltage applied and also against the cathode overvoltage. The upper straight part was extrapolated upon the line of zero current. The values obtained on the line of zero current are taken as the dynamic decomposition voltage and the metal overvoltage respectively.

The electrodes were treated with nitric acid after each run. After rotating them for some time in this acid they generally had the same potential as shown by the voltmeter or the potentiometer connecting them. The electrodes were thoroughly washed with

distilled water after which they were ready for another determination in water but to be used with liquid ammonia they first thoroughly dried. After using electrode a (Figure 2) as cathode for one of a pair of runs, switch No. 3 (Figure 3) was thrown the other way to bring electrode b into place to be used as cathode. Any difference in the two electrodes was thus compensated.

DATA.

The data is shown in the Tables I to XXXI. The "volts applied" is the voltage between electrodes a and b when the current was flowing and was measured by the potentiometer. The "volts reference" is the potential that existed between the reference electrode and the cathode, at the time when the corresponding current was read, and was also measured by the potentiometer. Whenever the reference electrode was negative with respect to the cathode there is a minus (-) sign before the voltage. This has been called an undervoltage. Whenever the reference electrode was the more positive, and this was the more general, then there is either a plus sign or no sign before the voltages. The "current" is the reading shown by the milliammeter during the above mentioned interval. The time between successive readings was generally about one-half minute.

The E. M. F. of the cell is the potential measured by the potentiometer in the way described on page 15.

All the values in the Tables are plotted on the Plates opposite the pages where the Tables occur. The decomposition voltages are the values read off the plots. The same is true for the metal overvoltages. The average decomposition and the average cathode overvoltages are obtained by averaging all the values obtained for that particular determination.

Table Number XXXII Page 75 is a summary of the averages from the Tables I to XXXI.

TABLE NUMBER I.

TABLE NUMBER I.

Silver Nitrate in liquid Ammonia.

Cur-ent.	Volts applied.	Volts reference.	Cur-ent.	Volts applied.	Volts reference.
<u>First Trial.</u>			8.85	1.396	0.476
See Plate I (1).			19.0	1.738	0.682
			31.0	2.108	0.926
			43.0	2.478	1.144
0.10	0.712	0.152	Decomposition		
0.25	0.780	0.170	Voltage 1.11 volts.		
0.60	0.880	0.210	Cathode Over-		
1.30	0.970	0.250	voltage 0.28 volts.		
3.44	1.078	0.322	<u>Third Trial.</u>		
7.00	1.104	0.350	See Plate I (3).		
9.75	1.144	0.372	0.12	0.700	0.172
Decomposition			0.28	0.798	0.222
Voltage 1.045 volts.			0.90	0.994	0.280
Cathode Over-			1.48	1.096	0.322
voltage 0.29 volts.			2.55	1.196	0.336
<u>Second Trial.</u>			9.20	1.432	0.466
See Plate I (2).			Decomposition		
			Voltage 1.11 volts.		
0.15	0.779	0.225	Cathode Over-		
0.96	0.988	0.308	voltage 0.30 volts.		
4.95	1.274	0.408			

Average Decomposition Voltage 1.09 volts.

Average Cathode Overvoltage 0.29 volts.

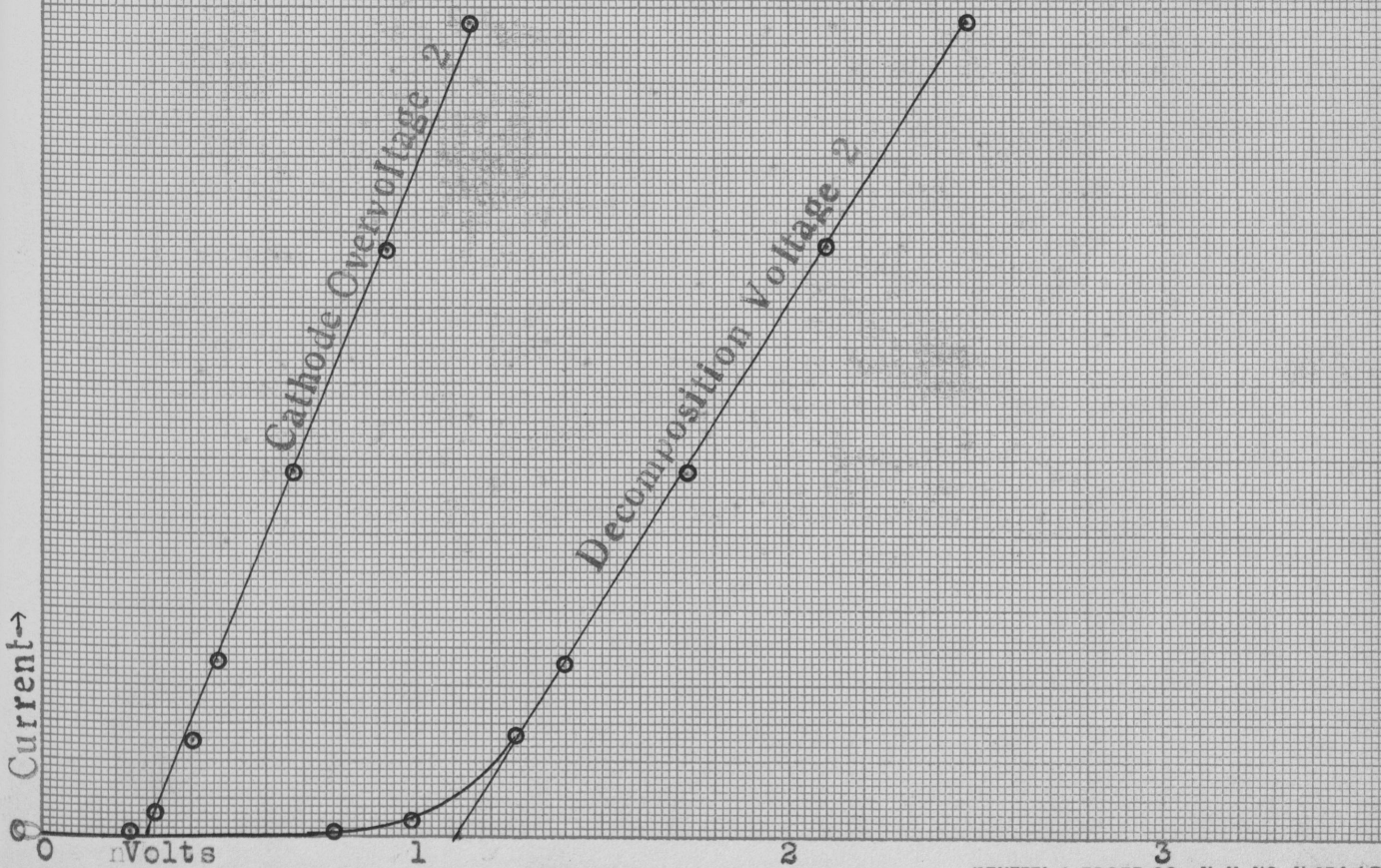
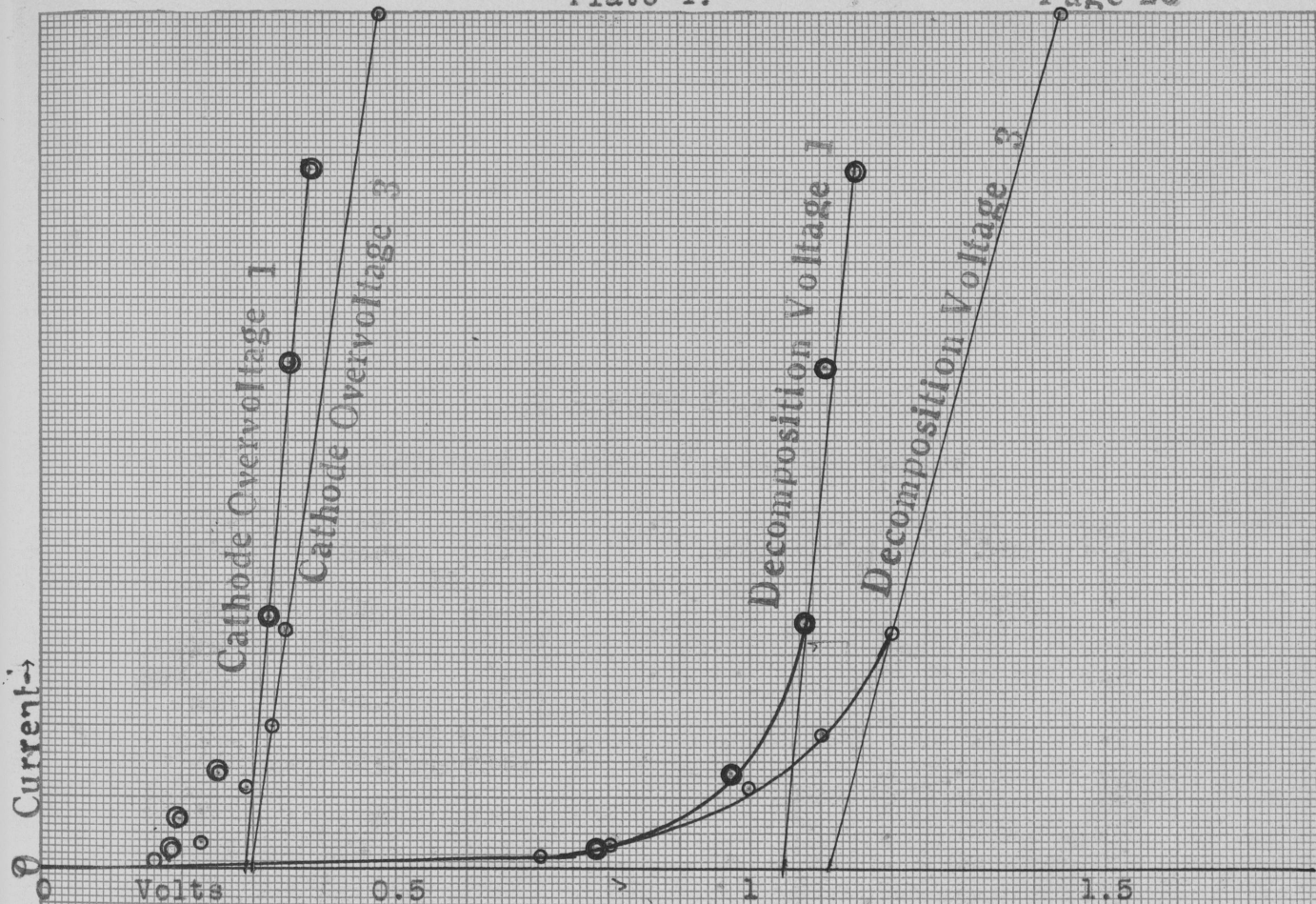


TABLE NUMBER II.

TABLE NUMBER II.

Silver Nitrate in Water.

Current. Volts Volts Current. Volts Volts
applied.reference. applied.reference.

First Trial.

See Plate II (1).

0.07 0.702 0.002
0.60 0.794 0.012
5.30 0.838 0.038
10.5 0.857 0.043

Decomposition
Voltage 0.82 volts.

Cathode Over-
voltage 0.01 volts.

E.M.F. 0.80 volts.

Second Trial.

See Plate II (2).

0.7 0.880 0.060
1.9 0.972 0.090
5.0 1.184 0.176
8.28 1.388 0.246

(Continued above)

11.0 1.596 0.340
15.0 1.796 0.440

Decomposition
Voltage 0.85 volts.

Cathode Over-
voltage 0.04 volts.

E.M.F. 0.80 volts.

Third Trial.

See Plate II (3).

1.2 0.984 0.060
4.2 1.184 0.140
7.4 1.354 0.328
11.0 1.592 0.366
15.0 1.800 0.458
19.5 1.994 0.582

Decomposition
Voltage 0.94 volts.

Cathode Over-
voltage 0.01 volts.

E.M.F. 0.83 volts.

Average Decomposition Voltage 0.87 volts.

Average Cathode Overvoltage 0.02 volts.

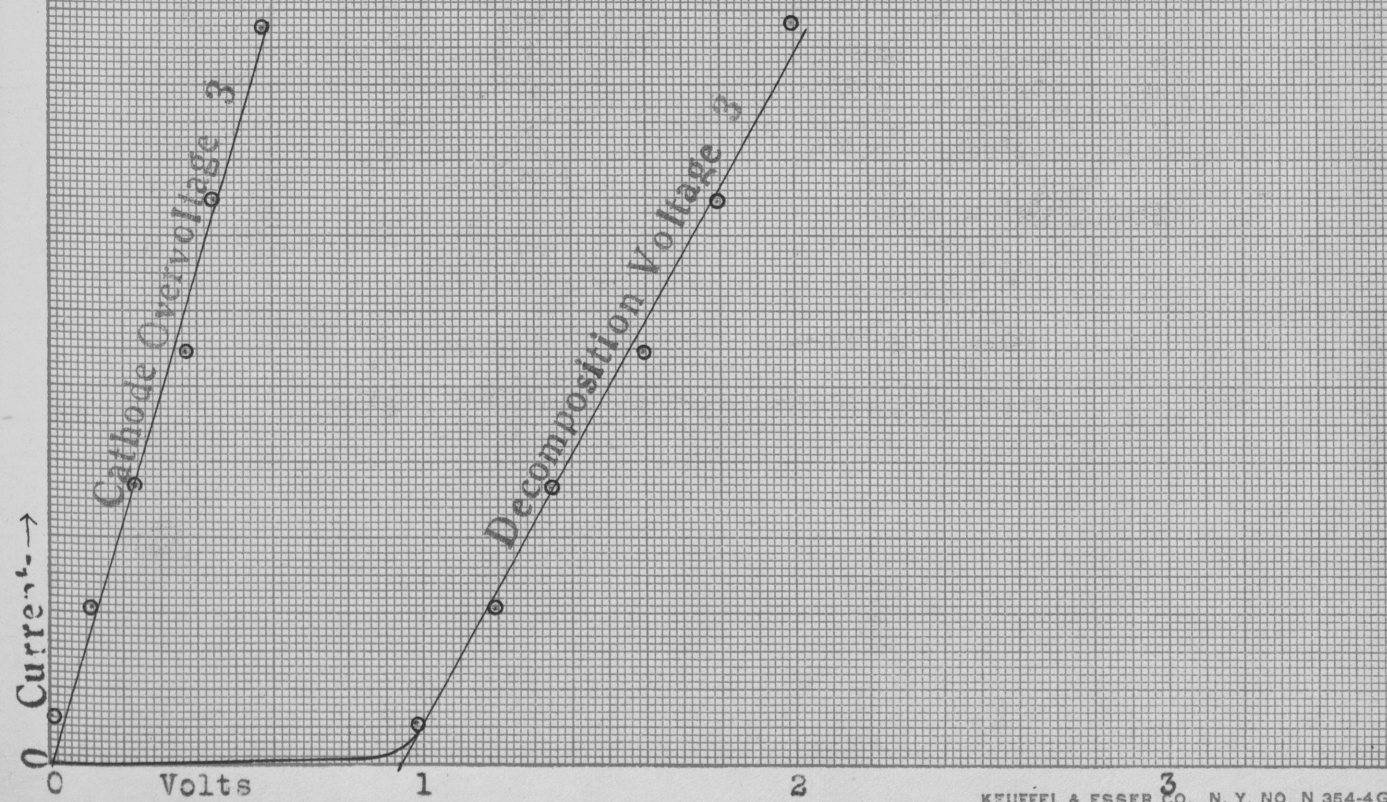
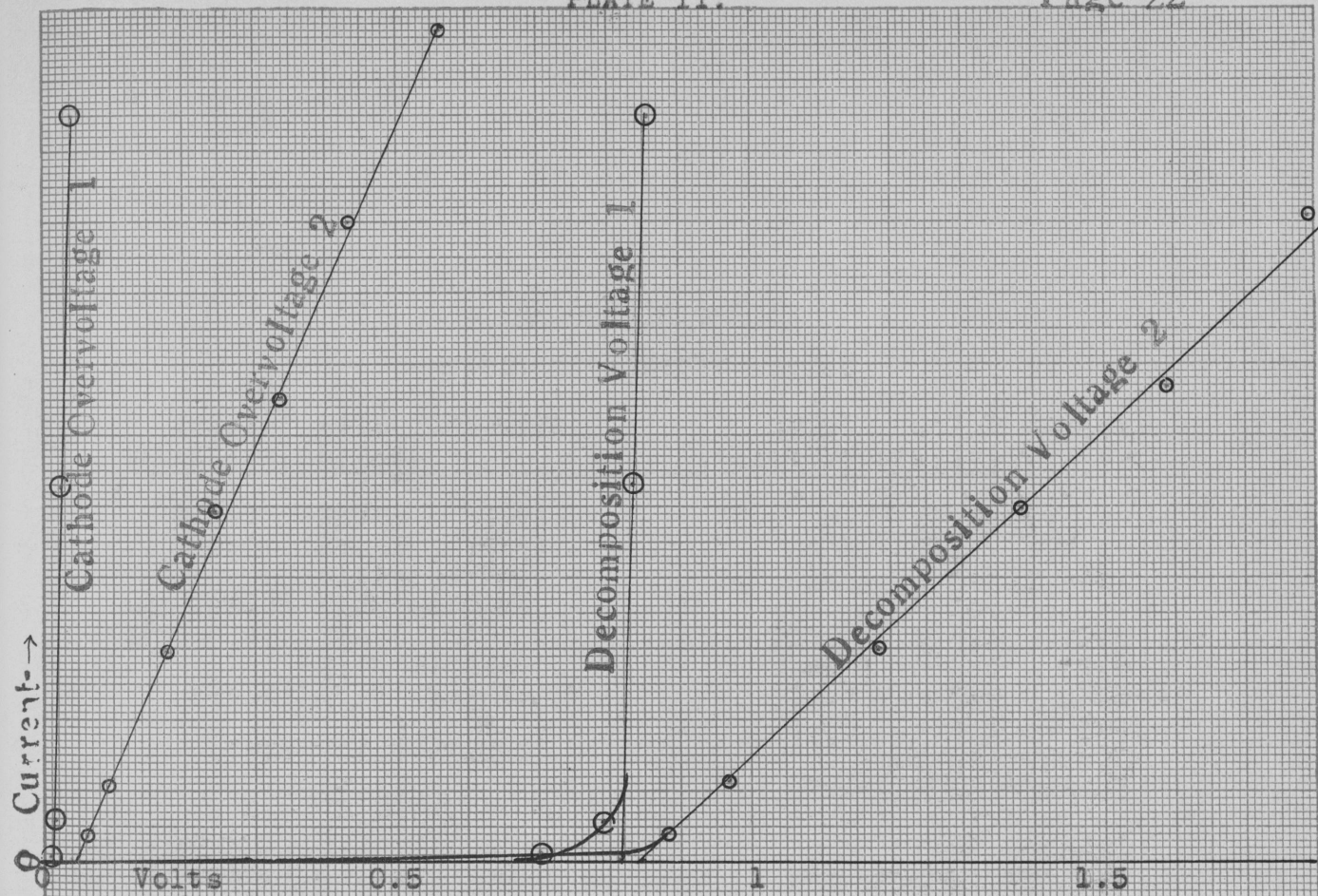


TABLE NUMBERV III.

TABLE NUMBER III.

Silver Nitrite in Liquid Ammonia.

Current. Volts	Volts	Current. Volts	Volts
applied.	reference.	applied.	reference.

First Trial.

See Plate III (1).

0.10	0.806	0.170
0.34	0.878	0.214
0.93	1.002	0.286
2.20	1.062	0.298
3.70	1.164	0.364
5.30	1.232	0.386
7.00	1.298	0.434
8.70	1.398	0.482

Decomposition
Voltage 0.97 volts.

Cathode Over-
voltage 0.26 volts.

Second Trial.

See Plate III (3).

0.14	0.806	0.228
0.38	0.894	0.272
1.00	0.976	0.308
2.17	1.088	0.244
3.55	1.154	0.380
5.30	1.210	0.410
7.40	1.316	0.460
9.50	1.372	0.484

Decomposition
Voltage 1.00 volts.

Cathode Over-
voltage 0.30 volts.

Third Trial.

See Plate III (3).

0.95	0.988	0.318
9.70	1.400	0.496
20.0	1.776	0.702
31.0	2.114	0.920
43.0	2.494	1.120

Decomposition
Voltage 1.10 volts.

Cathode Over-
voltage 0.30 volts.

Fourth Trial.

See Plate III (4)

0.99	0.984	0.238
4.10	1.200	0.332
8.60	1.392	0.430
12.5	1.584	0.558
17.0	1.778	0.636
21.0	1.980	0.752
25.0	2.168	0.850
30.0	2.358	0.930
35.0	2.530	1.000
39.0	2.714	1.106
44.0	2.924	1.190
48.0	3.118	1.292

Decomposition
Voltage 1.02 volts.

Cathode Over-
voltage 0.25 volts.

Average Decomposition Voltage 1.02 volts.

Average Cathode Overvoltage 0.28 volts.

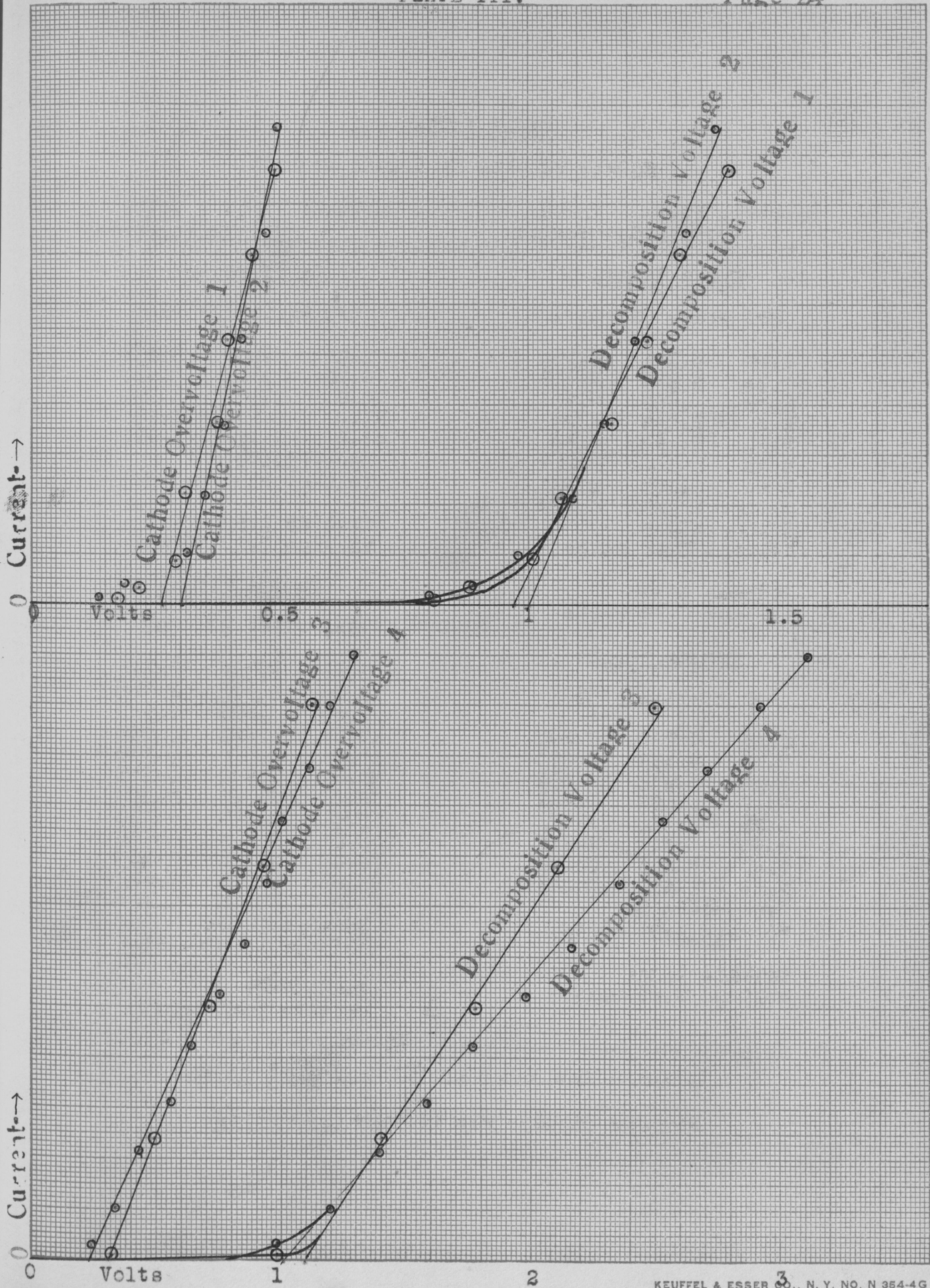


TABLE NUMBER IV.

TABLE NUMBER IV.

Silver Nitrite in Water.

Current.	Volts applied.	Volts reference	Current.	Volts applied.	Volts reference.
----------	-------------------	--------------------	----------	-------------------	---------------------

First Trial.

See Plate IV (1).

0.05	0.197	0.037
0.42	0.298	0.066
1.03	0.388	0.104
1.80	0.478	0.146
2.95	0.568	0.174
3.85	0.650	0.214
4.75	0.734	0.252
6.60	0.916	0.346
8.48	1.086	0.434
9.50	1.184	0.480

Decomposition
Voltage 0.30 volts.

Cathode Over-
voltage 0.10 volts.

Second Trial.

See Plate IV (2).

0.30	0.496	0.096
0.67	0.758	0.214
1.00	0.980	0.302
1.72	1.476	0.508
2.50	1.964	0.964
3.20	2.458	0.940

(Continued above).

4.15	2.918	1.328
5.00	3.426	1.582

Decomposition
Voltage 0.30 Volts.

Cathode Over-
voltage 0.02 volts.

Third Trial.

See Plate IV (3).

0.32	0.502	0.130
0.65	0.736	0.238
1.02	0.982	0.362
1.41	1.230	0.474
2.23	1.714	0.710
2.62	1.962	0.832
3.02	2.216	0.950
3.40	2.452	1.070
4.20	2.938	1.296
5.00	3.444	1.524
5.80	3.906	1.728
6.60	4.396	1.926
7.00	4.600	2.018

Decomposition
Voltage 0.350 volts.

Cathode Over-
voltage 0.05 volts.

E.M.F. 0.24 volts.

Average Decomposition Voltage 0.32 volts.

Average Cathode Overvoltage 0.06 volts.

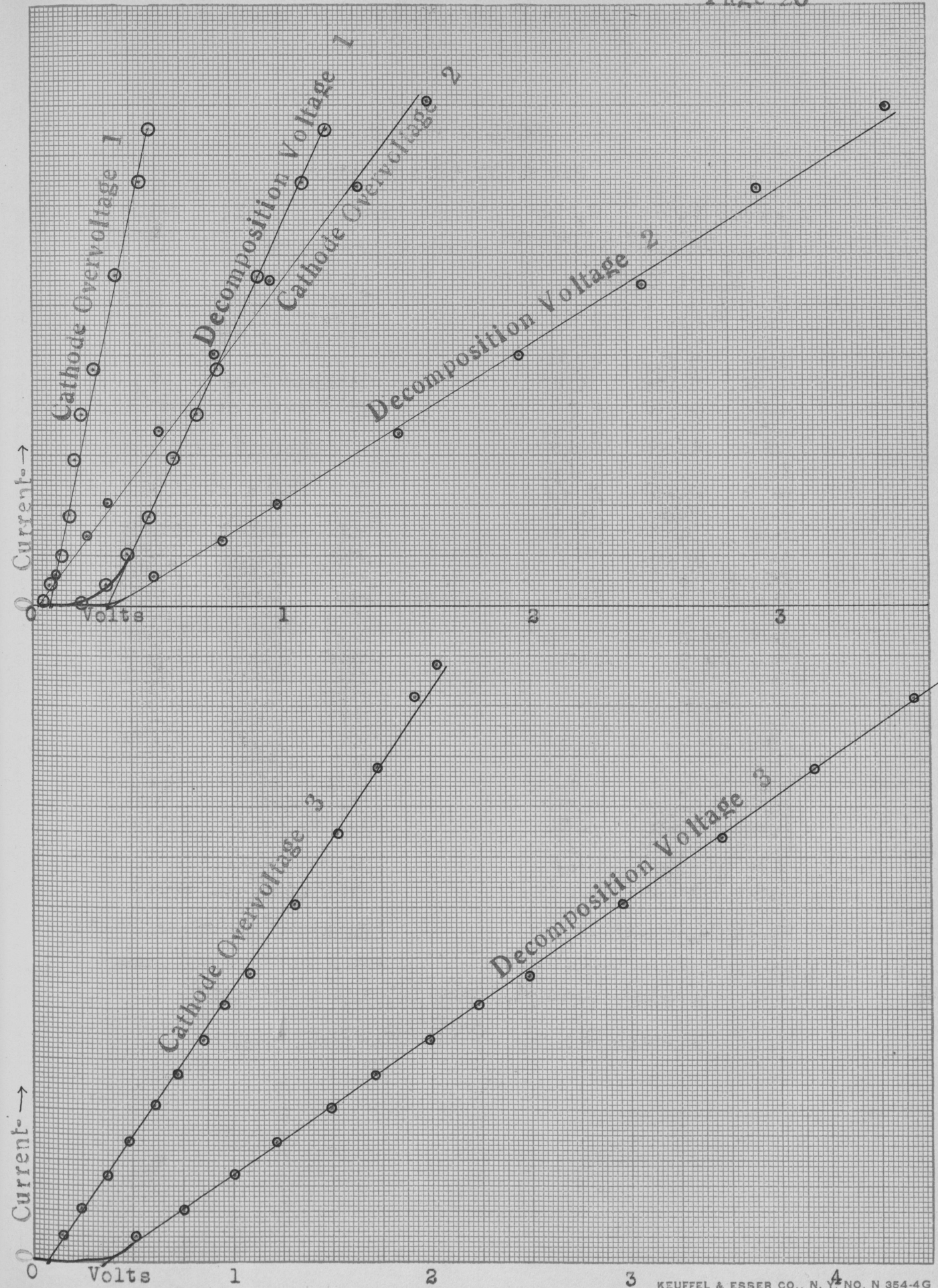


TABLE NUMBER V.

TABLE NUMBER V.

Silver Iodide in Liquid Ammonia.

Current. Volts	Volts	Current. Volts	Volts
applied.	reference.	applied.	reference.

First Trial.

Second Trial.

See Plate V (1).

See Plate V (2).

0.7	0.914	0.130
1.1	1.022	0.174
2.0	1.212	0.246
3.1	1.410	0.340
4.2	1.610	0.430
5.2	1.816	0.526
6.2	2.006	0.632
7.3	2.206	0.738
8.5	2.414	0.844
9.8	2.606	0.948
10.6	2.794	1.046
12.0	2.990	1.148

0.7	1.016	0.142
1.3	1.218	0.242
2.3	1.426	0.334
3.2	1.620	0.426
4.1	1.816	0.522
4.8	2.016	0.612
5.3	2.210	0.706
6.1	2.408	0.802

Decomposition
Voltage 0.85 volts.

Decomposition
Voltage 0.84 volts.

Cathode Over-
voltage 0.05 volts.

Cathode Over-
voltage 0.05 volts.

E.M.F. 0.45 volts.

Average Decomposition Voltage 0.85 volts.

Average Cathode Overvoltage 0.05 volts.

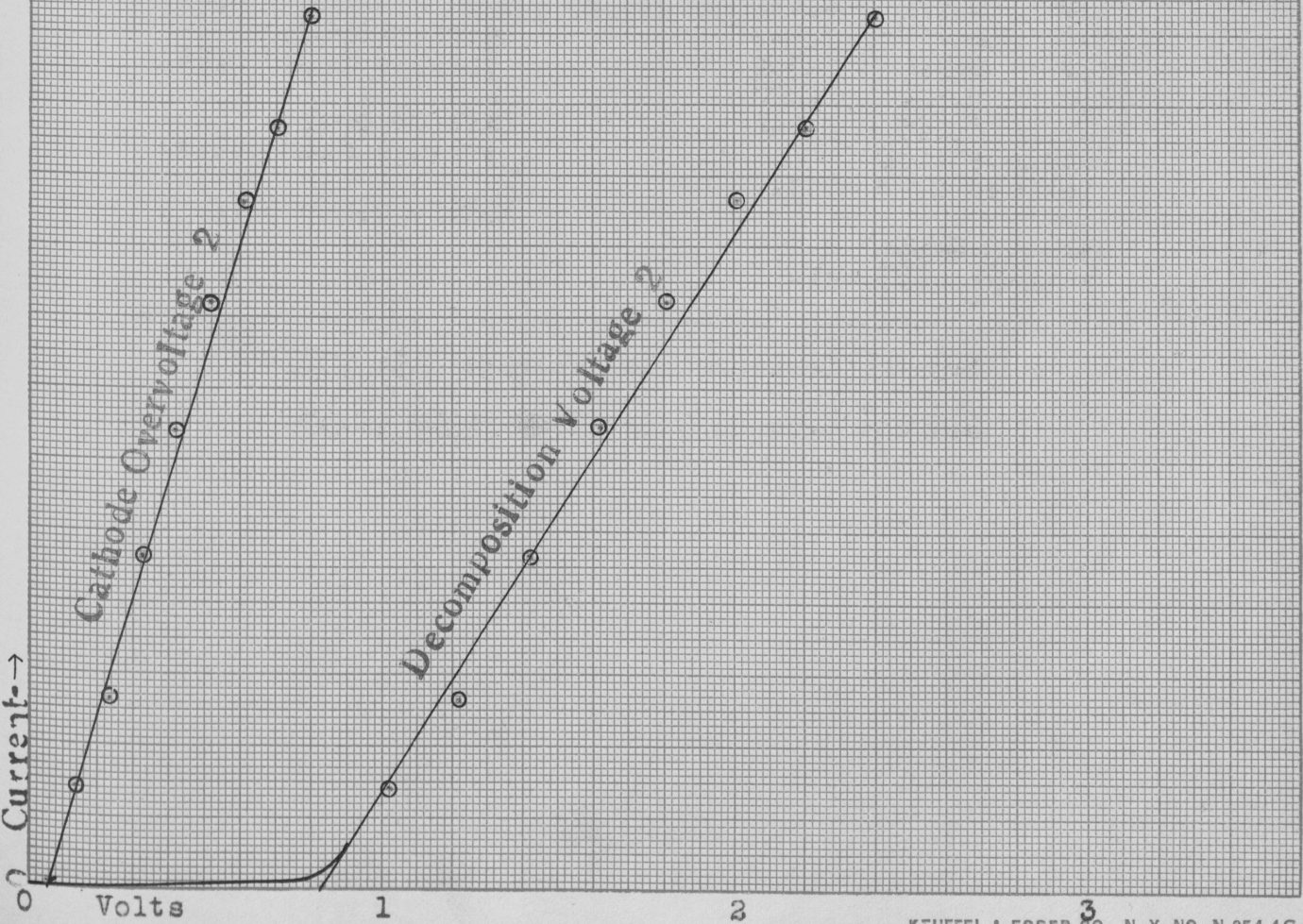
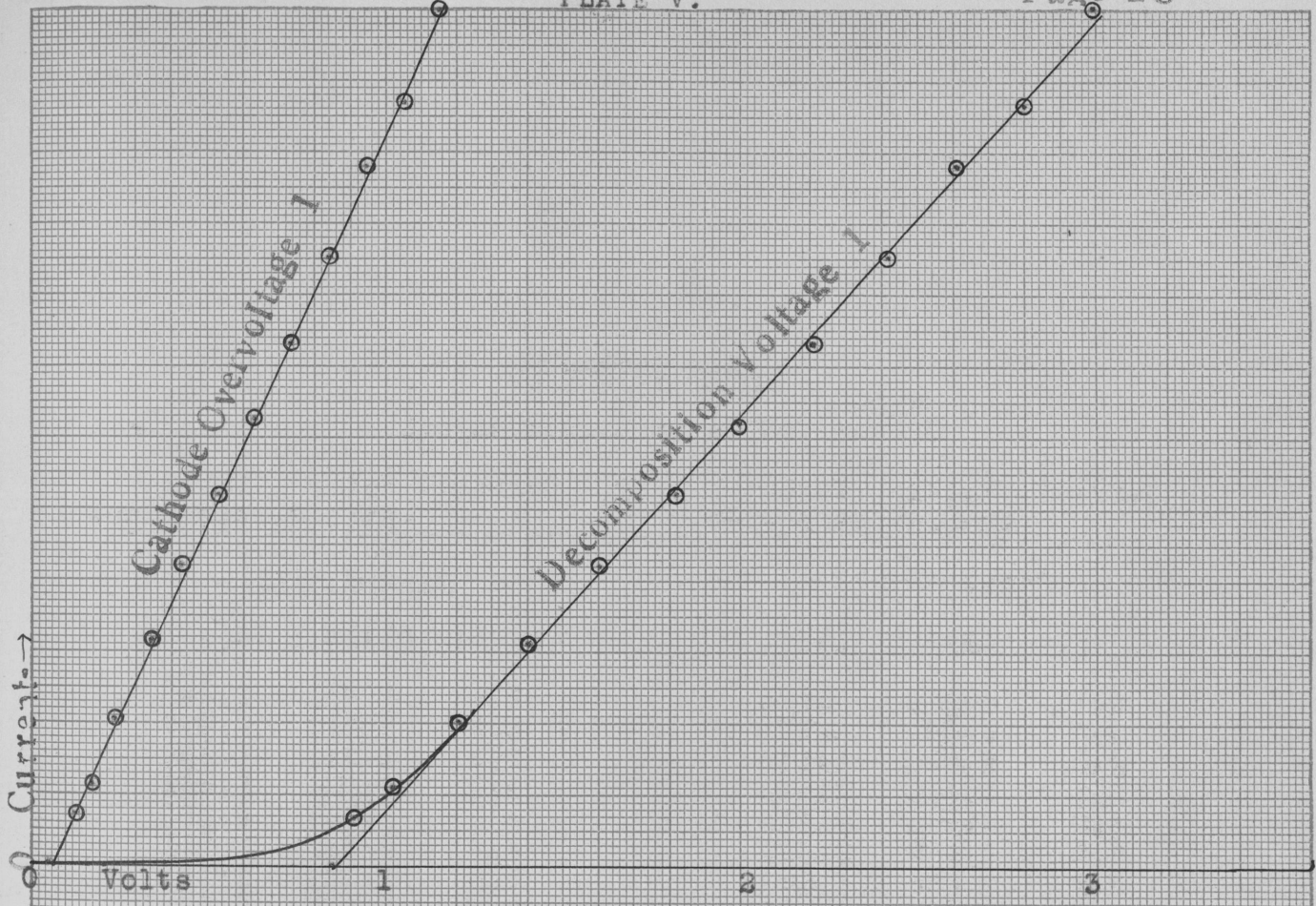


TABLE NUMBER VI.

TABLE NUMBER VI.

Nickel Nitrate in Liquid Ammonia.

Current.	Volts applied.	Volts reference.	Current.	Volts applied.	Volts reference.
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First Trial.

See Plate VI (1).

0.3	0.970	0.070
0.5	1.494	0.408
0.6	1.998	0.934
1.8	2.440	1.366
5.2	2.870	1.616
8.9	3.354	1.922
12.0	3.788	2.280

Decomposition
Voltage 2.175 volts.

Cathode Over-
voltage 1.20 volts.

Second Trial.

See Plate VI (2).

0.90	0.976	0.126
1.40	1.486	0.594
1.90	1.986	1.054
2.40	2.218	2.246
3.10	2.424	1.404
5.10	2.692	1.560
6.85	2.860	1.646

9.5	3.126	1.778
12.0	3.254	1.898
18.0	3.984	2.220
25.0	4.600	2.536

Decomposition
Voltage 2.20 volts.

Cathode Over-
voltage 1.30 volts.

Third Trial.

See Plate VI (3)

0.95	1.482	0.460
1.00	1.738	0.730
1.18	1.982	0.978
1.50	2.230	1.216
2.15	2.468	1.422
3.70	2.698	1.584
5.70	2.920	1.712
9.45	3.364	1.980
12.0	3.822	2.264

Decomposition
Voltage 2.20 volts.

Cathode Over-
voltage 1.25 volts.

Average Decomposition Voltage 2.19 volts.

Average Cathode Overvoltage 1.25 volts.

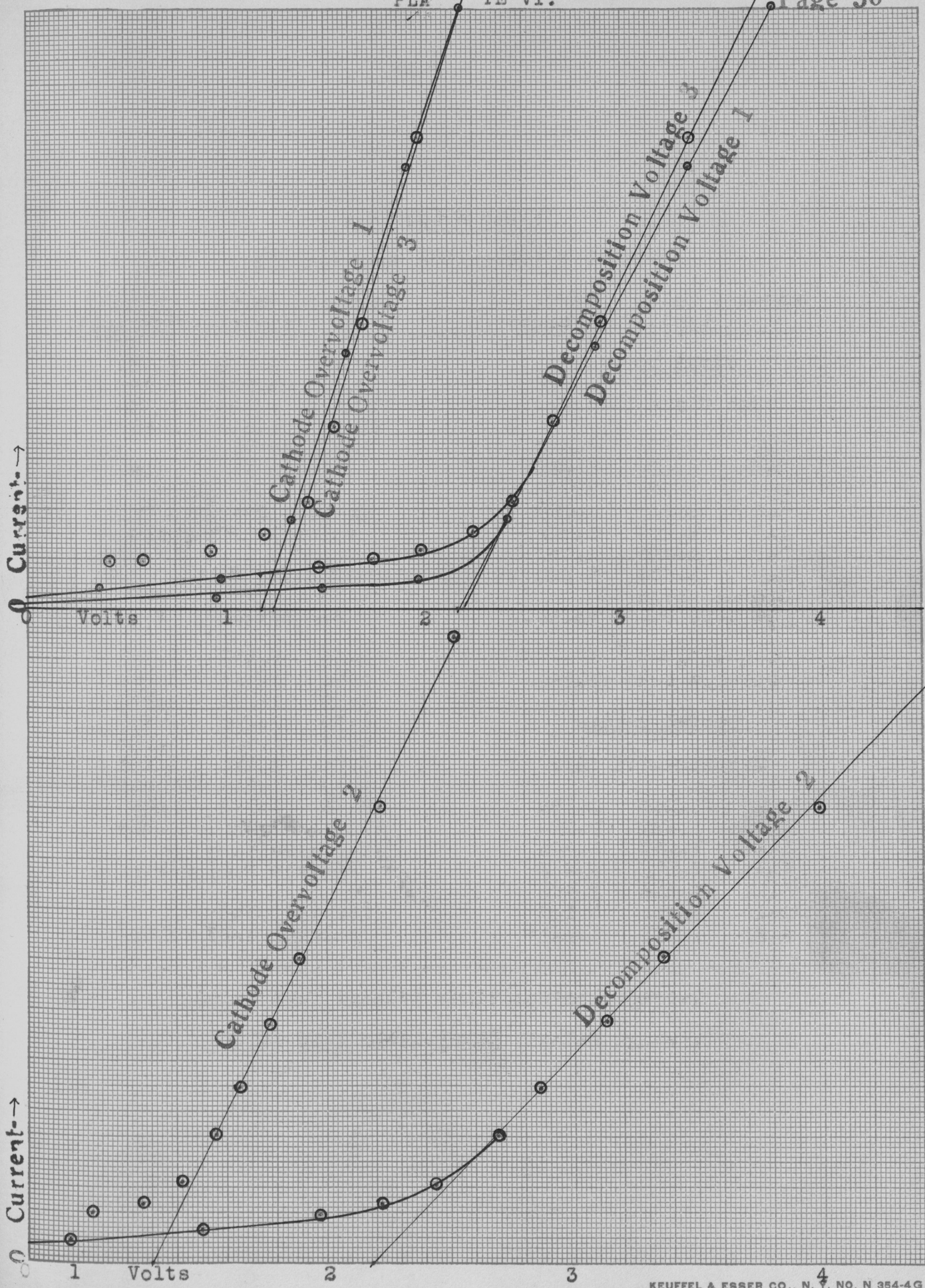


TABLE NUMBER VII.

TABLE NUMBER VII.

Nickel Nitrate in Water.

Current. Volts Volts Current. Volts Volts
 applied. reference. applied. reference.

First Trial.

Second Trial..

See Plate VII (1).

See Plate VII (2).

0.5	1.984	0.780
1.5	2.476	0.890
2.65	2.704	1.000
4.2	2.932	1.080
5.8	3.148	1.200
7.5	3.376	1.280
9.2	3.594	1.380
11.0	3.814	1.490
12.5	4.036	1.590
15.0	4.232	1.710

Decomposition
Voltage 2.40 volts.

Cathode Over
voltage 0.80 volts.

0.70	1.984	0.750
2.1	2.464	0.970
3.6	2.714	1.112
4.7	2.914	1.220
6.4	3.144	1.320
8.1	3.376	1.420
9.9	3.592	1.510
12.0	3.816	1.600
14.0	4.044	1.696
16.0	4.280	1.790
18.5	4.600	1.940

Decomposition
Voltage 2.33 volts.

Cathode Over-
voltage 0.98 volts.

Average Decomposition Voltage 2.36 volts.

Average Cathode Overvoltage 0.89 volts.

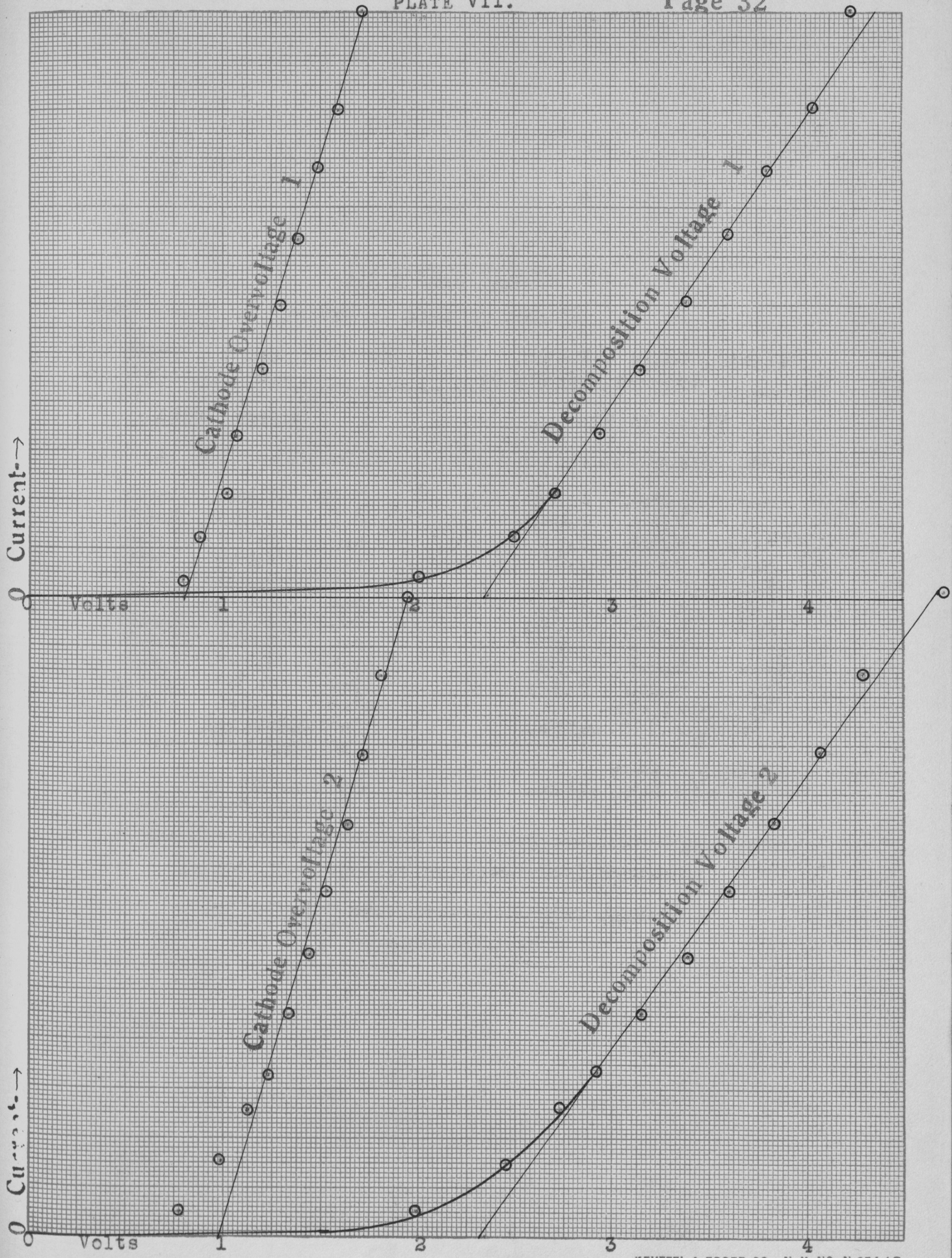


TABLE NUMBER VIII.

TABLE NUMBER VIII.

Cadmium Nitrate in Liquid Ammonia.

Current. Volts Volts Current. Volts Volts
 applied.reference. applied.reference.

First Trial.

Second Trial.

See Plate VIII (1).

See Plate VIII (2)

0.11	0.792	-0.652
0.21	0.998	0.490
0.31	1.500	0.036
1.30	1.982	+0.322
5.50	2.424	0.494
10.0	2.846	0.698
15.0	3.268	0.906
20.1	3.698	1.108

0.24	1.486	-0.200
1.13	1.972	+0.200
2.98	2.170	0.310
5.20	2.396	0.434
7.50	2.624	0.554
9.85	2.848	0.666
14.0	3.280	0.874
18.0	3.712	1.084
22.5	4.174	1.318

Decomposition
voltage 1.90 volts.

Decomposition
voltage 1.85 volts.

Cathode over-
voltage 0.29 volts.

Cathode over-
voltage 0.18 volts.

Average Decomposition Voltage 1.87 volts.

Average Cathode Overvoltage 0.23 volts.

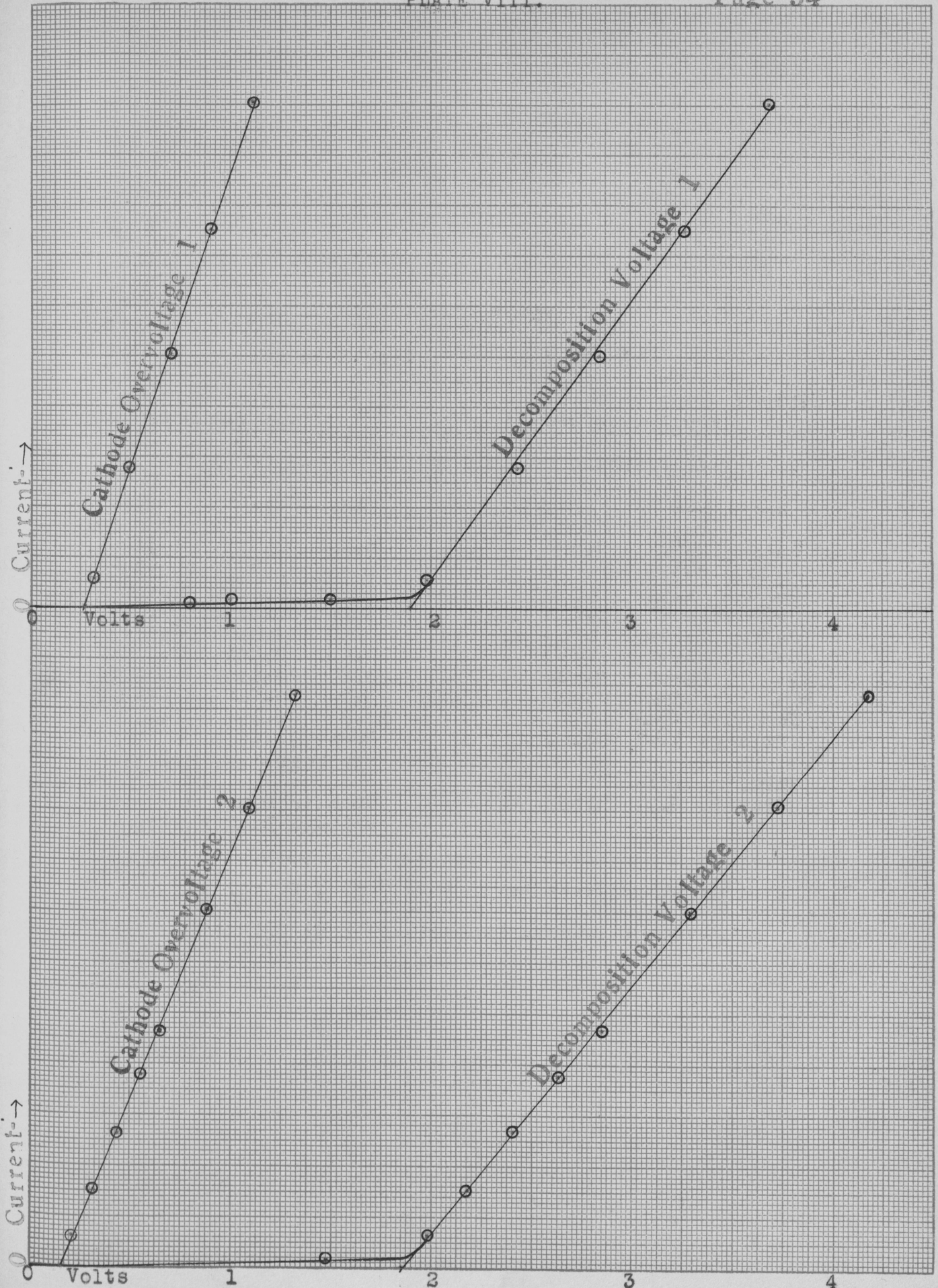


TABLE NUMBER IX.

TABLE NUMBER IX.

Cadmium Nitrate in Water.

Current. Volts	Volts	Volts	Current. Volts	Volts	Volts
applied.	reference.	reference.	applied.	reference.	reference.

First Trial.

See Plate IX (1).

0.10	1.232	-0.552
0.23	1.488	0.362
1.50	1.962	0.100
3.50	2.194	+0.078
4.80	2.426	0.240
12.0	2.794	0.396
23.0	3.160	0.568
33.0	3.508	0.738
45.0	3.860	0.912
56.0	4.194	1.076

Decomposition
voltage 2.40 volts.

Cathode over-
voltage 0.20 volts

E.M.F. 2.20 volts.

Second Trial.

See Plate IX (2).

0.20	1.986	0.076
1.10	2.470	0.202
2.95	2.718	0.264
4.70	2.910	
6.50	3.128	0.454
8.15	3.354	0.570
10.0	3.596	0.680
12.0	3.884	0.792

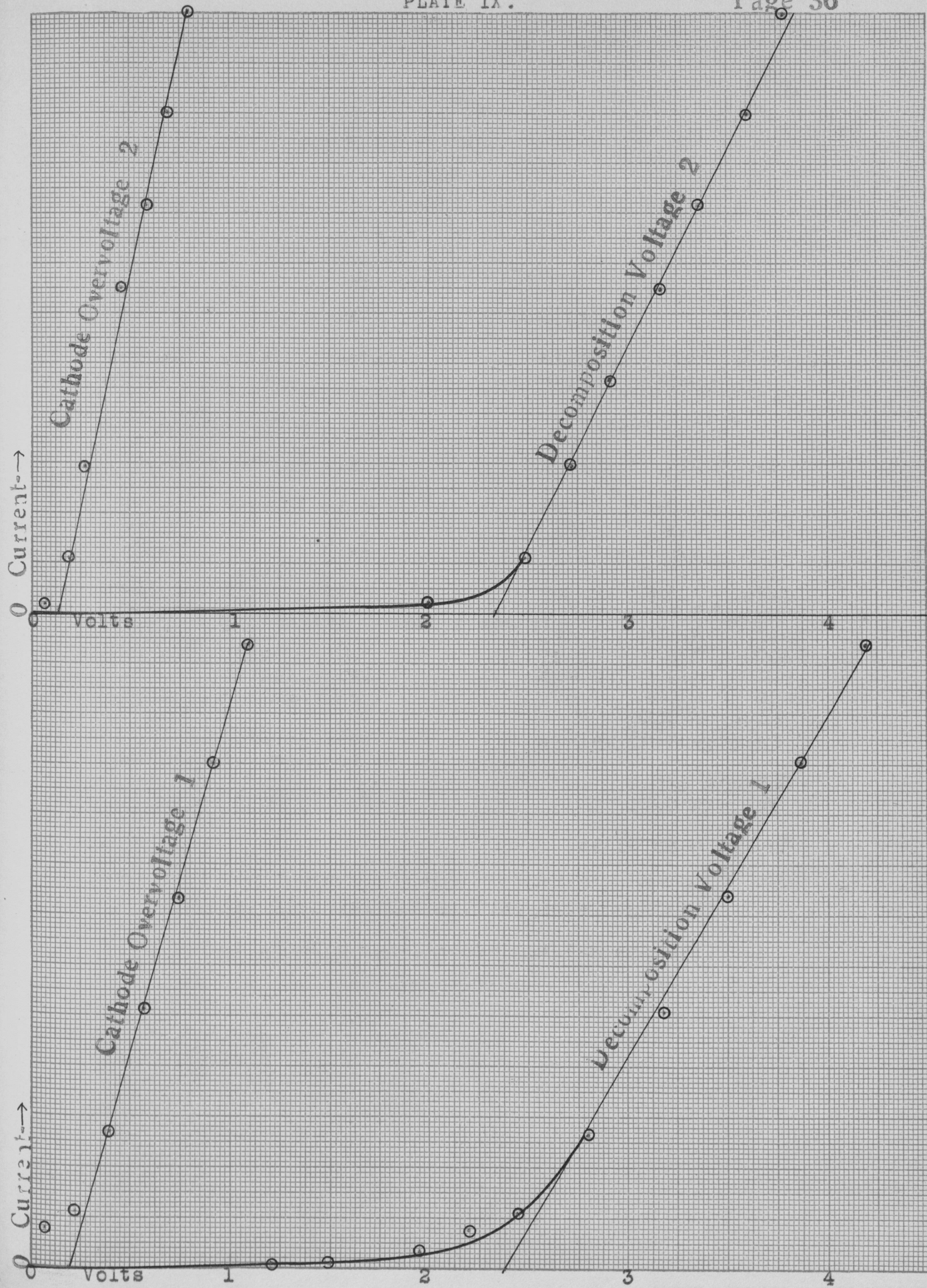
Decomposition
voltage 2.33 volts.

Cathode over-
voltage 0.13 volts.

E.M.F. 2.16 volts.

Average Decomposition Voltage 2.36 volts.

Average Cathode Overvoltage 0.16 volts.



TABLES NUMBER X and XI.

TABLE NUMBER X.

Cadmium Iodide in Liquid Ammonia.

Current. Volts Volts Current. Volts Volts
applied.reference. applied.reference.

First Trial.

Second Trial.

See Plate X (1).
0.10 1.000
0.20 1.502
0.50 1.742 0.104
1.07 1.986 0.186
2.40 2.460 0.384
3.85 2.944 0.610
5.30 3.424 0.834
Decomposition
voltage 1.66 volts.
Cathode over-
voltage 0.04 volts.

See Plate X (2).
0.25 1.510
3.80 1.728 0.042
9.80 1.8540. 0.090
27.0 2.150 0.228
45.0 2.420 0.356
61.0 2.688 0.472
80.0 2.940 0.600
100.0 3.218 0.728
Decomposition
voltage 1.68 volts.
Cathode over-
voltage 0.02 volts.

Average Decomposition Voltage 1.67 volts.

Average Cathode Overvoltage 0.02 volts.

PLATE NUMBER XI.

Cadmium Iodide in Water.

First Trial.

Second Trial.

See Plate X (3).
0.25 1.000
1.20 1.244 0.110
2.95 1.460 0.190
4.80 1.692 0.282
6.25 1.906 0.332
7.25 2.130 0.342
Decomposition
voltage 1.10 volts.
Cathode over-
voltage 0.03 volts.

See Plate X (4).
0.05 0.998
0.90 1.240 0.110
2.15 1.472 0.228
3.40 1.708 0.344
4.60 1.922 0.456
5.90 2.180 0.578
7.10 2.400 0.684
8.50 2.662 0.806
9.50 2.858 0.894
Decomposition
voltage 1.10 volts.
Cathode over-
voltage 0.02 volts.

Average Decomposition Voltage 1.10 volts.

Average Cathode Overvoltage 0.025 volts.

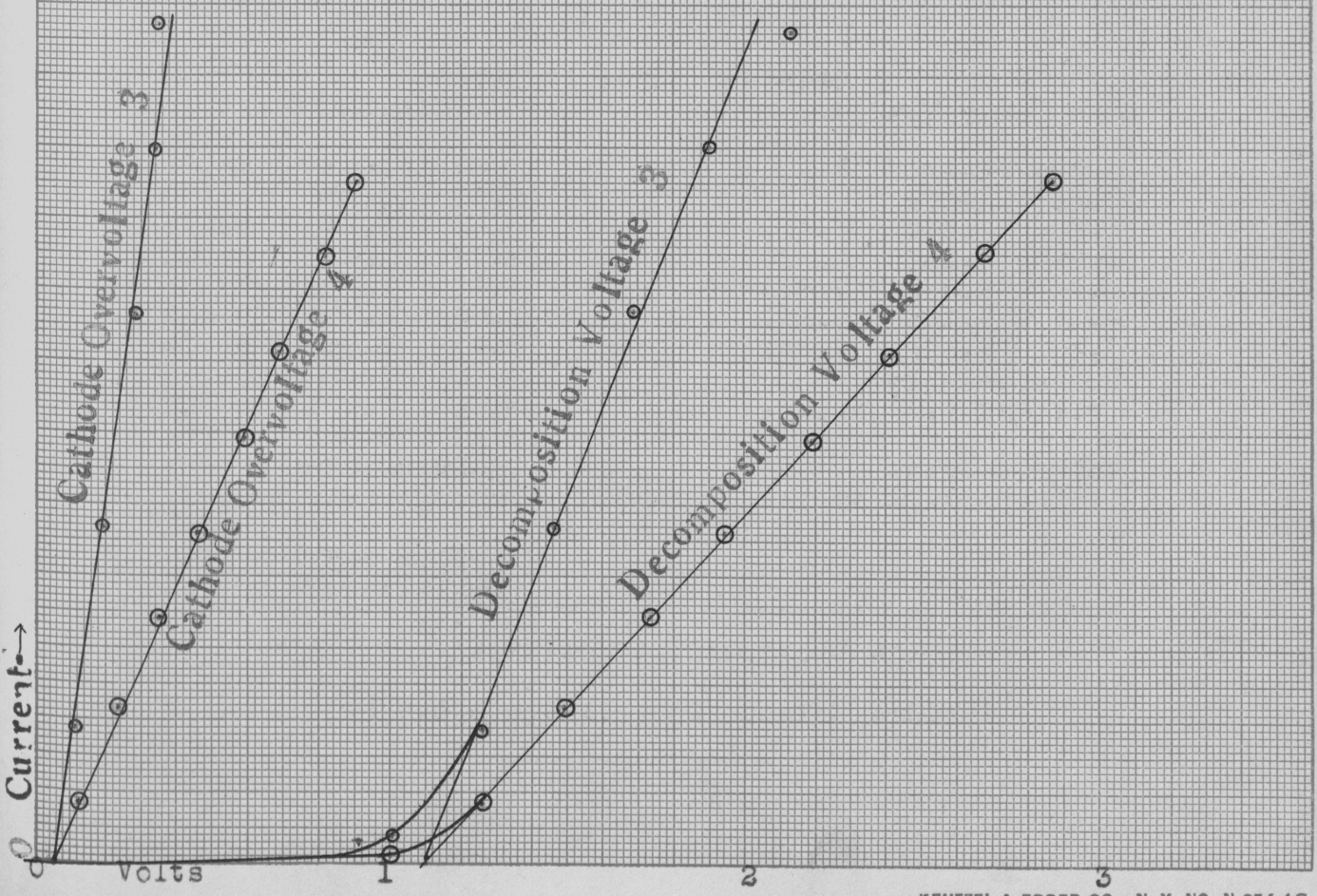
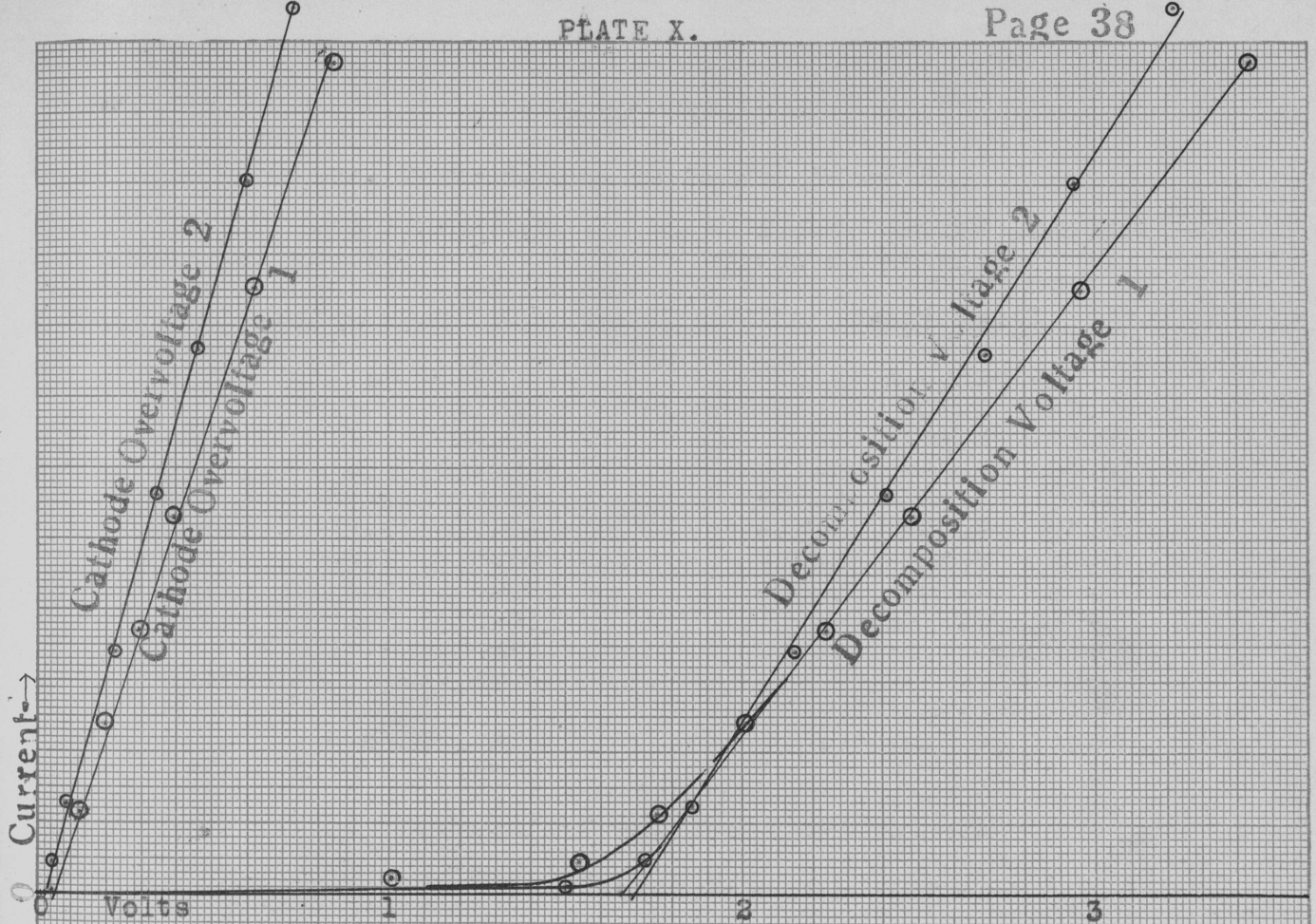


TABLE NUMBER XII.

TABLE NUMBER XII.

Mercuric Nitrate in Liquid Ammonia.

Current. Volts applied. reference.	Current. Volts applied. reference.
---------------------------------------	---------------------------------------

First Trial.

See Plate XI (1).

1.8	1.073	0.154
5.9	1.600	0.386
10.1	2.094	0.608
13.5	2.554	0.832
18.0	3.046	1.048
22.5	3.534	1.300
25.0	3.890	1.450

Decomposition
voltage 0.88 volts.

Cathode over-
voltage 0.08 volts.

Second Trial.

See Plate XI (2).

0.17	0.738	0.082
1.10	0.984	0.162
2.50	1.224	0.274
5.40	1.690	0.304
6.90	1.912	0.616
8.40	2.140	0.736
9.90	2.360	0.844
11.5	2.600	0.964
13.0	2.834	1.074
15.5	3.274	1.300
20.0	3.738	1.518
22.0	4.194	1.740
25.0	4.600	1.938

Decomposition
voltage 0.83 volts.

Cathode over-
voltage 0.07 volts.

Third Trial.

See Plate XI (3).

2.0	0.976	0.172
3.5	1.210	0.280
5.0	1.442	0.398
6.6	1.686	0.520
8.15	1.912	0.636
9.6	2.130	0.748
10.8	2.360	0.866
14.0	2.816	1.100
17.0	3.272	1.338
20.0	3.730	1.576
23.0	4.180	1.812
26.0	4.600	2.028

Decomposition
voltage 0.70 volts.

Cathode over-
voltage 0.00 volts.

Fourth Trial.

See Plate XI (4).

1.75	0.984	0.170
3.2	1.214	0.272
4.8	1.450	0.384
6.4	1.682	0.490
8.0	1.898	0.592
9.7	2.132	0.700
11.0	2.352	0.806
15.0	2.800	
18.0	3.266	1.238
21.0	3.716	1.454

Decomposition
voltage 0.75 volts.

Cathode over-
voltage 0.07 volts.

Average Decomposition Voltage 0.79 volts.

Average Cathode Overvoltage 0.07 volts.

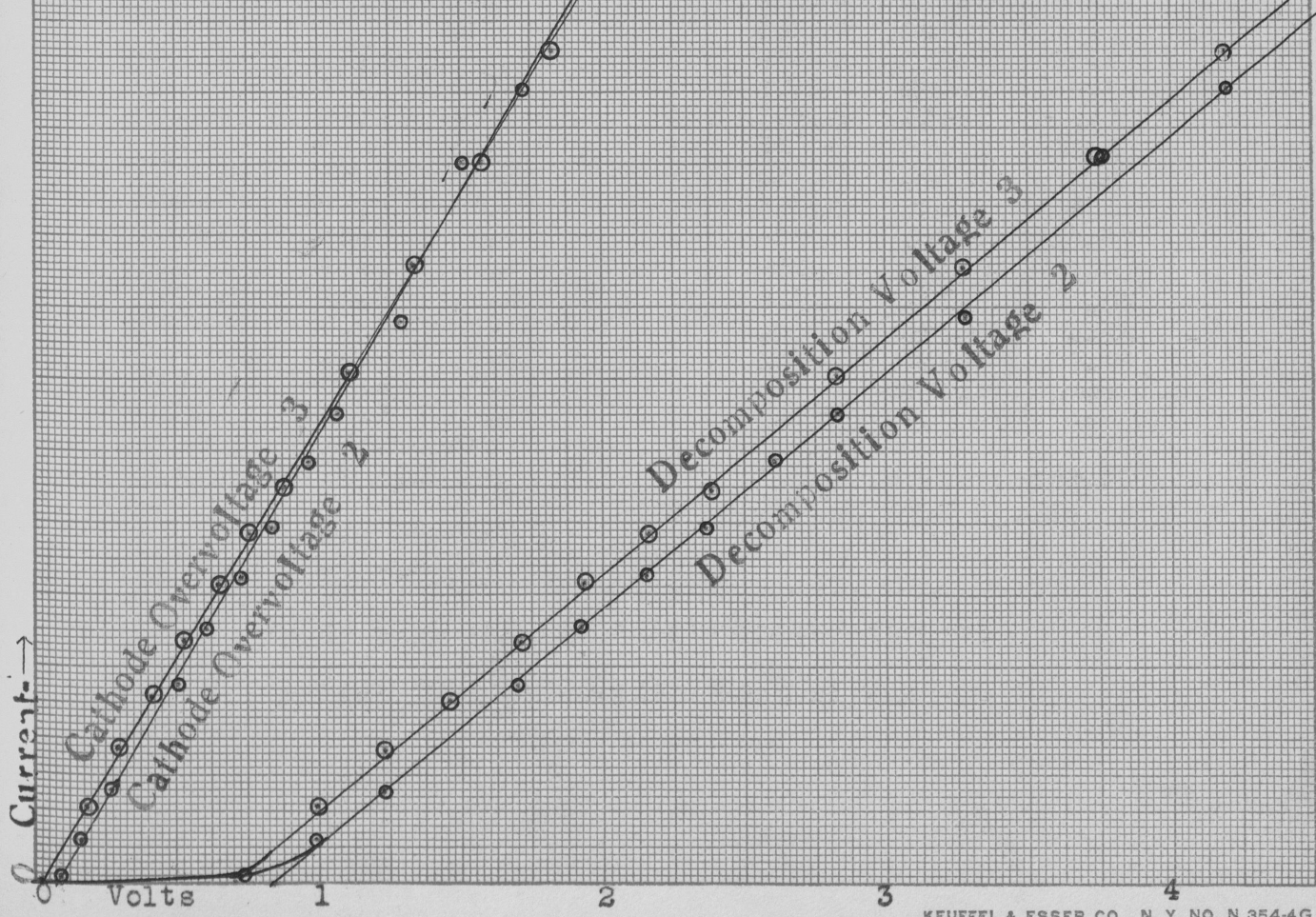
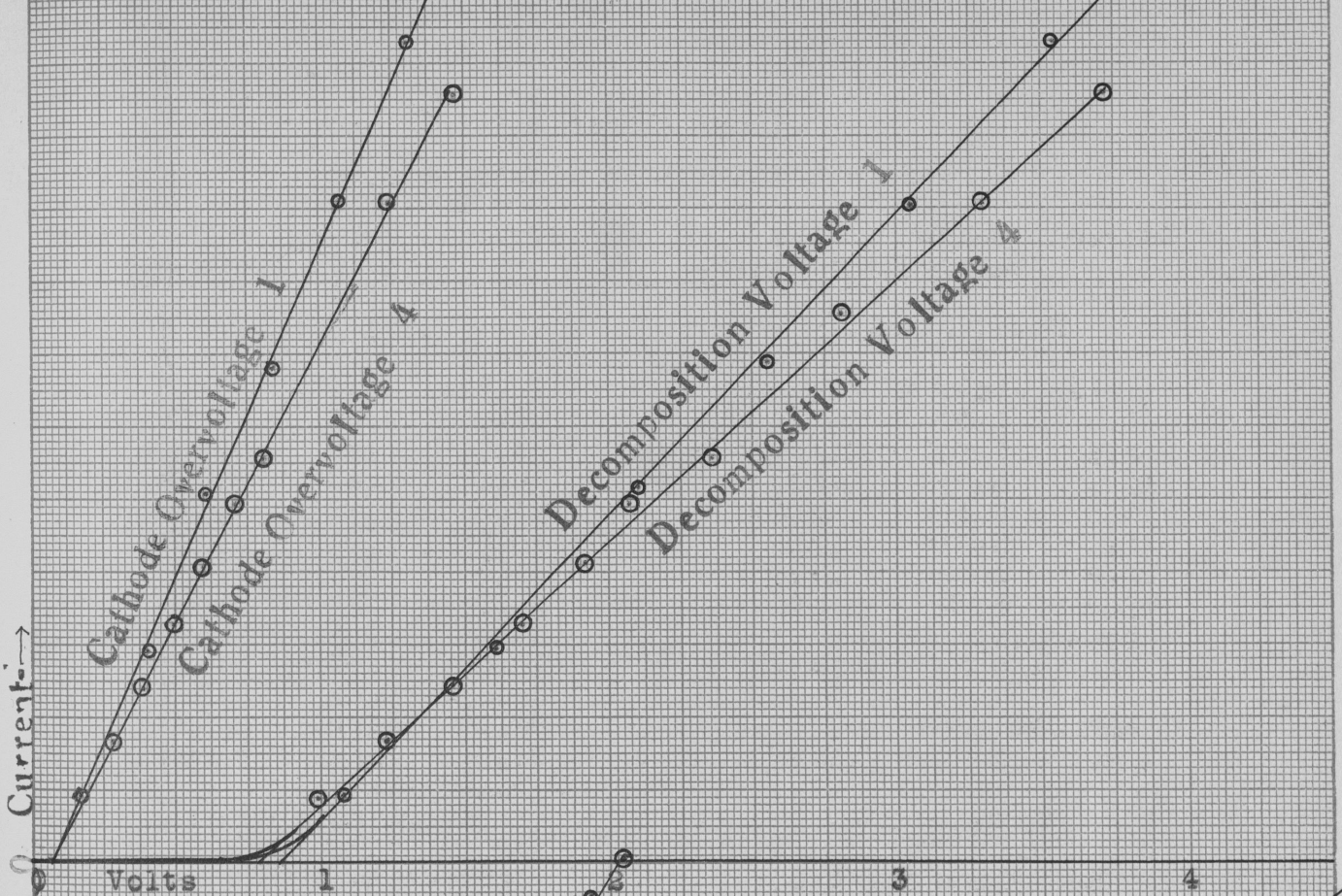


TABLE NUMBER XIII.

TABLE NUMBER XIII.

Mercuric Iodide in Liquid Ammonia.

Current.	Volts applied.	Volts reference.	Current.	Volts applied.	Volts reference.
<u>First Trial.</u>			8.2	1.712	0.392
			10.0	1.878	0.470
			15.5	2.388	0.714
			20.0	2.804	0.912
			30.0	3.696	1.336
			Decomposition voltage 0.89 volts.		
			Cathode over-voltage 0.01 volts.		
			<u>Third Trial.</u>		
			See Plate XII (3).		
			0.13	0.600	0.030
			2.40	0.976	0.150
			4.40	1.208	0.232
			6.50	1.444	0.360
			8.40	1.662	0.460
			9.90	1.816	0.534
			12.5	2.116	0.672
			14.5	2.328	0.772
			19.0	2.794	0.992
			23.0	3.234	1.200
			27.0	3.674	1.412
			Decomposition voltage 0.76 volts.		
			Cathode Over-voltage 0.02 volts.		
<hr/>					
Average Decomposition Voltage <u>0.82 volts.</u>					
Average Cathode Overvoltage <u>0.02 volts.</u>					

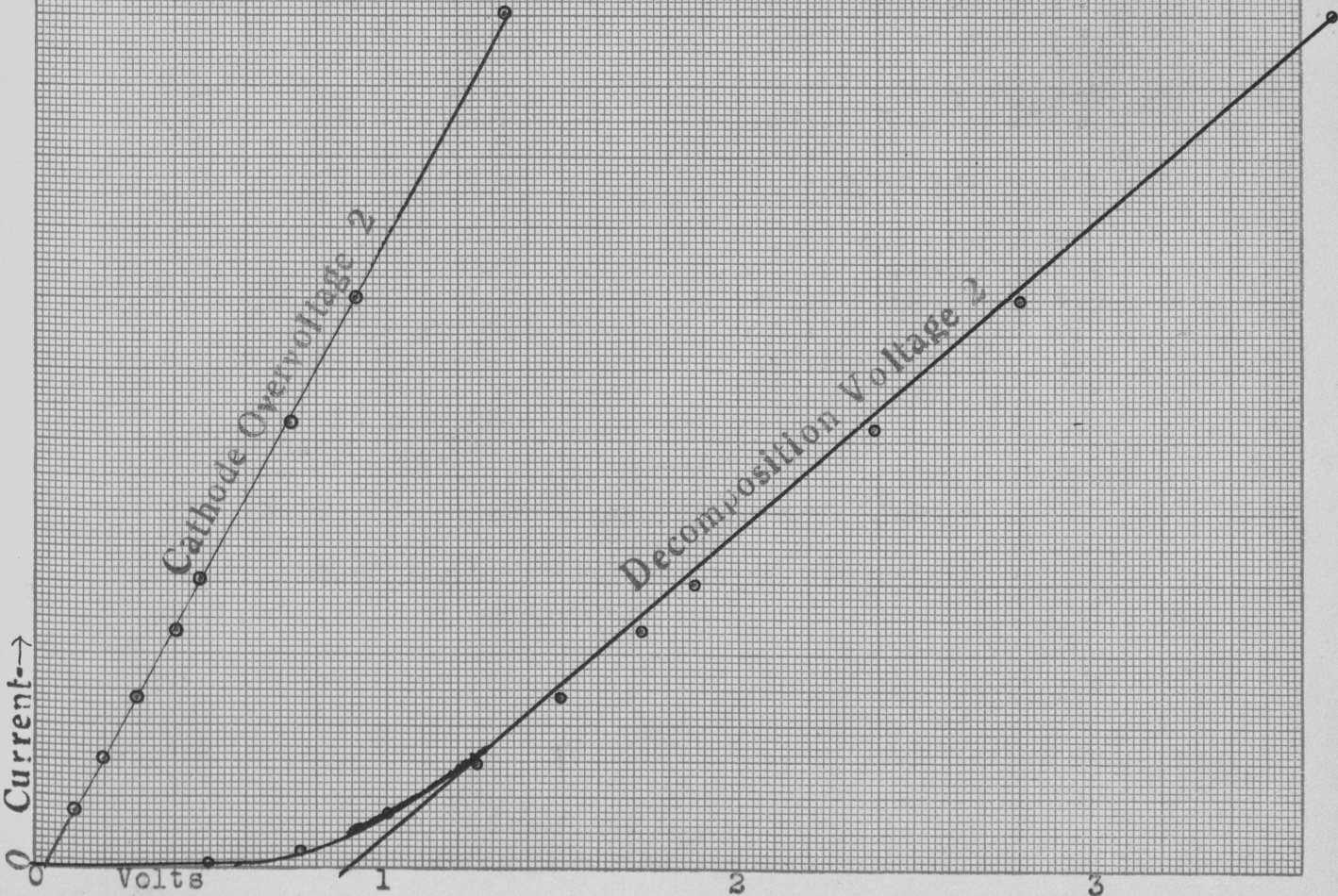
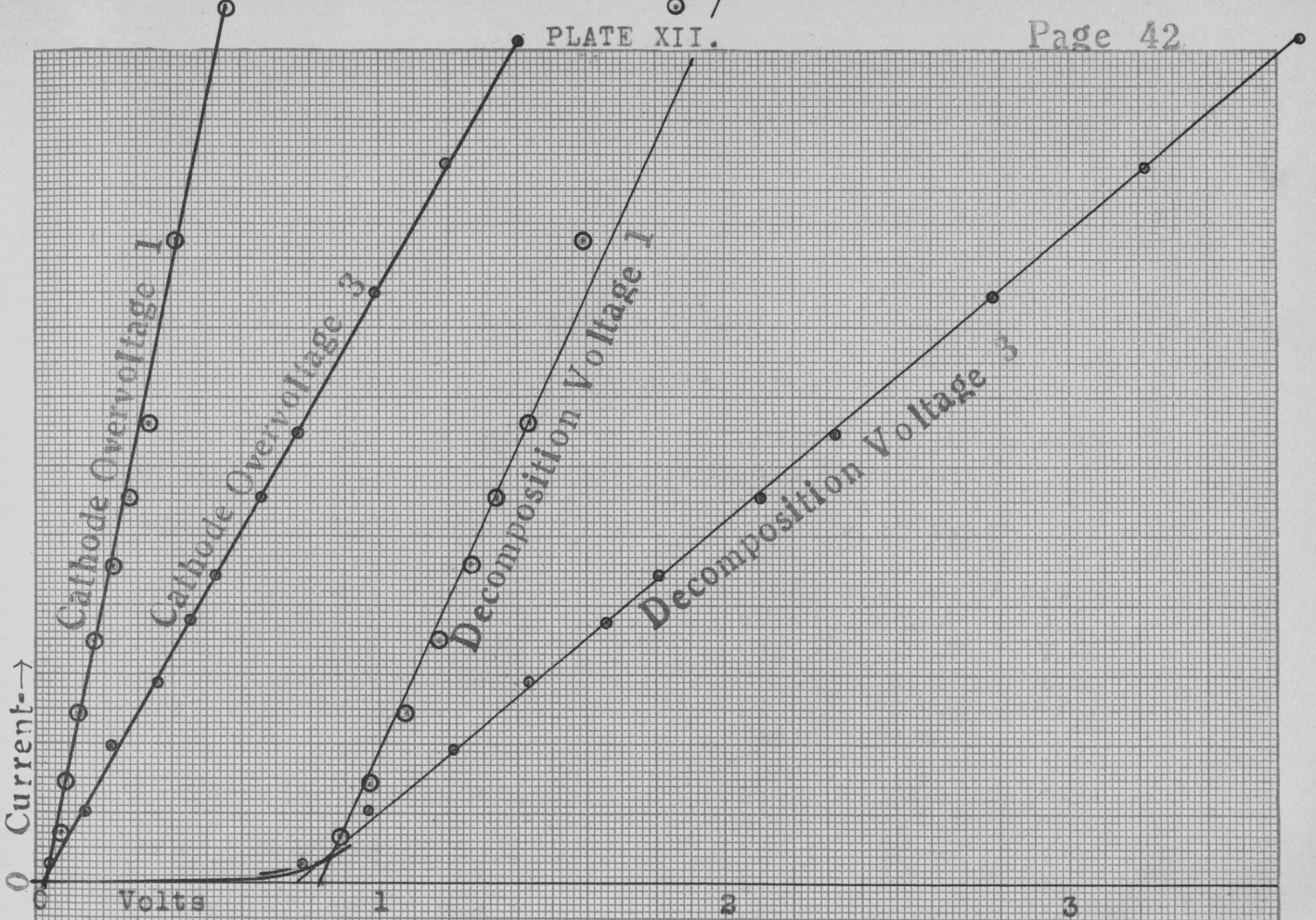


TABLE NUMBER XIV.

TABLE NUMBER XIV.

Other Mercuric Salts in Liquid Ammonia.

Current. Volts Volts Current. Volts Volts
applied. reference. applied. reference.

Mercuric Acetate.

See Plate XIII (1).

0.08	1.000	0.096
0.33	1.206	0.232
0.59	1.396	0.366
0.72	1.496	0.428
1.06	1.794	0.614
1.30	1.998	0.750
1.68	2.280	0.918
2.01	2.600	1.120
2.48	2.870	1.360
3.60	3.960	1.960
4.80	4.990	2.600

Decomposition
voltage 0.92 volts.

Cathode over-
voltage 0.04 volts.

Mercuric Chloride..

See Plate XIII (2).

0.29	0.972	0.106
0.48	1.082	0.162
0.80	1.274	0.270
0.98	1.372	0.324
1.52	1.678	0.486
2.08	1.958	0.648
2.75	2.336	0.860
3.47	2.732	1.072
4.15	3.094	1.280
5.60	3.866	1.704
6.50	4.332	1.970

Decomposition
voltage 0.85 volts.

Cathode over-
voltage 0.04 volts.

Average Decomposition Voltage 0.88 volts.

Average Cathode Overvoltage 0.04 volts.

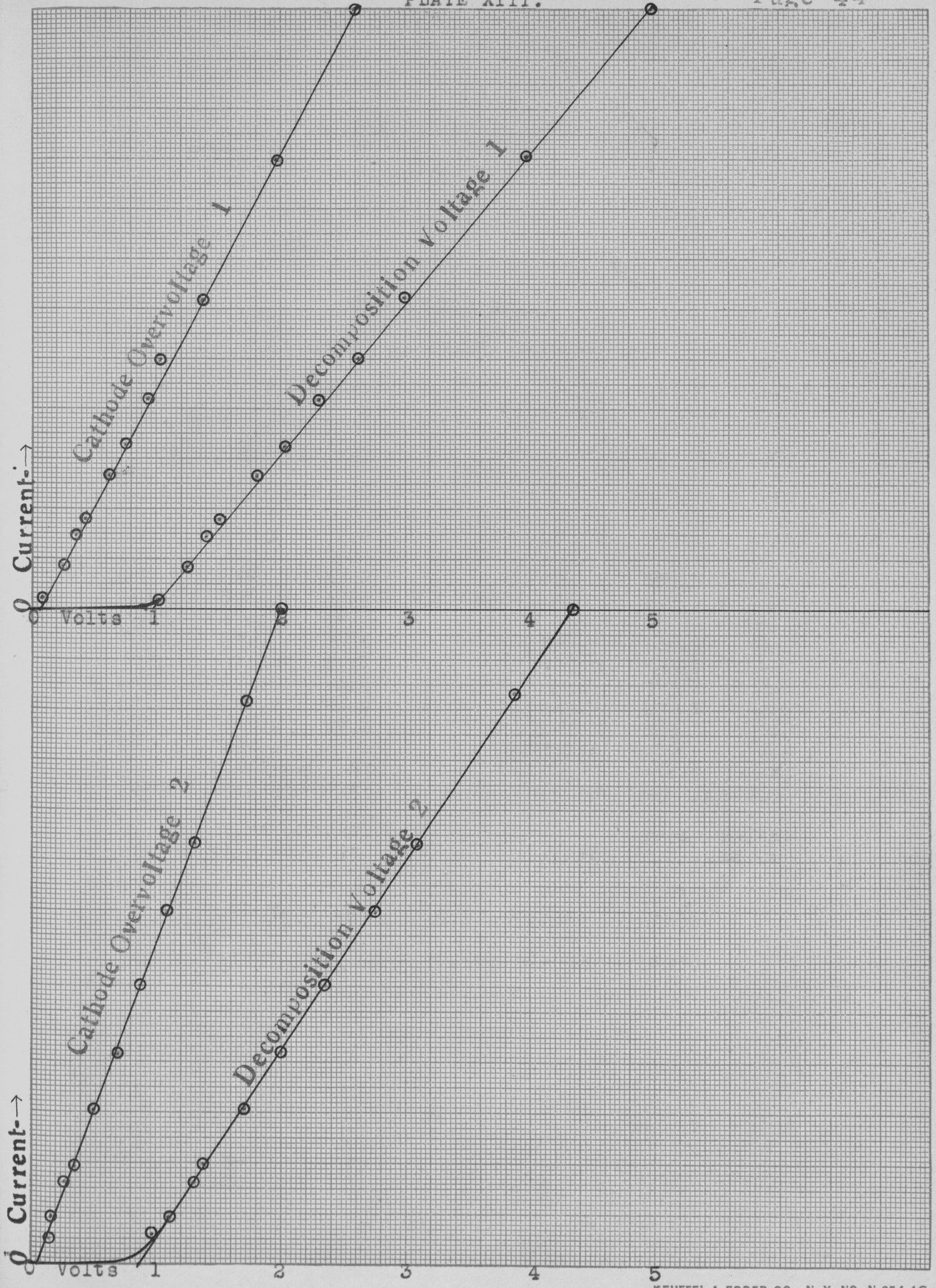


TABLE NUMBER XV.

TABLE NUMBER XV.

Mercuric Salts in Water.

Current. Volts applied.	Volts reference.	Current. Volts applied; reference.
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Mercuric Nitrate.

First Trial.

See Plate XIV (1).

0.95	1.250	0.040
8.37	1.718	0.204
17.0	2.240	0.432
26.0	2.716	0.660
29.0	2.850	0.714
37.0	2.250	0.914
46.0	3.692	1.124

Decomposition
voltage 1.35 volts.

Cathode over-
voltage 0.02 volts.

Second Trial.

See Plate XIV (2).

0.70	1.496	0.074
1.75	1.728	0.156
2.90	1.958	0.240
4.15	2.186	0.338
5.45	2.414	0.436
8.20	2.876	0.650
11.0	3.310	0.864

Decomposition
voltage 1.40 volts.

Cathode over-
voltage 0.01 volts.

Third Trial.

See Plate XIV (3).

0.70	1.480	0.092
1.75	1.720	0.172
2.90	1.950	0.268
4.20	2.198	0.370
5.40	2.420	0.472
6.70	2.648	0.578
7.90	2.864	0.686
9.20	3.106	0.814
11.0	3.332	0.954

Decomposition
voltage 1.40 volts.

Cathode over-
voltage 0.01 volts.

Mercuric Acetate.

See Plate XIV (4).

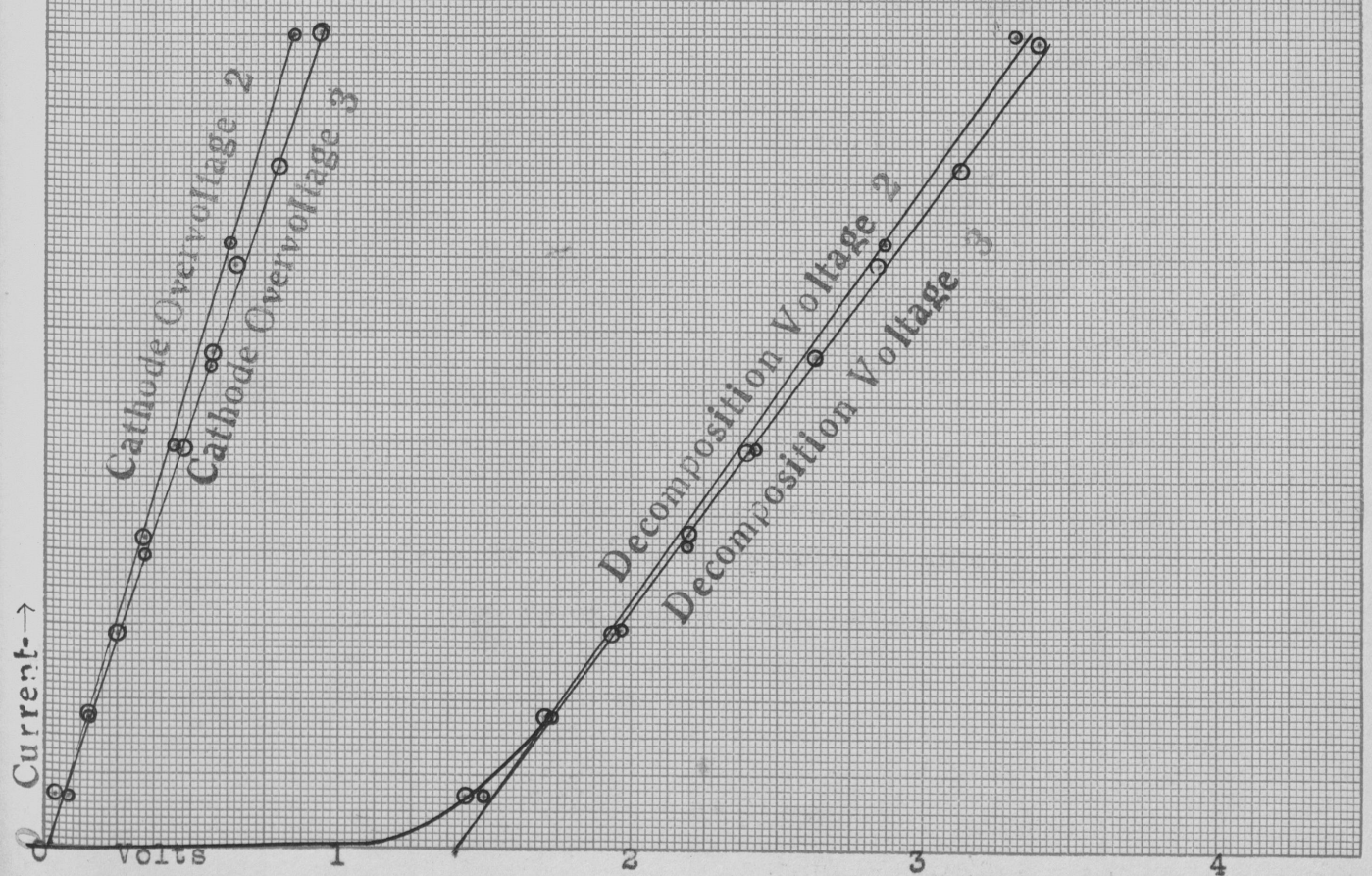
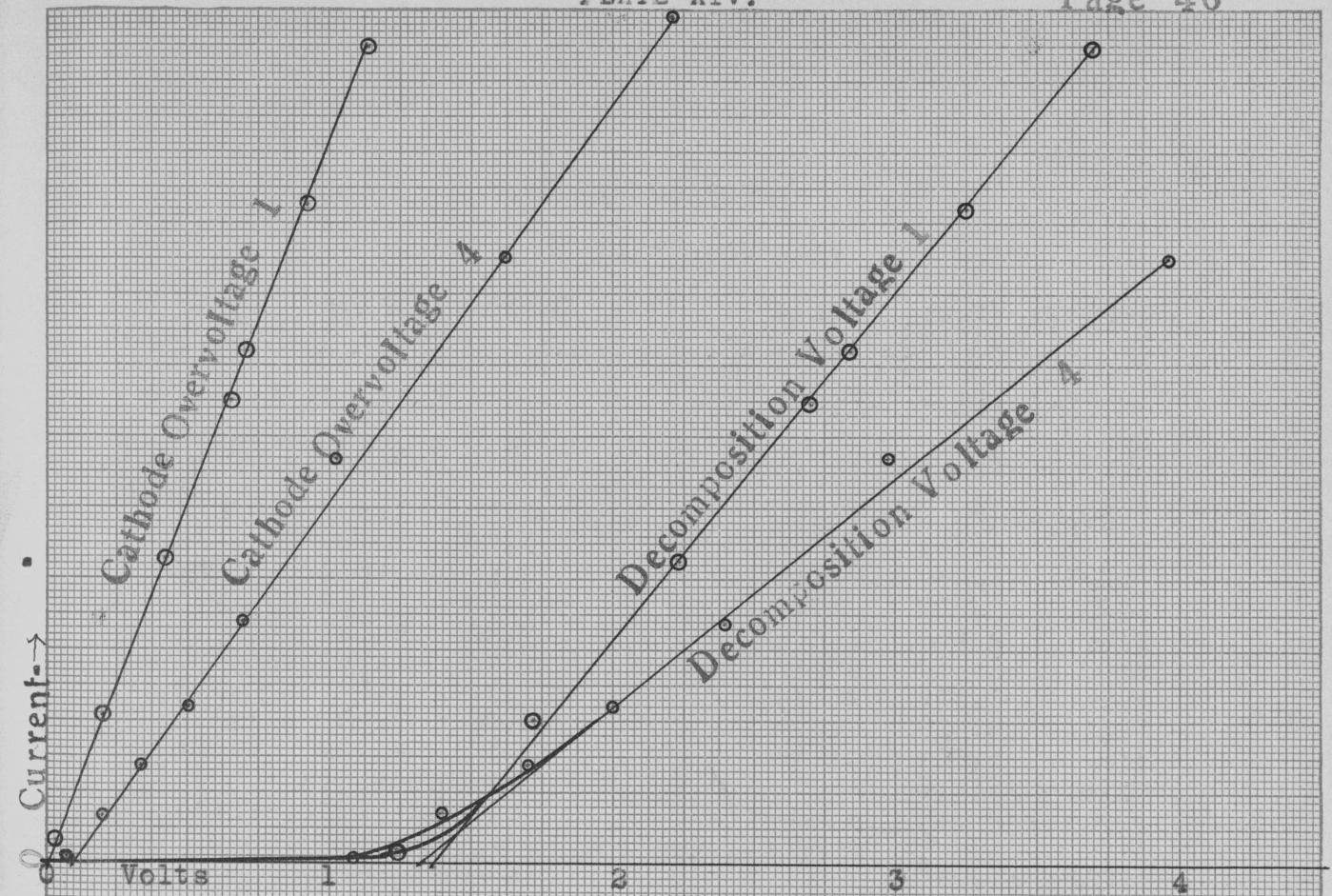
0.03	1.086	0.860
0.20	1.418	0.214
0.40	1.686	0.336
0.65	2.002	0.486
1.00	2.394	0.708
1.67	2.980	1.030
2.50	3.964	1.604
3.50	5.000	2.200

Decomposition
voltage 1.33 volts.

Cathode over-
voltage 0.10 volts.

Average Decomposition Voltage 1.37 volts.

Average Cathode Overvoltage 0.03 volts.



TABLES NUMBER XVI and XVII.

TABLE NUMBER XVI.

Lead Nitrate in Liquid Ammonia.

Current. Volts applied.	Volts reference.	Current. Volts applied.	Volts reference.
<u>First Trial.</u>		<u>Second Trial.</u>	
See Plate XV (1).		See Plate XV (2).	
0.10	1.410	0.068	
0.37	1.494	0.094	
1.30	1.590	0.112	
3.60	1.662	0.138	
6.00	1.740	0.156	
8.50	1.800	0.160	
10.2	1.842	0.170	
Decomposition voltage 1.58 volts.		Decomposition voltage 1.64 volts.	
Cathode over- voltage 0.13 volts,		Cathode over- voltage 0.18 volts.	

Average Decomposition Voltage 1.61 volts.

Average Cathode Overvoltage 0.15 volts.

TABLE NUMBER XVII.

Lead Nitrate in Water.

Current. Volts applied.	Volts reference.	Current. Volts applied.	Volts reference.
<u>First Trial.</u>		<u>Second Trial.</u>	
See Plate XV (3).		See Plate XV (4).	
0.10	1.514	1.0	1.824
0.20	1.597	2.50	2.012
0.40	1.696	0.000	0.216
0.83	1.796	0.006	0.298
2.78	1.976	0.020	0.390
7.40	2.218	0.042	0.480
9.80	2.306	0.050	0.562
Decomposition voltage 1.82 volts.		Decomposition voltage 1.83 volts.	
Cathode over- voltage 0.01 volts.		Cathode over- voltage 0.06 volts.	
E.M.F. 1.83 volts.			

Average Decomposition Voltage 1.84 volts.

Average Cathode Overvoltage 0.03 volts.

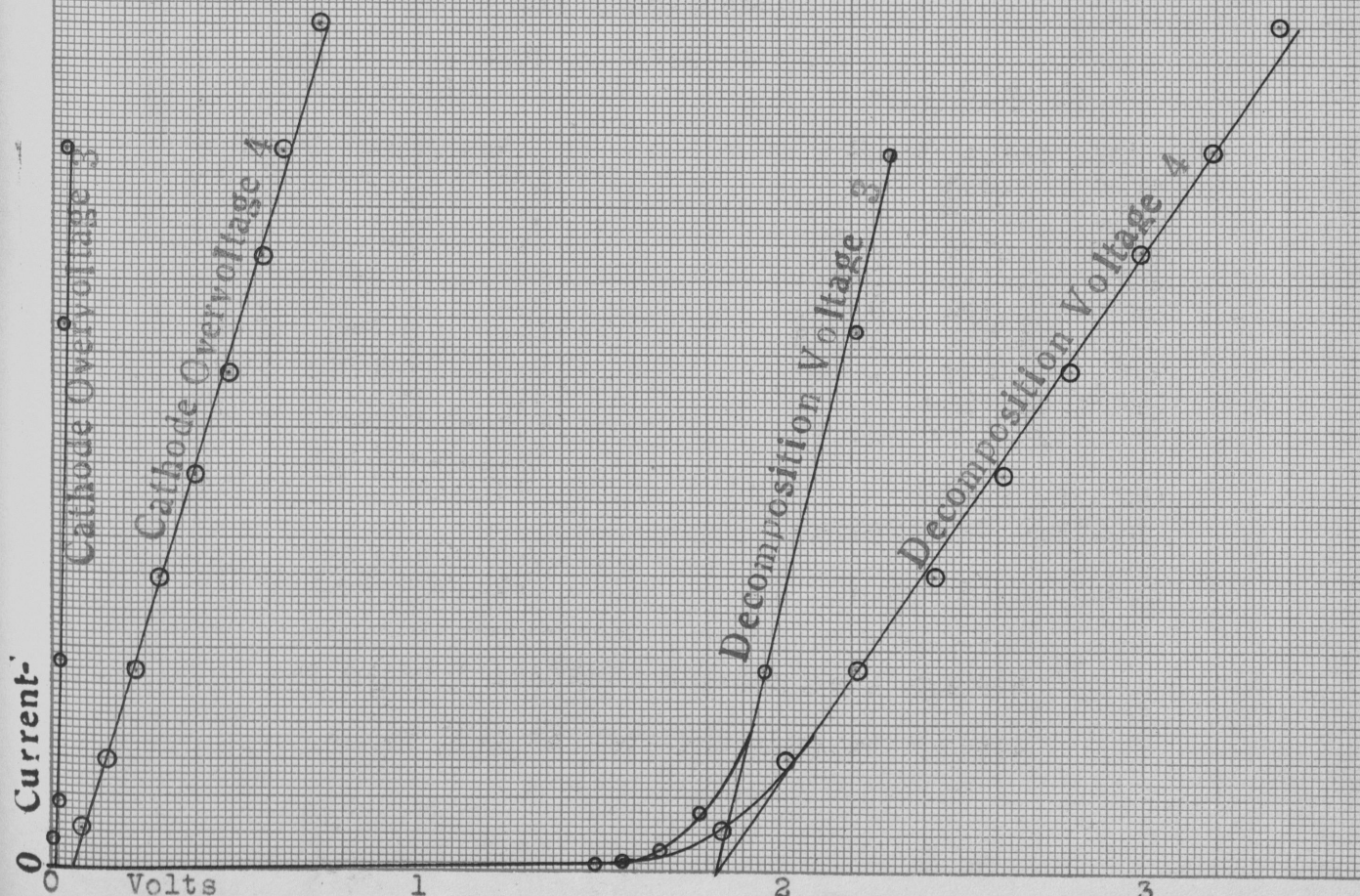
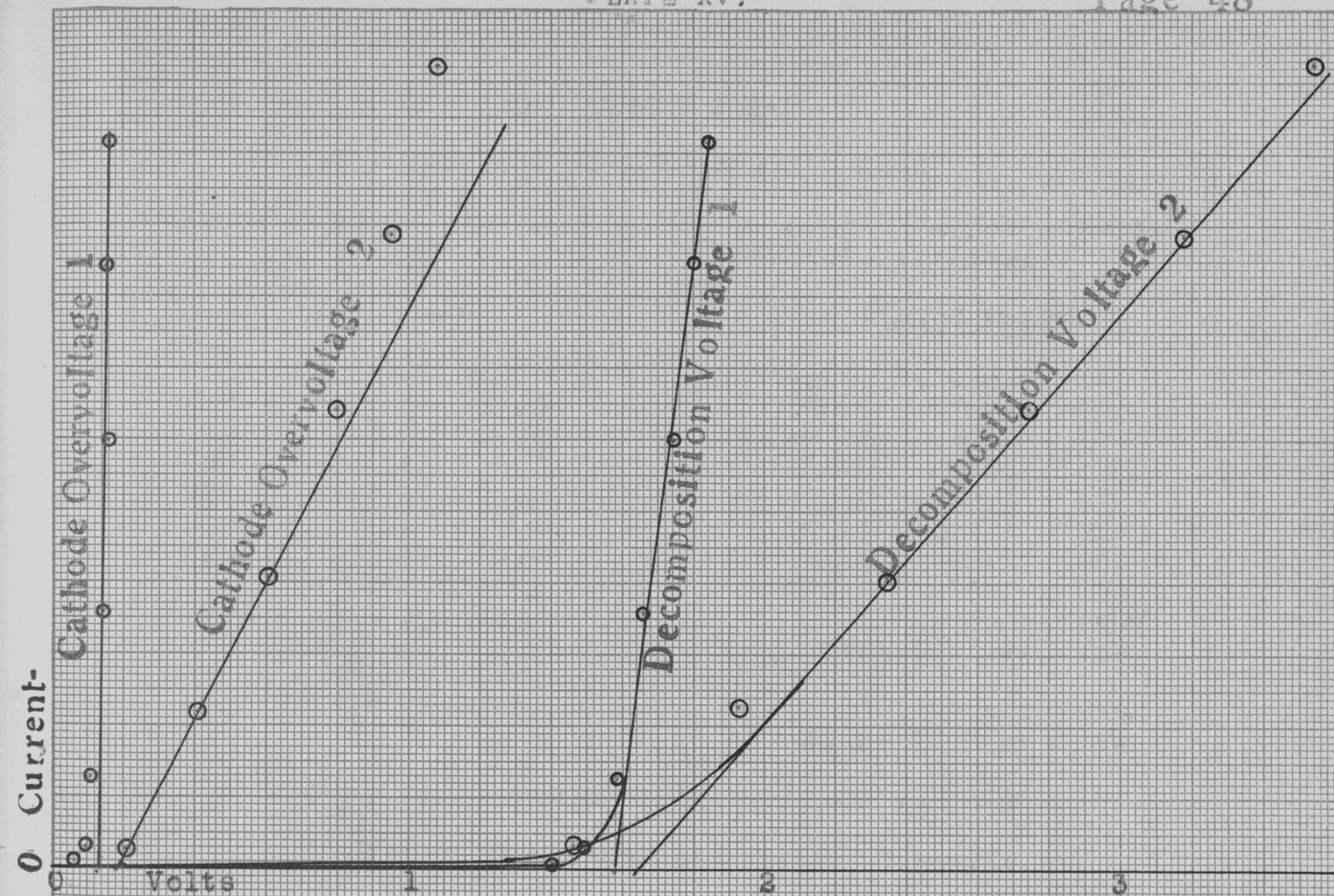


TABLE NUMBER XVIII.

TABLE NUMBER XVIII.

Zinc Nitrate in Liquid Ammonia.

Current.	Volts applied.	Volts reference.	Current.	Volts applied.	Volts reference.
<u>First Trial.</u>			13.0	3.310	0.680
See Plate XVI (1).			15.0	3.476	0.732
0.40	2.012		17.0	3.728	0.880
0.78	2.102	0.046	22.0	4.188	1.104
1.10	2.132	0.058	26.0	4.600	1.320
1.80	2.176	0.074	Decomposition		
2.80	2.194	0.074	voltage 2.05 volts.		
3.90	2.186	0.086	Cathode over-		
6.15	2.236	0.108	voltage 0.02 volts.		
9.60	2.312	0.132	<u>Third Trial.</u>		
Decomposition			See Plate XVI (3).		
voltage 2.15 volts.			0.2	2.006	
Cathode over-			1.8	2.210	0.098
voltage 0.05 volts.			4.0	2.438	0.202
<u>Second Trial.</u>			6.5	2.666	1.316
See Plate XVI (2).			8.7	2.850	0.408
1.00	2.004	0.080	11.0	3.086	0.534
2.40	2.220	0.156	14.0	3.306	0.650
4.24	2.436	0.254	16.0	3.512	0.758
6.25	2.658	0.360	Decomposition		
8.30	2.880	0.472	voltage 2.08 volts.		
9.90	3.040	0.540	Cathode over-		
			voltage 0.03 volts.		

Average Decomposition Voltage 2.09 volts.

Average Cathode Overvoltage 0.03 volts.

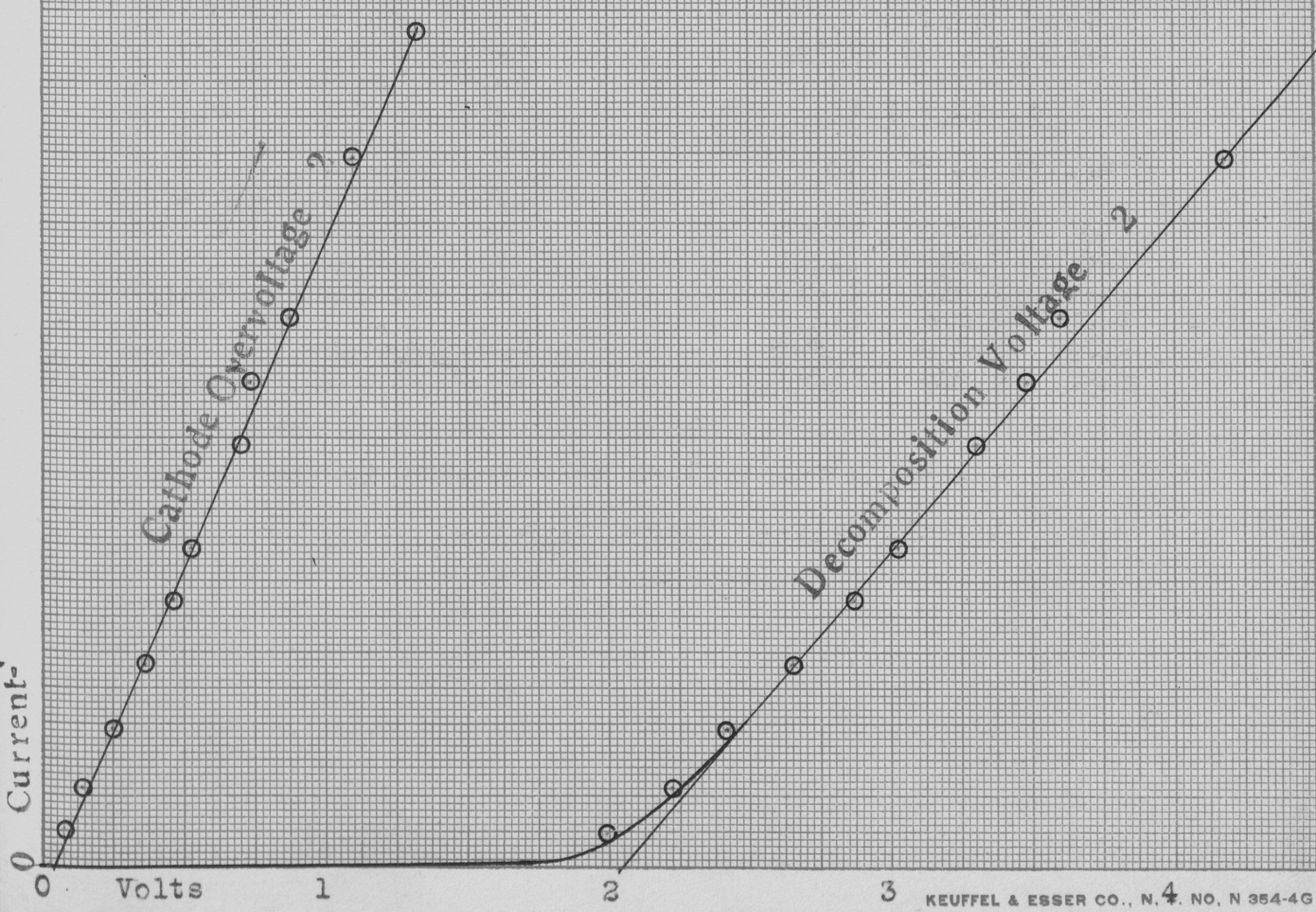
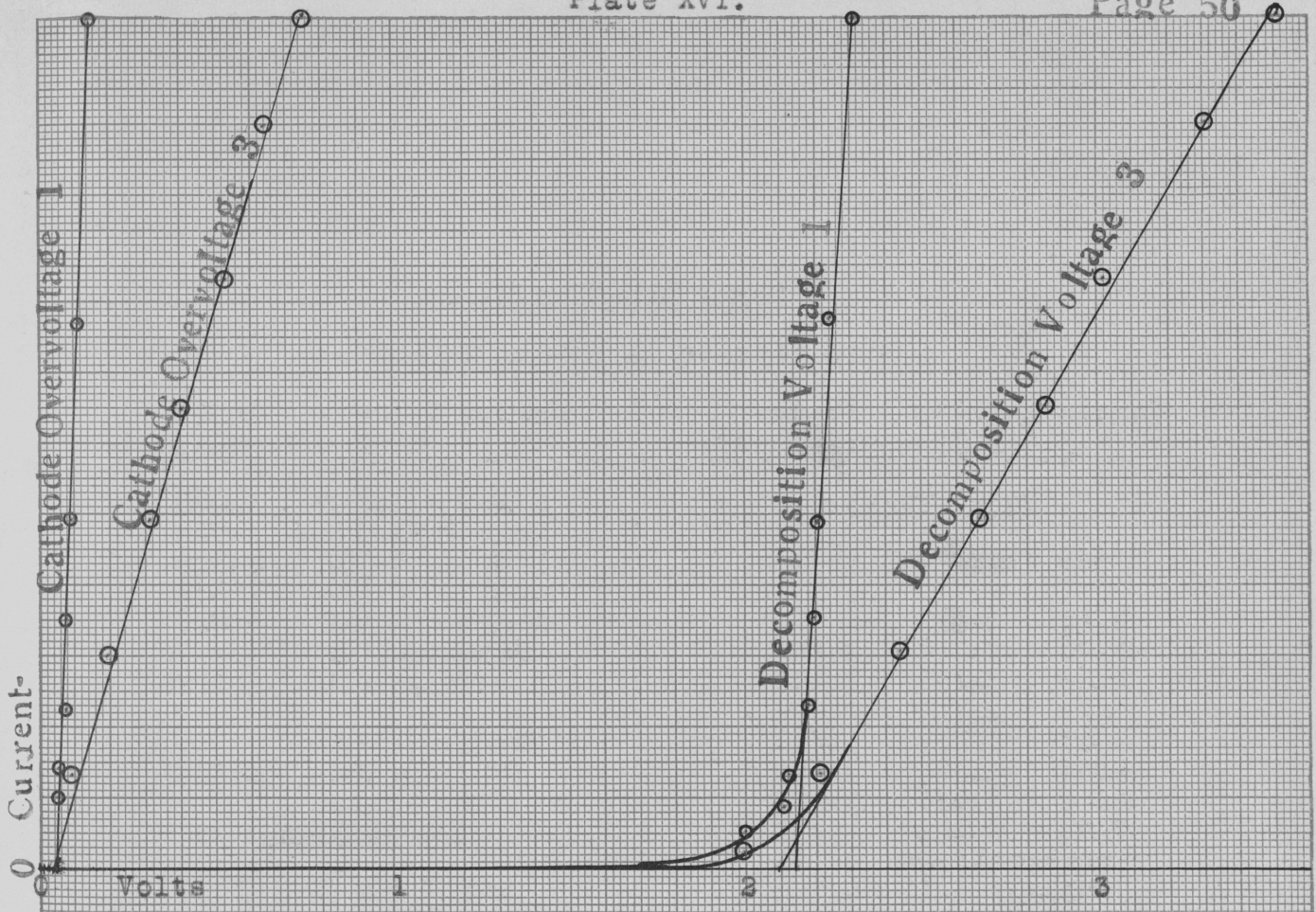


TABLE NUMBER XIX.

TABLE NUMBER XIX.

Zinc Nitrate in Water.

Current. Volts applied.	Volts reference.	Current. Volts applied.	Volts reference.
<u>First Trial.</u>		18.0	3.728 0.808
See Plate XVII (1).		Decomposition	voltage 2.88 volts.
0.10	2.022 0.190	Cathode over-	voltage 0.44 volts.
0.23	2.652 0.400	E.M.F.	2.60 volts.
0.50	2.756 0.470		
1.25	2.810 0.476	<u>Third Trial.</u>	
3.30	2.896 0.516	See Plate XVII(3).	
6.20	2.976 0.554	0.25	2.244
9.40	3.044 0.574	0.40	2.484 0.114
Decomposition	voltage 2.77 volts.	0.50	2.728 0.350
Cathode over-	voltage 0.51 volts.	1.50	2.970 0.486
E.M.F.	2.56 volts.	4.60	3.172 0.564
		8.15	3.362 0.636
<u>Second Trial.</u>		12.0	3.560 0.710
See Plate XVII (2).		16.0	3.748 0.772
0.16	2.482 0.166	25.0	4.128 0.906
0.20	2.738 0.390	Decomposition	voltage 2.90 volts.
1.65	2.948 0.472	Cathode over-	voltage 0.47 volts.
5.10	3.160 0.550	E.M.F.	2.60 volts.
8.95	3.348 0.628		
13.0	3.560 0.740		

Average Decomposition Voltage 2.86 volts.

Average Cathode Overvoltage 0.48 volts.

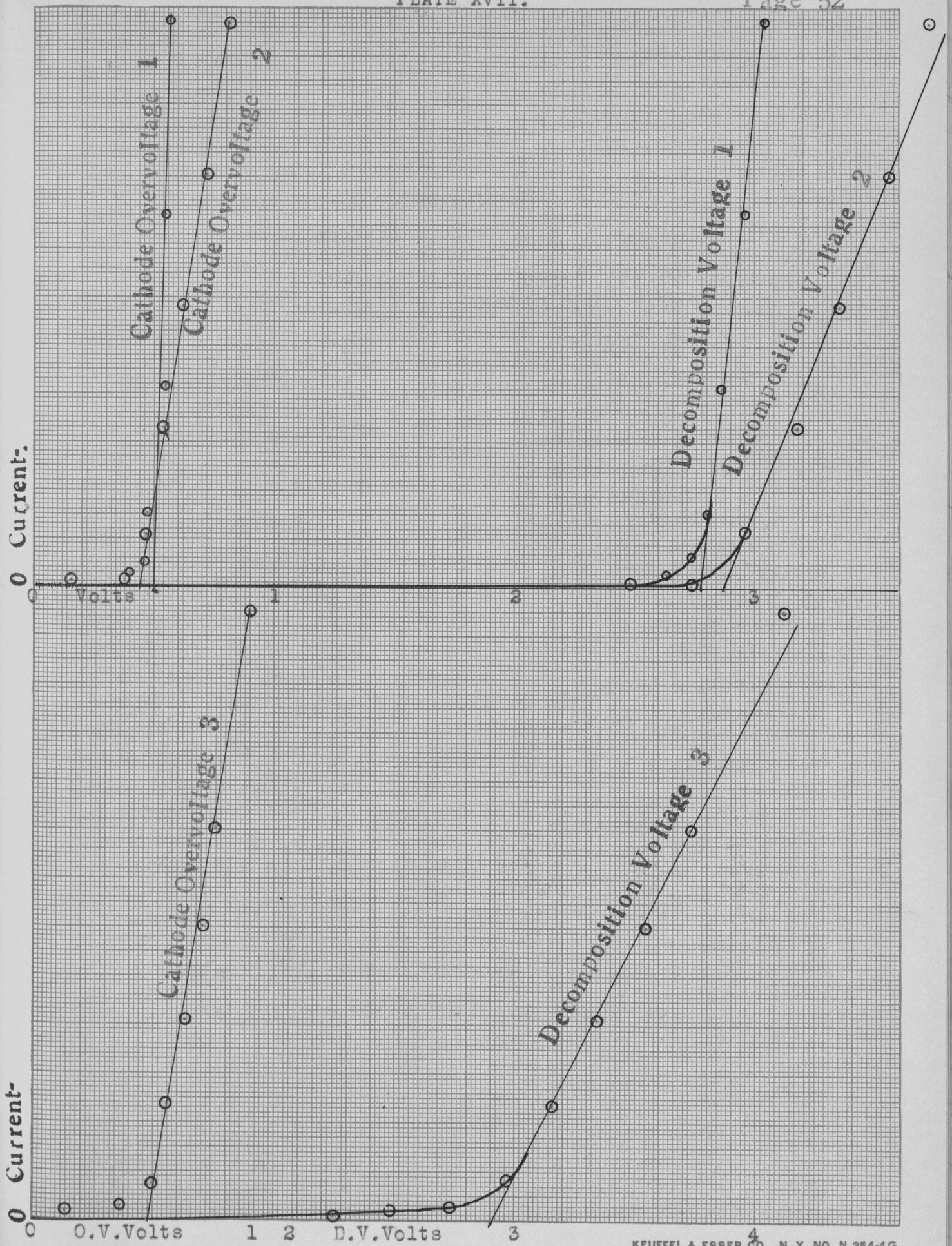


TABLE NUMBER XX.

TABLE NUMBER XX.

Zinc Iodide in Liquid Ammonia.

Current. Volts	Volts	Current. Volts	Volts
applied.	reference.	applied.	reference.

First Trial.

See Plate XVIII (1).

0.02	1.048	
0.10	1.570	
0.22	1.917	0.173
0.43	1.996	0.196
0.78	2.130	0.232
2.05	2.284	0.284
3.00	2.402	0.328
4.00	2.480	0.380
6.00	2.686	0.468
8.20	2.856	0.570
9.25	2.964	0.620

Decomposition
voltage 2.13 volts.

Cathode over-
voltage 0.20 volts.

Second Trial.

See Plate XVIII (3).

0.15	2.032	0.032
0.25	2.096	0.030
0.50	2.208	0.052
0.98	2.292	0.074
1.70	2.442	0.154
3.70	2.596	0.178
6.90	2.866	0.304
9.20	3.016	0.384

Decomposition
voltage 2.30 volts.

Cathode over-
voltage 0.05 volts.

Third Trial.

See Plate XVIII (3).

0.09	1.886	0.016
0.18	2.008	0.022
0.30	2.108	0.038
0.70	2.198	0.580
1.25	2.294	0.882
2.15	2.418	0.114
3.20	2.496	0.156
5.43	2.650	0.232
8.10	2.820	0.320
9.70	2.918	0.376

Decomposition
voltage 2.28 volts.

Cathode over-
voltage 0.04 volts.

Fourth Trial.

See Plate XVIII (4).

0.1	1.474	
0.28	1.994	0.024
1.5	2.210	0.080
3.0	2.424	0.130
5.1	2.670	0.210
7.1	2.850	0.268
9.7	3.058	0.370
12.0	3.272	0.464
14.0	3.470	0.564
17.0	3.688	0.666

Decomposition
voltage 2.21 volts.

Cathode over-
voltage 0.03 volts.

Average Decomposition Voltage 2.23 volts.

Average Cathode Overvoltage 0.08 volts.

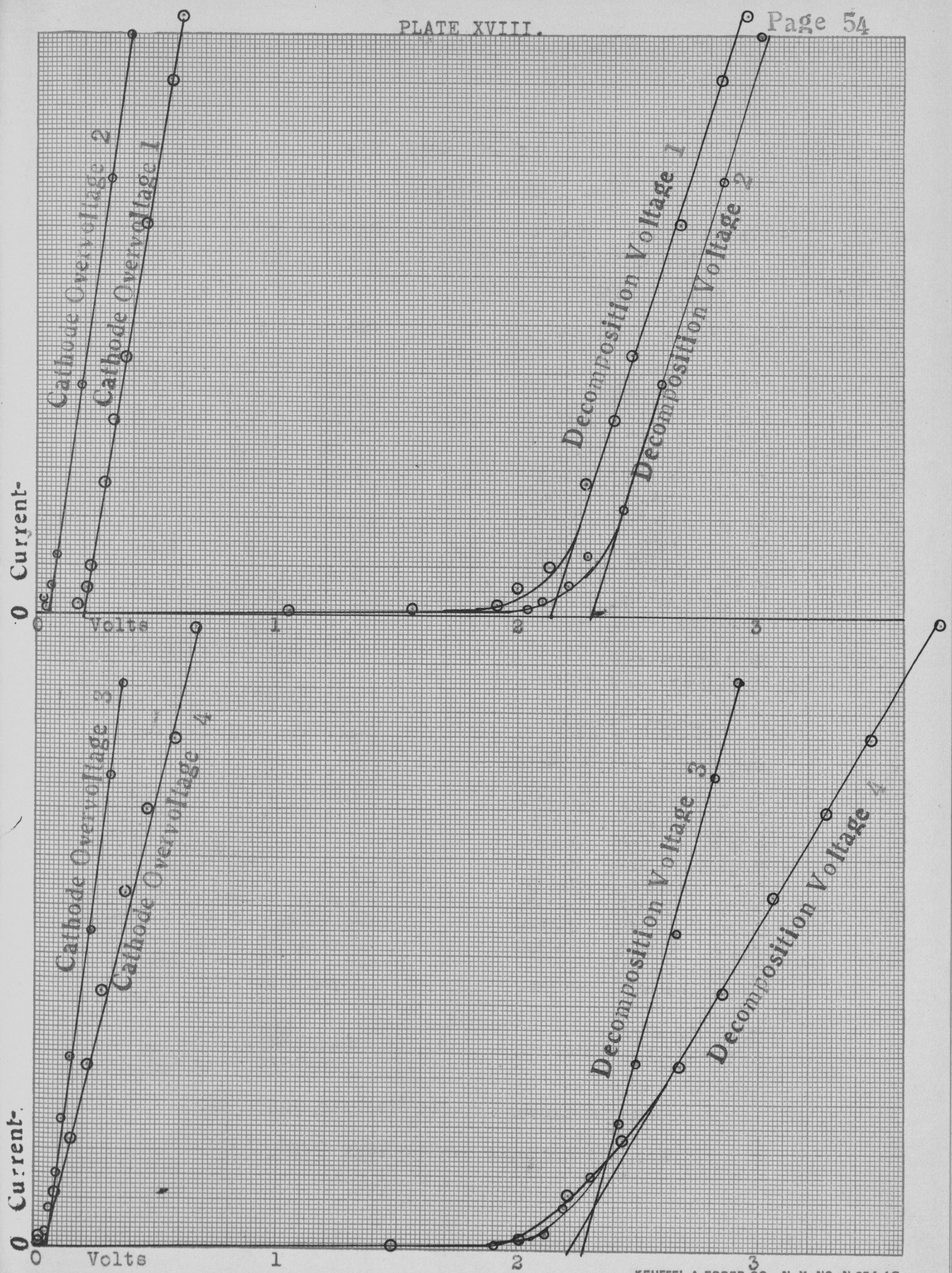


TABLE NUMBER XXI.

TABLE NUMBER XXI.

Zinc Iodide in Water.

Current. Volts applied. reference.	Volts reference.	Current. Volts applied. reference.	Volts reference.
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First Trial.

See Plate XIX (1).

0.10	1.048	
0.25	1.372	0.070
2.40	1.456	0.106
5.48	1.516	0.136
8.20	1.582	0.172
10.30	1.620	0.200

Decomposition
voltage 1.38 volts.

Cathode over-
voltage 0.07 volts.

E.M.F. 1.30 volts.

Second Trial.

See Plate XIX (2).

0.7	0.992	
1.8	1.476	0.074
4.1	1.684	0.180
6.8	1.892	0.292
12.0	2.390	0.490
18.0	2.790	0.682

(Continued above).

23.0	3.108	0.852
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Decomposition
voltage 1.36 volts.

Cathode over-
voltage 0.04 volts.

E.M.F. 1.30 volts.

Third Trial.

See Plate XIX (3).

0.3	0.800	
0.5	0.986	
1.7	1.462	0.070
4.9	1.682	0.206
7.7	1.896	0.316
11.0	2.104	0.440
13.5	2.284	0.534
17.0	2.508	0.652
20.0	2.702	0.750
23.0	2.920	0.862
26.0	3.118	0.952
29.0	3.310	1.046

Decomposition
voltage 1.35 volts.

Cathode over-
voltage 0.04 volts.

Average Decomposition Voltage 1.36 volts.

Average Cathode Overvoltage 0.04 volts.

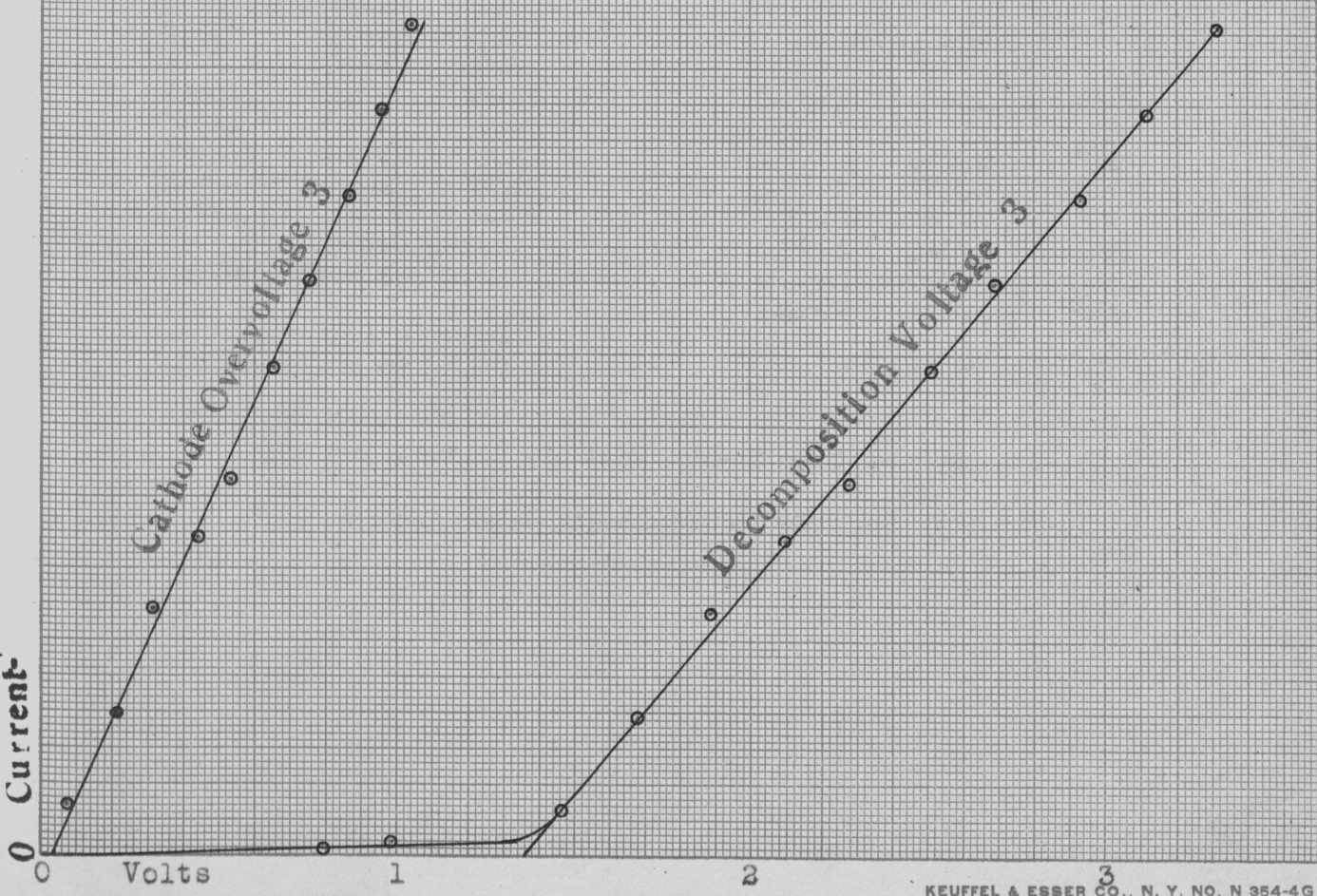
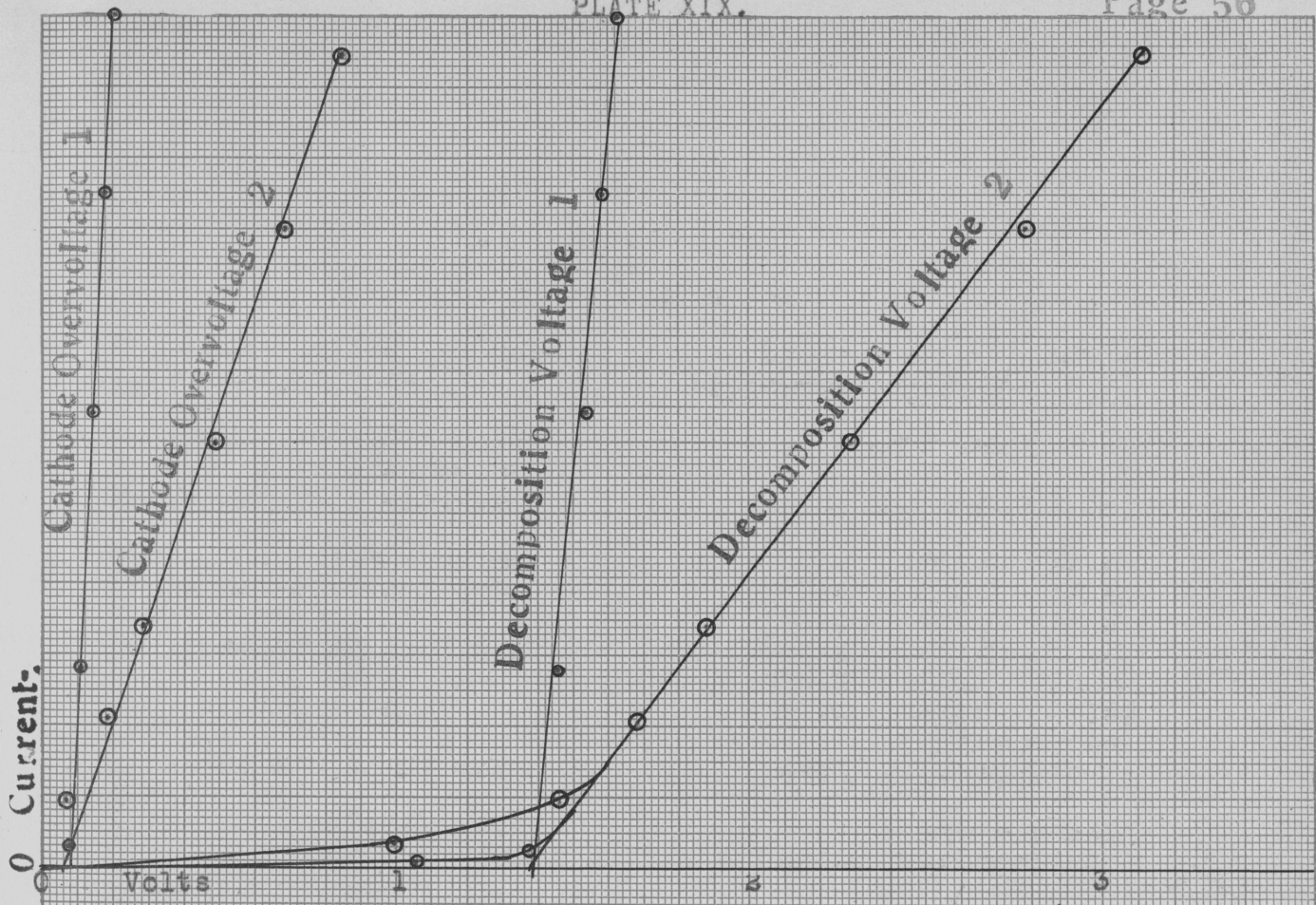


TABLE NUMBER XXII.

TABLE NUMBER XXII.

Copper Nitrate in Liquid Ammonia.

Current. Volts applied.	Volts reference.	Current. Volts applied.	Volts reference.
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First Trial. $\text{Cu}(\text{NO}_3)_2 \cdot x\text{NH}_3$.

See Plate XX (1).

0.9	0.986	0.040
2.5	1.224	0.152
4.2	1.454	0.264
6.0	1.686	0.372
7.7	1.904	0.478
9.55	2.144	0.582
11.0	2.366	0.700
15.0	2.810	0.916
18.0	3.258	1.136
22.0	3.736	1.370
25.0	4.170	1.580

Decomposition
voltage 0.94 volts.

Cathode over-
voltage 0.02 volts.

Second Trial. $\text{Cu}(\text{NO}_3)_2 \cdot x\text{NH}_3$.

See Plate XX (2).

1.1	0.994	0.062
2.9	1.230	0.162
5.1	1.454	0.264
9.7	1.902	0.468
14.5	2.352	0.694
29.0	3.656	1.326
34.0	4.110	1.556

Decomposition
voltage 0.94 volts.

Cathode over-
voltage 0.02 volts.

Third Trial. $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$.

See Plate XX (3).

2.0	1.004	0.032
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3.0	1.108	0.082
4.1	1.208	0.134
5.0	1.308	0.192
7.0	1.508	0.308
9.0	1.700	0.426
12.2	2.000	0.602
14.5	2.180	0.704
16.8	2.368	0.806
19.9	2.572	0.906
22.0	2.752	1.004
24.8	2.962	1.120
26.9	3.134	1.222
29.8	3.348	1.336
32.0	3.536	1.442

Decomposition
voltage 0.82 & 1.03 volts.

Cathode over-
voltage -0.10 & 0.09 volts.

Fourth Trial. $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$.

See Plate XX (4).

0.7	0.992	
3.8	1.200	0.098
6.7	1.406	0.206
9.9	1.624	0.316
13.0	1.824	0.416
15.5	2.026	0.520
19.0	2.234	0.622
22.0	2.430	0.724
25.0	2.636	0.828
29.0	2.846	0.936
32.0	3.044	1.036

Decomposition
voltage 0.94 & 1.05 volts.

Cathode over-
voltage -0.04 & 0.05 volts.

Average Decomposition Voltage (1) & (2) 0.94 volts.

Average Decomposition Voltage (3) & (4) 0.88 & 1.04 volts.

Average Cathode Overvoltage (1) & (2) 0.02 volts.

Average Cathode Overvoltage (3) & (4) -0.04 & 0.05 volts.

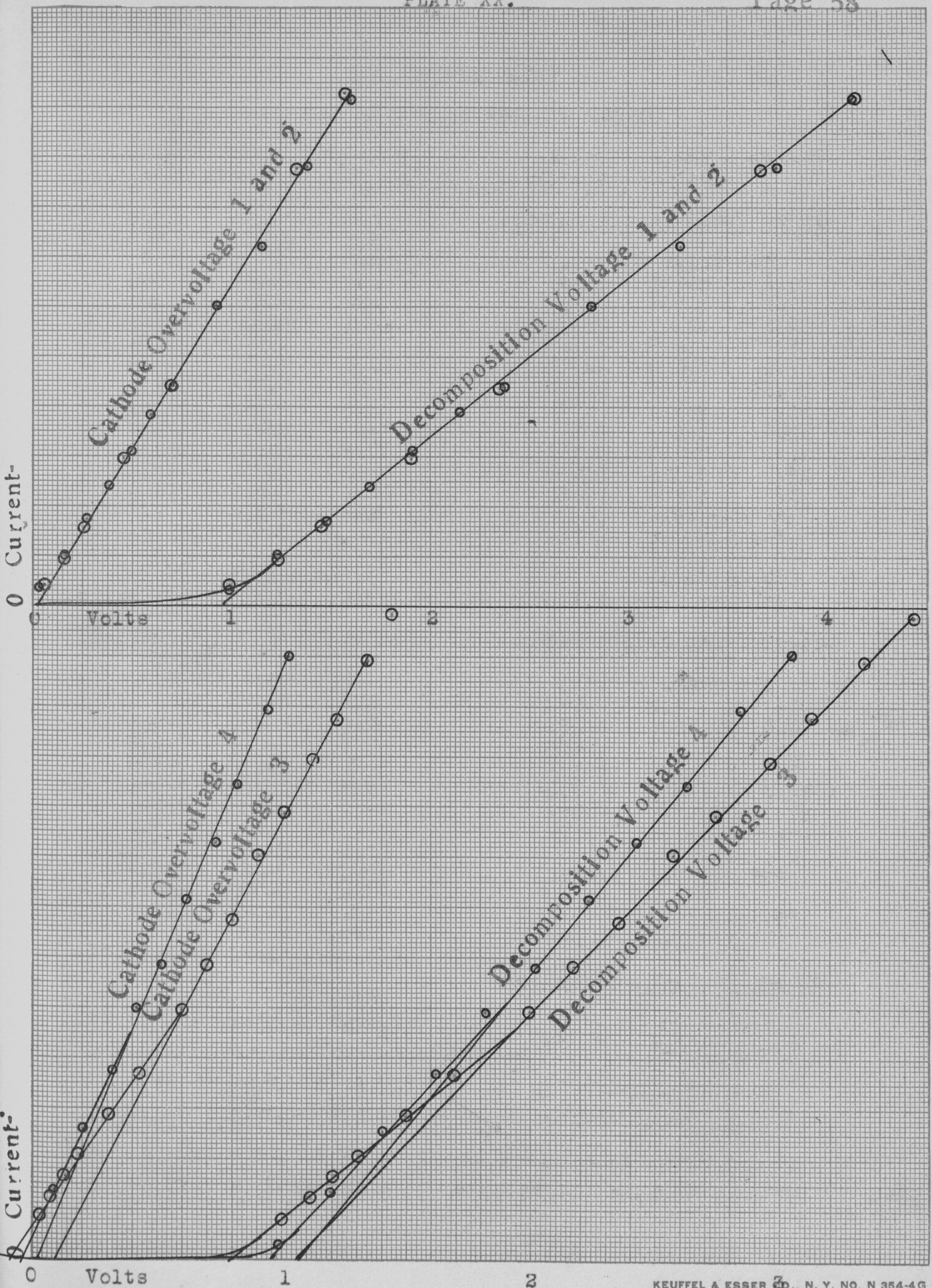


TABLE NUMBER XXIII.

TABLE NUMBER XXIII.

Copper Nitrate in Water.

Current. Volts applied. reference.	Current. Volts applied. reference.
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First Trial.

See Plate XXI (1).

0.2	0.968	0.020
0.9	1.476	0.090
2.1	1.708	0.156
4.5	1.916	0.220
7.9	2.132	0.280
11.0	2.306	0.376
14.0	2.514	0.474
18.0	2.712	0.566
21.0	2.900	0.656
25.0	3.098	0.756
32.0	3.474	0.936
39.0	3.864	1.136

Decomposition
voltage 1.80 volts.

Cathode over-
voltage 0.08 volts.

Second Trial.

See Plate XXI (2).

2.1	1.936	0.212
5.5	2.142	0.298
8.2	2.348	0.394
11.0	2.560	0.494
13.0	2.760	0.606
16.0	3.002	0.726
18.0	3.172	0.810
22.0	3.388	0.912
25.0	3.596	1.008

Decomposition
voltage 1.81 volts.

Cathode over-
voltage 0.10 volts.

Third Trial. Ammonia Added.

See Plate XXI (3).

3.5	1.430	0.100
6.0	1.646	0.200
8.7	1.868	0.304
11.0	2.060	0.390
14.0	2.284	0.500
16.5	2.504	0.608
22.5	2.908	0.802
25.0	3.104	0.900
31.0	3.526	1.110

Decomposition
voltage 1.12 & 1.15 volts.

Cathode over-
voltage -0.02 volts.

Fourth Trial. Ammonia Added.

See Plate XXI (4).

1.3	1.206	
3.2	1.416	0.076
5.0	1.608	0.190
6.4	1.808	0.314
8.002	2.002	0.444
9.9	2.190	0.550
12.0	2.398	0.666
14.1	2.600	0.768
16.0	2.772	0.864
18.0	2.968	0.964
20.0	3.162	1.074
24.2	3.560	1.290

Decomposition
voltage 1.05 & 1.24 volts.

Cathode over-
voltage 0.05 volts.

Average Decomposition Voltage (1) & (2) 1.80 volts.

Average Decomposition Voltage (3) & (4) 1.08 & 1.25 volts.

Average Cathode Overvoltage (1) & (2) 0.09 volts.

Average Cathode Overvoltage (3) & (4) 0.01 volts.

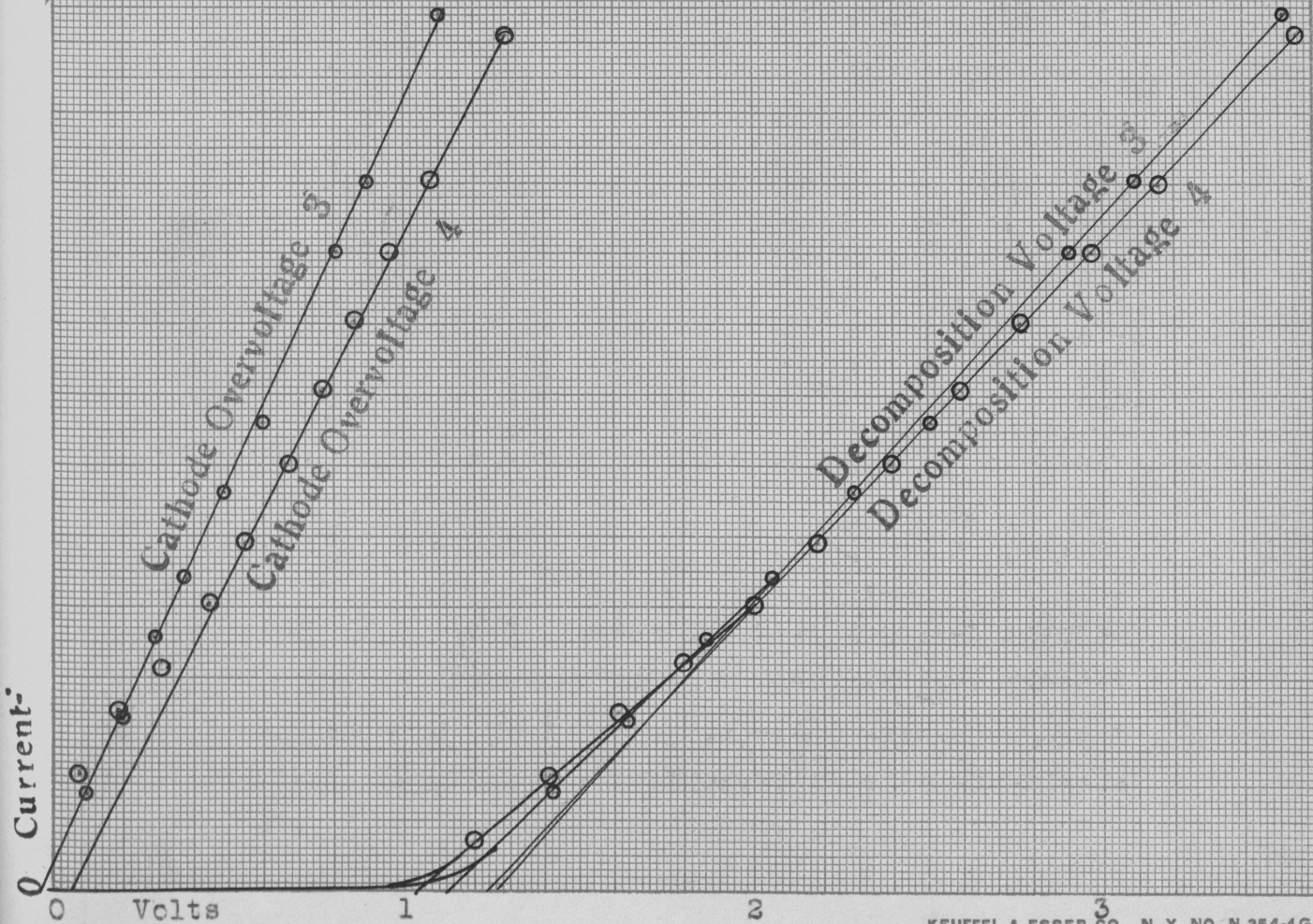
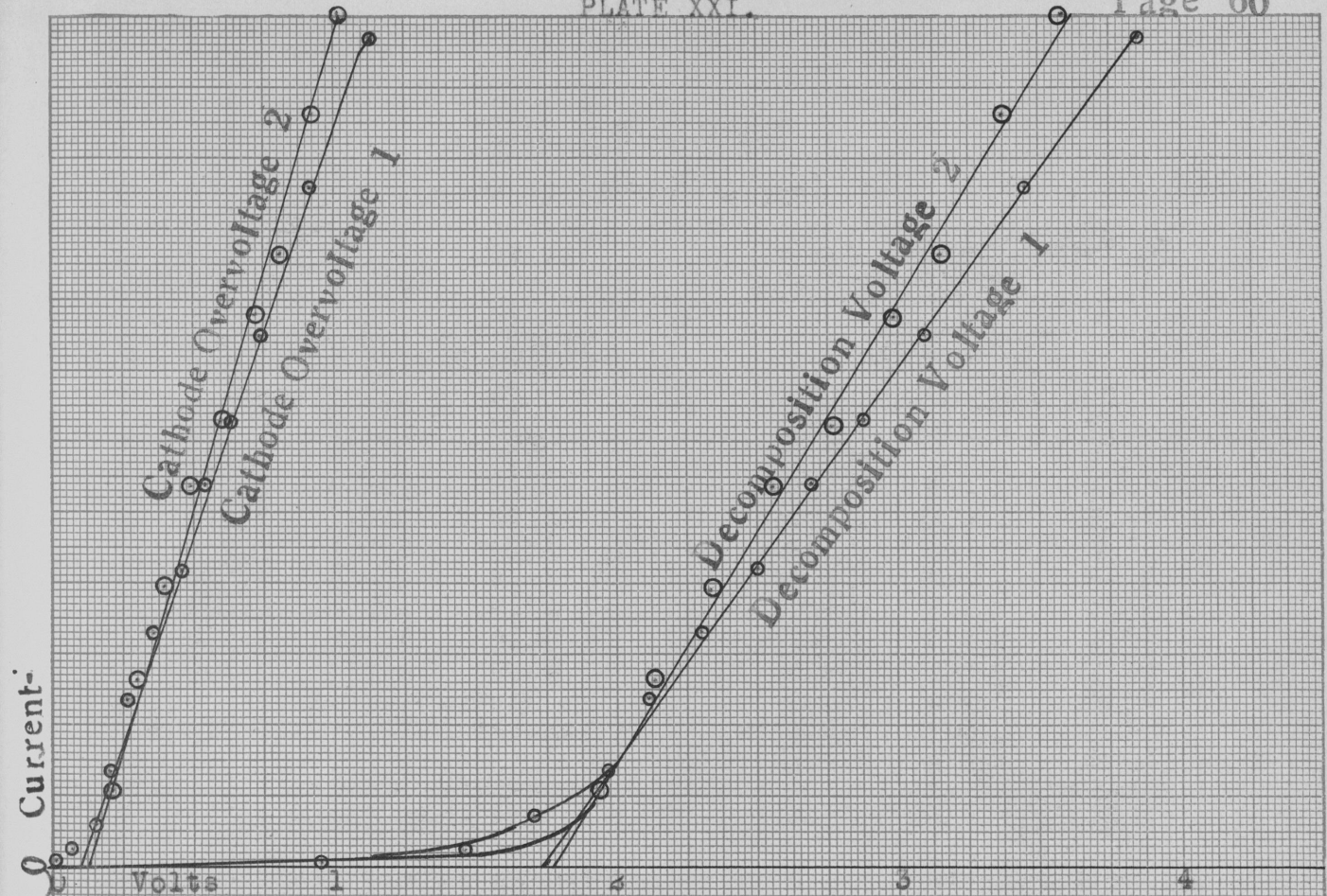


TABLE NUMBER XXIV.

TABLE NUMBER XXIV.

Copper Sulphate in Water.

Current. Volts Volts
applied. reference.

Current. Volts Volts
applied. reference.

First Trial.

See Plate XXII (1).

0.3	1.626	0.144
1.2	1.826	0.220
2.3	2.028	0.296
3.3	2.222	0.368
4.5	2.428	0.458
5.2	2.610	0.540
6.2	2.806	0.626
7.3	3.000	0.714
9.7	3.410	0.904
10.3	3.588	0.986

Decomposition
voltage 1.62 volts.

Cathode over-
voltage 0.12 volts.

E.M.F. 1.48 volts.

Second Trial.

See Plate XXII (2).

0.8	1.700	0.112
3.2	2.000	0.234
5.0	2.200	0.334
6.9	2.400	0.422
8.7	2.600	0.528
10.2	2.800	0.638
12.4	3.000	0.746
14.4	3.200	0.850
16.2	3.400	0.960
18.2	3.600	1.062

Decomposition
voltage 1.63 volts.

Cathode over-
voltage 0.06 volts.

E.M.F. 1.50 volts.

Third Trial. Ammonia Added.

See Plate XXII (3).

1.0	1.222	
2.1	1.428	0.080
3.5	1.632	0.184
5.7	2.016	0.384
8.0	2.416	0.600
9.2	2.618	0.714
11.1	2.996	0.930
13.5	3.412	1.186

Decomposition
voltage 1.05 volts.

Cathode over-
voltage -0.15 volts.

E.M.F. 0.90 volts.

Fourth Trial. Ammonia Added.

See Plate XXII (4).

1.2	1.200	
3.0	1.400	0.088
4.9	1.600	0.140
6.5	1.800	0.250
8.5	2.000	0.366
10.2	2.200	0.474
12.3	2.400	0.596
14.3	2.600	0.718
16.0	2.800	0.836
18.0	3.000	0.958
19.9	3.200	1.084
21.7	3.400	1.214

Decomposition
voltage 1.08 volts.

Cathode over-
voltage -0.17 volts.

E.M.F. 0.90 volts.

Average Decomposition Voltage 1.63 volts.

Average Decomposition Voltage with Ammonia 1.06 volts.

Average Cathode Overvoltage 0.09 volts.

Average Cathode Overvoltage with Ammonia -0.16 volts.

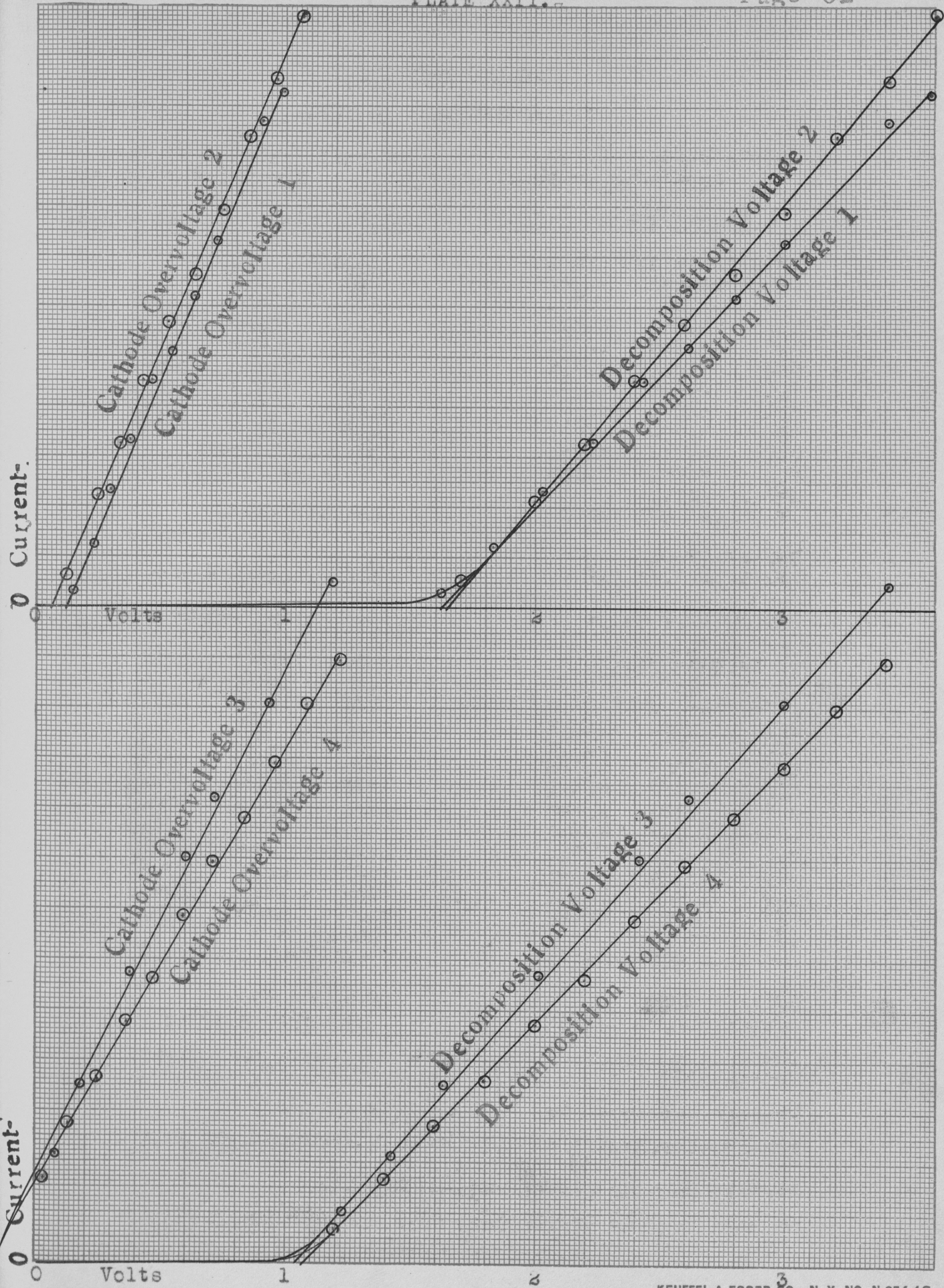


TABLE NUMBER XXV.

TABLE NUMBER XXV.

Ferric Nitratetin Liquid Ammonia.

Current. Volts applied.	Volts reference.	Current. Volts applied.	Volts reference.
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First Trial.

See Plate XXIII (1).

0.25	1.242	0.290
0.30	1.486	0.550
0.30	1.738	0.824
0.62	1.980	1.052
1.5	2.210	1.230
3.1	2.444	1.380
5.0	2.666	1.540
7.0	2.880	1.640
9.0	3.102	1.738
11.0	3.324	1.856
12.5	3.484	1.944
15.0	3.744	2.062
18.5	4.164	2.270
22.5	4.600	2.486

Decomposition
voltage 2.09 volts.

Cathode over-
voltage 1.27 volts

Second Trial.

See Plate XXIII (2).

0.7	0.982	0.170
2.7	1.222	0.340
6.3	1.412	0.440
9.1	1.638	0.620
11.0	1.860	0.800
13.0	2.080	0.980

10.0	2.408	1.360
13.0	2.556	1.466
17.0	2.754	1.600
21.0	2.946	1.680
25.0	3.138	1.752
30.0	3.332	1.820
35.0	3.520	1.922
43.0	3.910	2.112

Decomposition
voltage 1.04 & 1.96 volts.

Cathode over-
voltage 0.11 & 1.25 volts.

Third Trial.

See Plate XXIII (3).

1.0	0.980	0.258
3.2	1.204	0.432
5.9	1.408	0.614
6.3	1.668	0.860
6.4	1.886	1.200
7.3	2.120	1.372
13.5	2.298	1.500
20.0	2.444	1.586
27.0	2.600	1.672
35.0	2.730	1.726
43.0	2.870	1.800

Decomposition
voltage 1.00 & 2.02 volts.

Cathode over-
voltage 0.20 & 1.40 volts.

Average Decomposition Voltage 1.02 & 2.02 volts.

Average Cathode Overvoltage 0.15 & 1.33 volts.

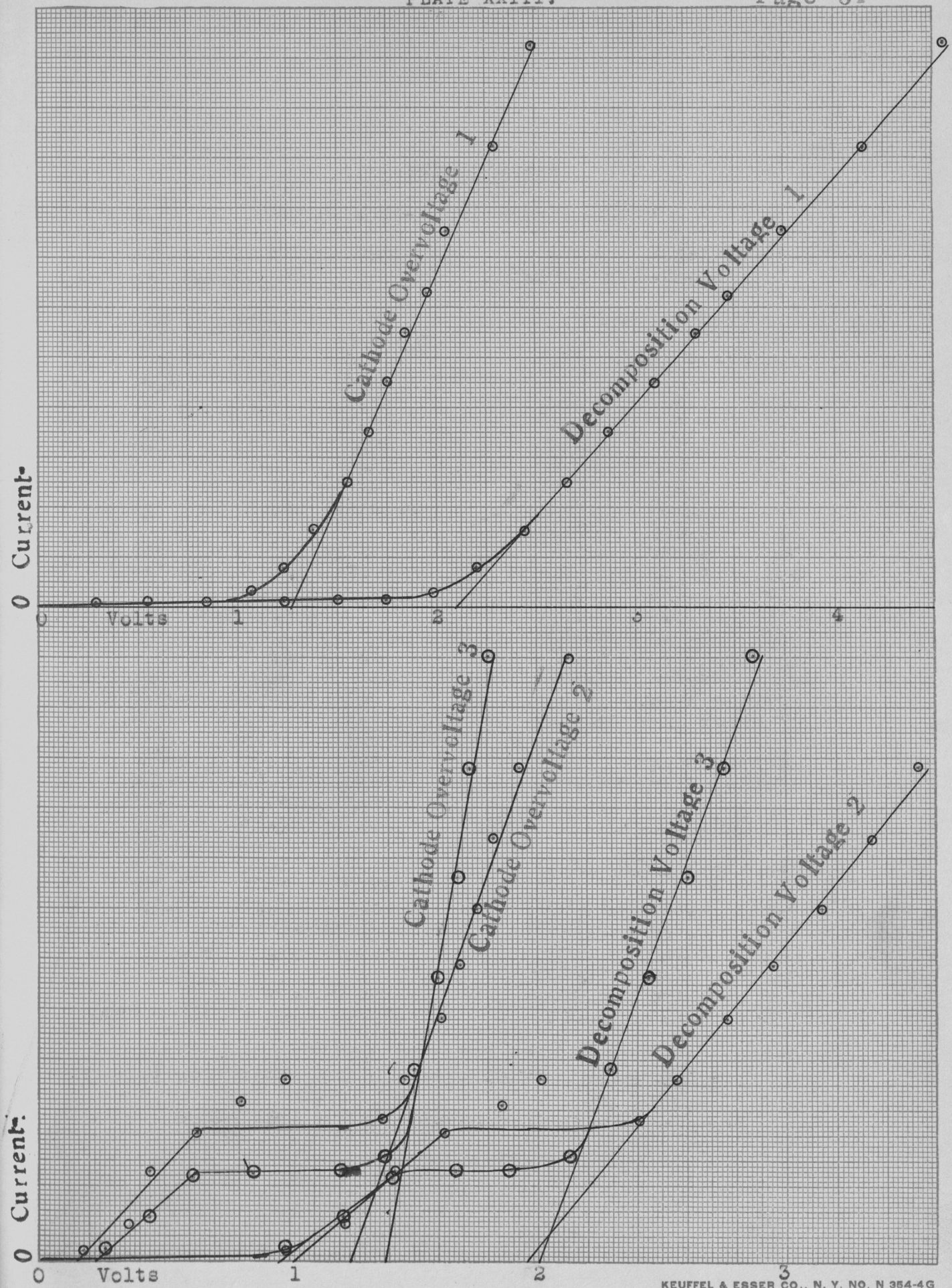


TABLE NUMBER XXVI.

TABLE NUMBER XXVI.

Ferric Nitratet in Water.

Current.	Volts applied.	Volts reference.	Current.	Volts applied.	Volts reference.
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First Trial.

Second Trial.

See Plate XXIV (1).

See Plate XXIV (2).

0.2	0.990	-0.932
1.3	1.234	0.828
3.3	1.446	0.726
5.9	1.668	0.610
8.7	1.882	0.494
10.5	2.040	0.406
14.0	2.322	0.234
15.5	2.538	0.090
17.0	2.768	0.084
18.0	2.986	0.276
20.0	3.228	0.460
25.0	3.630	0.740
30.0	4.000	0.954
38.0	4.502	1.236

1.13	0.978	-0.600
1.35	1.236	0.590
2.70	1.470	0.490
4.65	1.668	0.340
6.50	1.912	0.204
8.00	2.154	0.016
8.80	2.392	0.192
12.0	2.854	0.540
16.0	3.298	0.860
21.0	3.750	1.170
25.0	4.136	1.500
29.0	4.600	1.736

Decomposition
voltage 1.22 & 1.76 volts.

Decomposition
voltage 1.15 & 1.80 volts.

Cathode over-
voltage -0.9 & -0.2 volts.

Cathode over-
voltage -0.7 & -0.2 volts.

Average Decomposition Voltage 1.19 & 1.78 volts.

Average Cathode Overvoltage -0.8 & -0.2 volts.

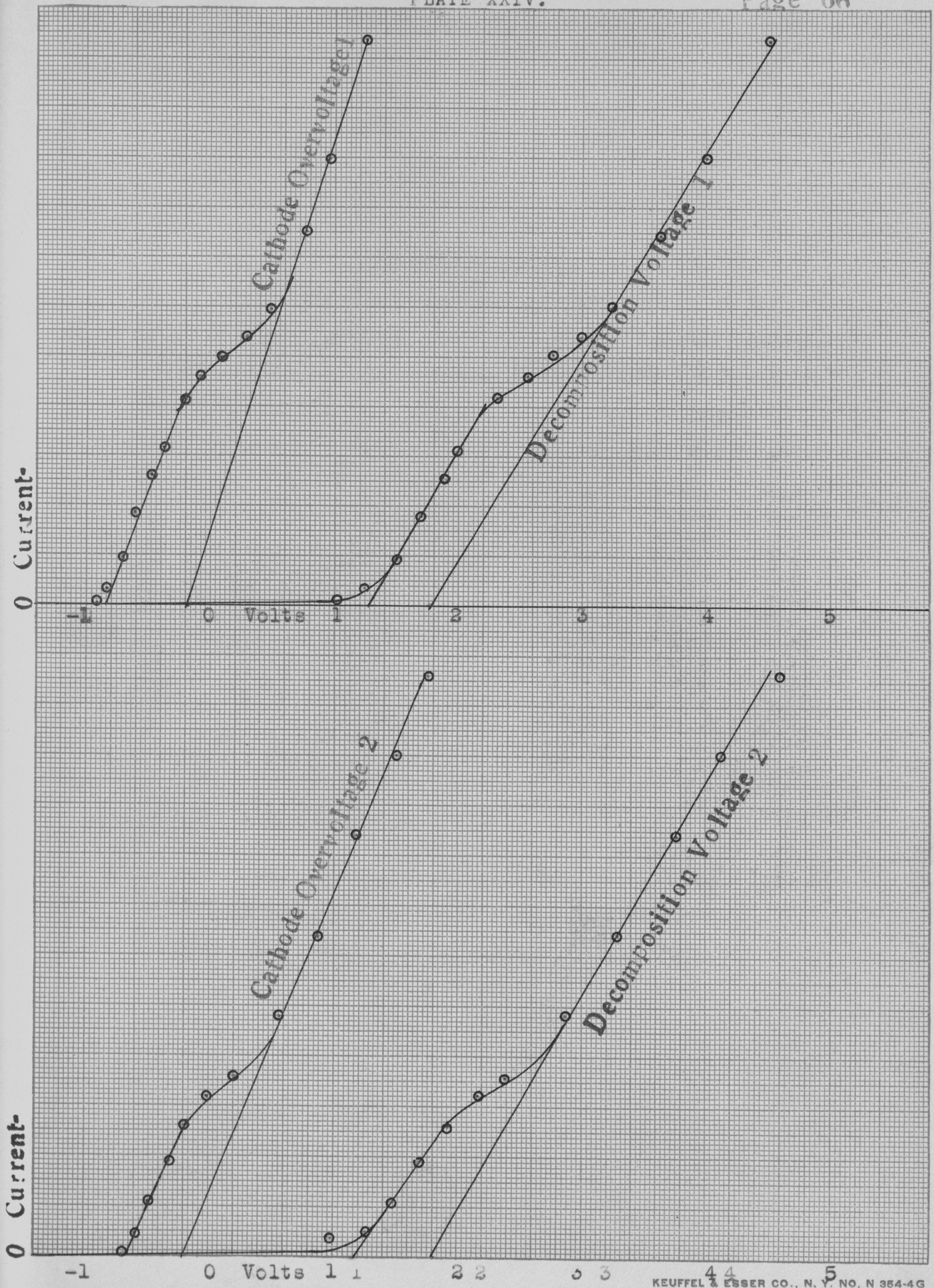


TABLE NUMBER XXVII.

TABLE NUMBER XXVII.

Ammonium Nitrate in Liquid Ammonia.

Current.	Volts applied.	Current.	Volts applied.	Current.	Volts applied.
<u>First Trial.</u>		13.3	2.300	2.8	1.850
		15.7	2.400	5.5	2.050
See Plate XXV (1).		21.8	2.600	6.2	2.100
		28.0	2.800	7.0	2.150
0.3	1.600			7.9	2.200
0.9	1.650	Decomposition		9.1	2.250
1.3	1.700	voltages 1.57,		10.0	2.300
2.0	1.750	1.65 & 1.89 volts.		12.3	2.400
2.9	1.800			18.7	2.600
3.8	1.850	<u>Second Trial.</u>		25.3	2.800
4.8	1.900				
5.3	1.950	See Plate XXV (2).		Decomposition	
6.2	2.000			voltages 1.49,	
7.6	2.050	0.6	1.600	1.65, 1.86 and	
8.6	2.100	0.9	1.650	2.01 volts.	
9.7	2.150	1.1	1.750		
10.5	2.200	1.5	1.750		
11.9	2.250	2.1	1.800		

Average Decomposition Voltages 1.53, 1.65, 1.88 and

2.01 volts.

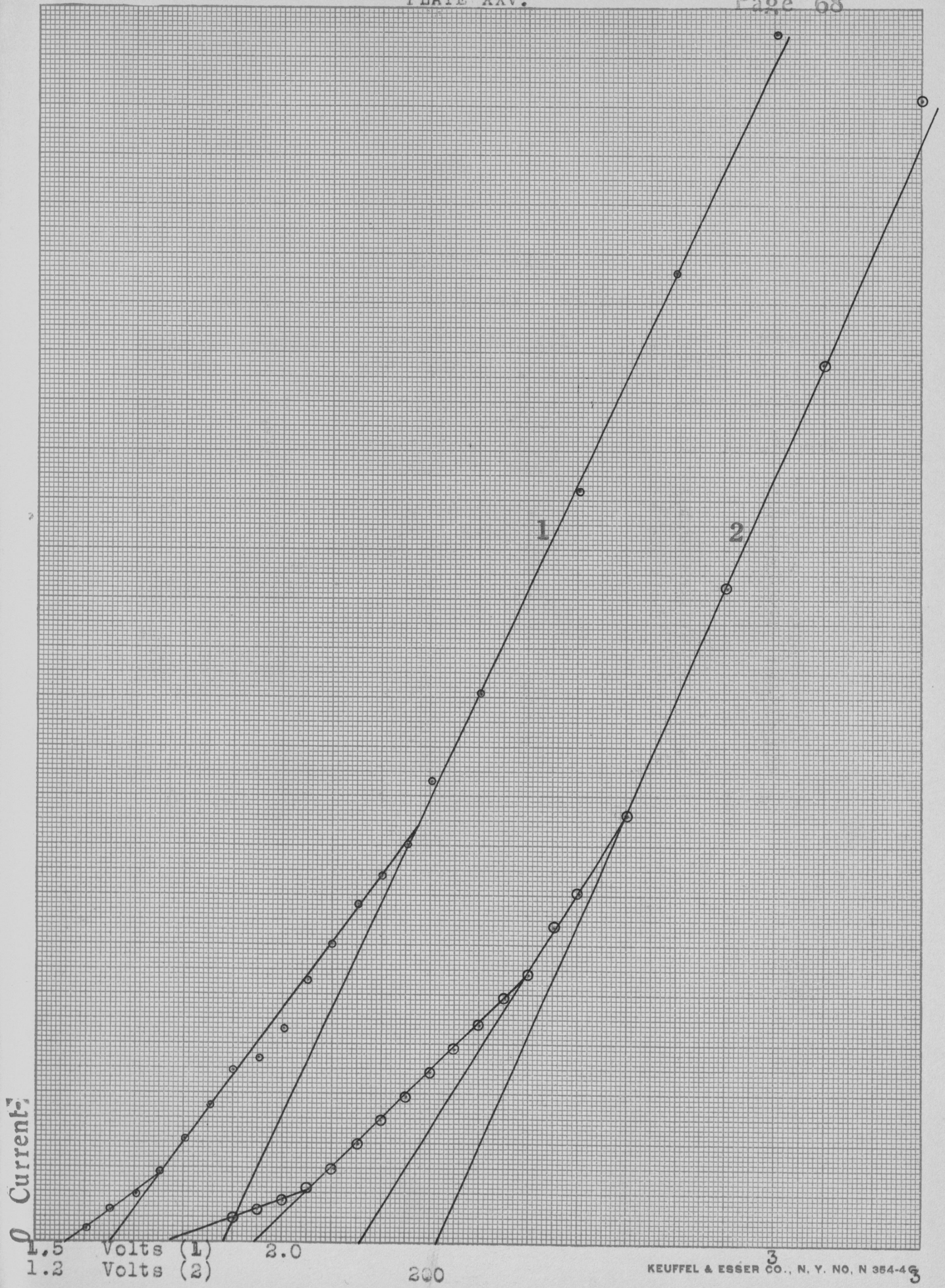


TABLE NUMBER XXVIII.

TABLE NUMBER XXVIII.

Ammonium Chloride in Liquid Ammonia.

Current. Volts applied.		Current. Volts applied.		Current. Volts applied.	
<u>First Trial.</u>		31.0	3.430	<u>Fourth Trial.</u>	
		35.7	3.576		
See Plate XXVI (1)		40.0	3.720	See Plate XXVI (4).	
		42.3	3.818		
0.2	1.520	44.5	3.890	0.5	1.756
1.2	1.780	47.2	3.990	1.6	1.992
3.4	2.010	50.0	4.074	5.2	2.246
6.9	2.212			10.0	2.480
12.0	2.396	Decomposition voltage 2.16 volts.		15.0	2.714
17.0	2.558			20.1	2.932
23.0	2.722				
36.0	3.060	<u>Third Trial.</u>		Decomposition Voltage 2.03 volts.	
48.0	3.380	See Plate XXVI (3).			
62.0	3.716			<u>Fifth Trial.</u>	
Decomposition voltage 2.13 volts.		0.85	1.762	See Plate XXVI (5).	
		2.10	1.996		
		4.45	2.190		
<u>Second Trial.</u>		8.20	2.380	0.3	1.496
		12.0	2.550	1.0	1.742
See Plate XXVI (2).		16.0	2.730	2.4	1.970
		26.0	3.060	5.1	2.184
1.0	1.762	37.0	3.414	8.8	2.384
2.8	2.008	48.0	3.758	13.0	2.580
5.3	2.254			18.0	2.782
16.3	2.798	Decomposition voltage 2.16 volts.		23.0	2.990
20.0	2.964			28.0	3.168
23.6	3.114				
27.5	3.270			Decomposition voltage 2.04 volts.	

Average Decomposition Voltage 2.11 volts.

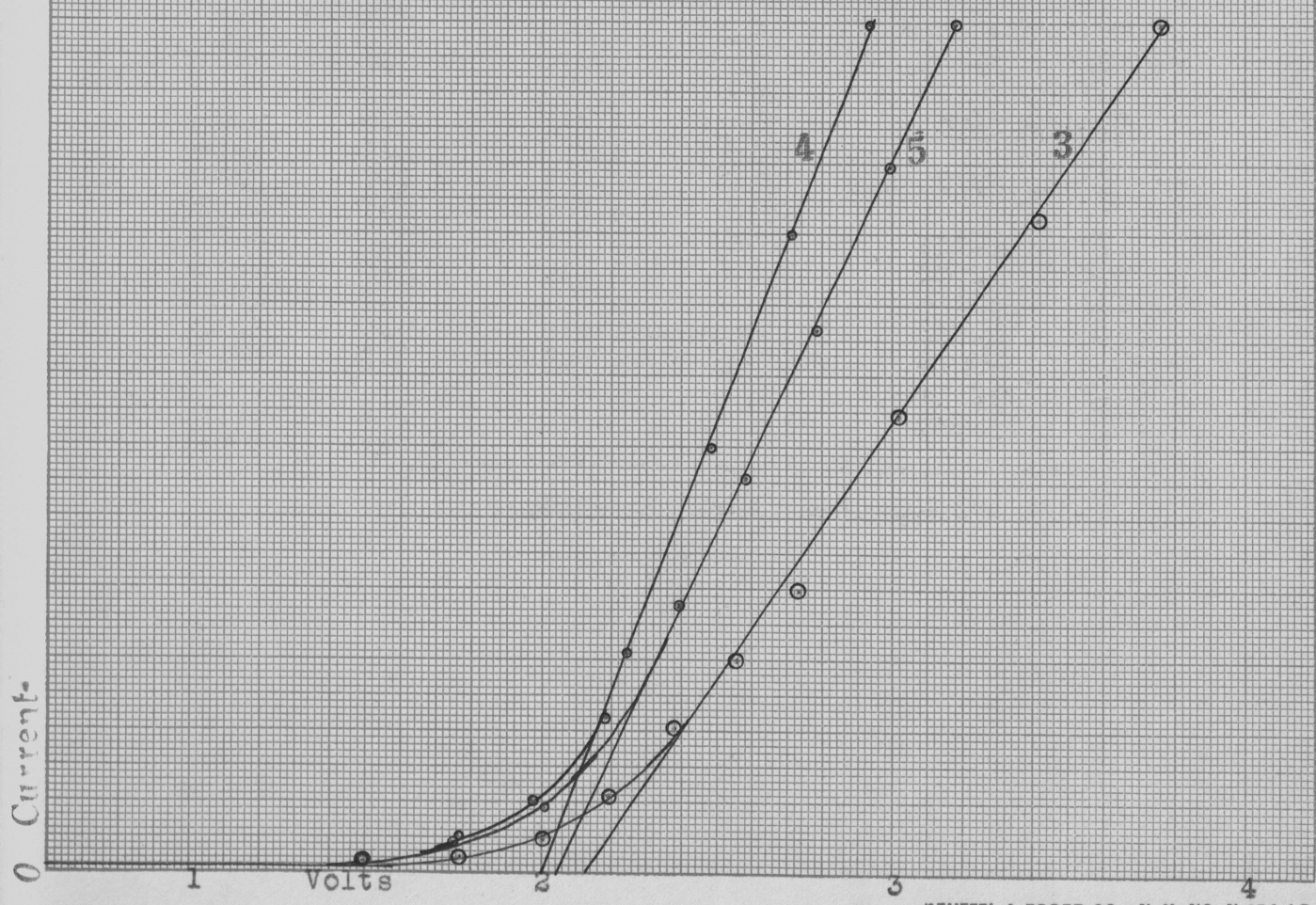
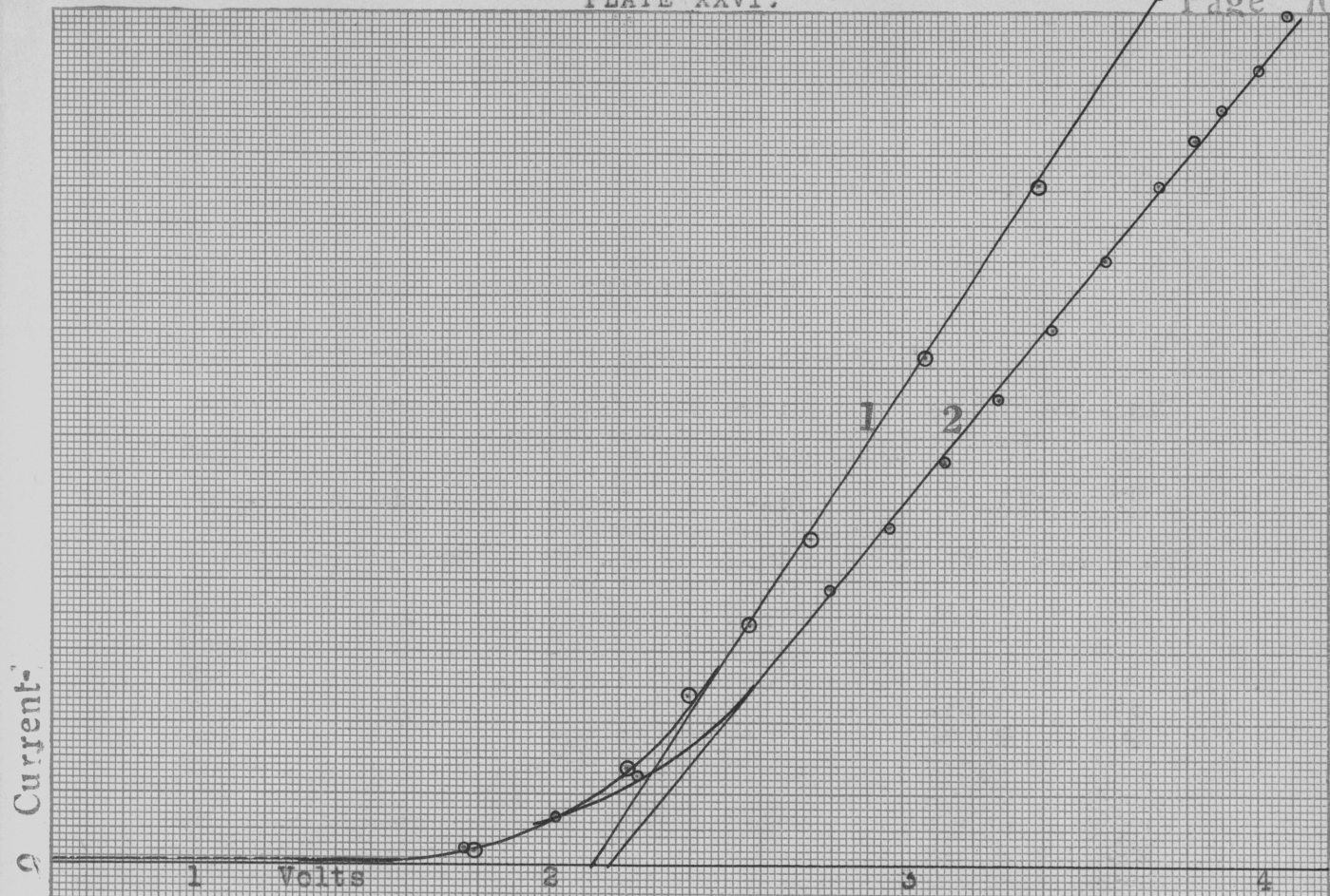


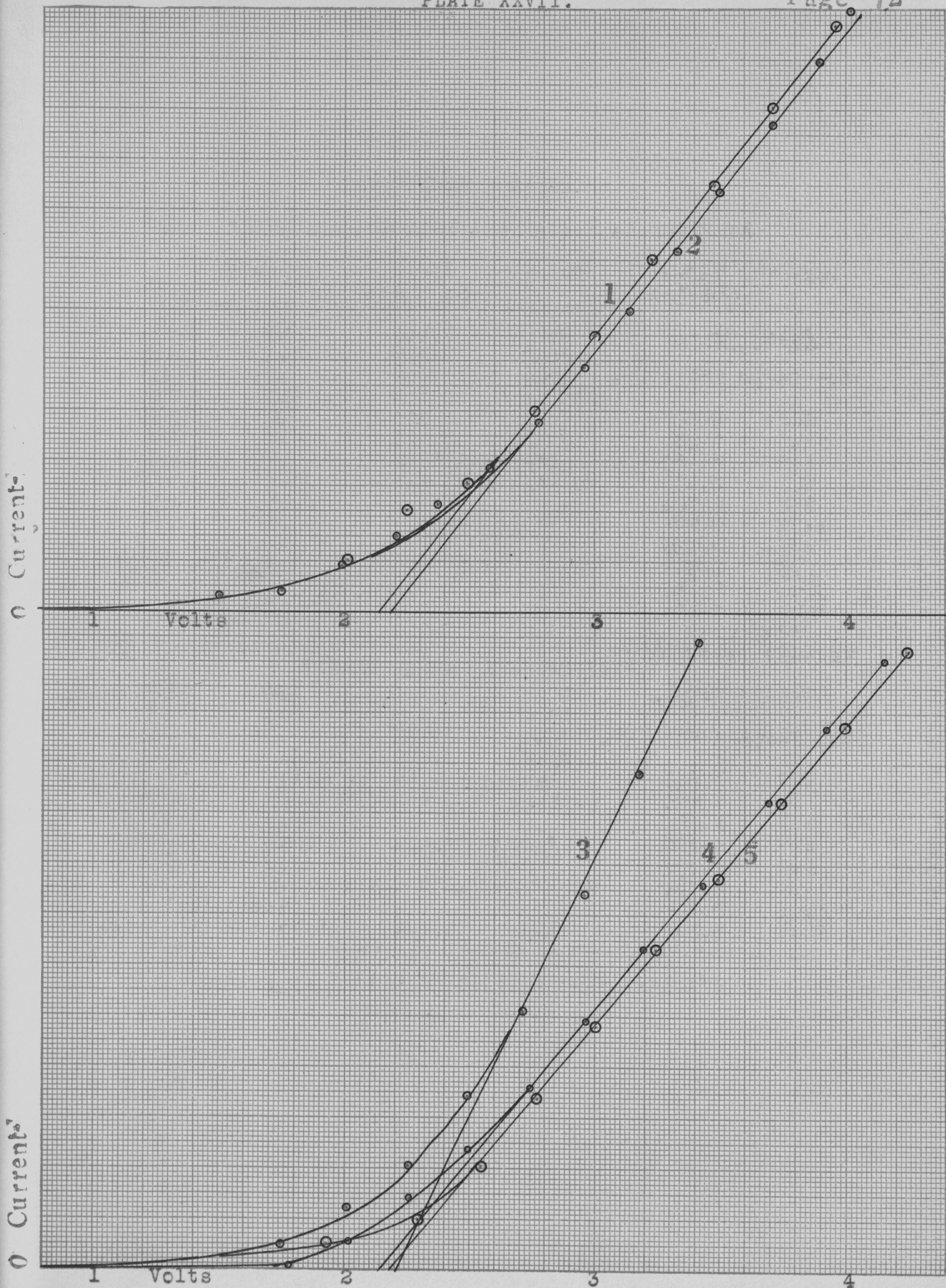
TABLE NUMBER XXIX.

TABLE NUMBER XXIX.

Ammonium Chloride in Liquid Ammonia at -60 C.

Current.	Volts applied.	Current.	Volts applied.	Current.	Volts applied.
<u>First Trial.</u>					
		25.0	3.144	1.2	2.014
		30.0	3.332	3.0	2.248
See Plate XXVII (1).		35.0	3.508	5.2	2.492
		40.5	3.700	8.0	2.740
2.0	2.010	46.0	3.886	10.8	2.970
4.0	2.250	50.0	4.012	14.0	3.204
4.7	2.400	Decomposition		17.0	3.444
5.1	2.498	voltage 2.18 volts.		20.5	3.702
8.0	2.760			23.8	3.938
11.0	2.994	<u>Third Trial.</u>		26.7	4.174
14.0	3.226			Decomposition	
17.0	3.482	See Plate XXVII (3).		voltage 2.15 volts.	
20.1	3.716			<u>Fifth Trial.</u>	
23.5	3.954	1.2	1.760	See Plate XXVII (5).	
Decomposition		3.0	2.004		
voltage 2.14 volts.		5.0	2.244		
		8.5	2.494		
<u>Second Trial.</u>		12.7 ^{2.71}	2.712	1.0	1.930
		18.5	2.960	2.0	2.280
See Plate XXVII (2).		24.5	3.186	4.0	2.530
		31.0	3.422	6.8	2.770
1.3	1.506	Decomposition		9.7	3.002
1.8	1.750	voltage 2.21 volts.		12.7	3.250
4.0	1.994			15.5	3.494
6.2	2.200	<u>Fourth Trial.</u>		18.5	3.740
9.0	2.380			21.5	3.988
12.0	2.580	See Plate XXVII (4).		24.5	4.226
15.0	2.770			Decomposition	
20.3	2.956	0.2	1.770	voltage 2.19 volts.	

Average Decomposition Voltage 2.17 volts.



TABLES NUMBER XXX and XXXI.

TABLE NUMBER XXX.

Ammonium Bromide in Liquid Ammonia.

Current.	Volts applied.	Current.	Volts applied.	Current.	Volts applied.
<u>First Trial.</u>		Decomposition		12.3	2.573
See Plate XXVIII (1).		voltage 1.61 and		14.8	2.674
		2.10 volts.		16.8	2.766
		<u>Second Trial.</u>		18.6	2.858
1.2	1.744	See Plate XXVIII (2).		20.8	2.944
5.0	1.984			23.0	3.040
8.7	2.200			25.2	3.140
14.0	2.434	2.0	1.752	27.5	3.232
20.0	2.656	3.1	1.884	30.0	3.326
27.0	2.872	4.1	2.000	32.1	3.418
35.0	3.096	5.0	2.094	Decomposition	
42.5	3.320	8.3	2.380	voltage 1.67 and	
		10.0	2.482	2.10 volts.	

Average Decomposition Voltages 1.64 and 2.10 volts.

TABLE NUMBER XXXI.

Ammonium Iodide in Liquid Ammonia.

<u>First Trial.</u>		22.3	3.056	8.3	2.214
See Plate XXVIII (3).		24.2	3.150	11.2	2.318
		26.7	3.256	13.7	2.400
		28.7	3.346	16.8	2.494
0.8	1.766	31.0	3.434	19.9	2.578
1.7	1.904	Decomposition		22.6	2.672
2.5	2.010	voltage 2.06 volts.		25.7	2.770
2.0	2.098			28.5	2.858
3.5	2.210	<u>Second Trial.</u>		31.5	2.996
5.0	2.296	See Plate XXVIII (4).		34.0	3.070
7.5	2.400			36.8	3.150
10.0	2.492	0.5	1.540	40.2	3.238
12.0	2.580	0.5	1.540	46.0	3.366
14.0	2.694	1.3	1.730	51.0	3.464
17.5	2.866	3.0	1.940	Decomposition	
20.1	2.966	6.0	2.116	voltage 2.00 volts.	

Average Decomposition Voltage 2.03 volts.

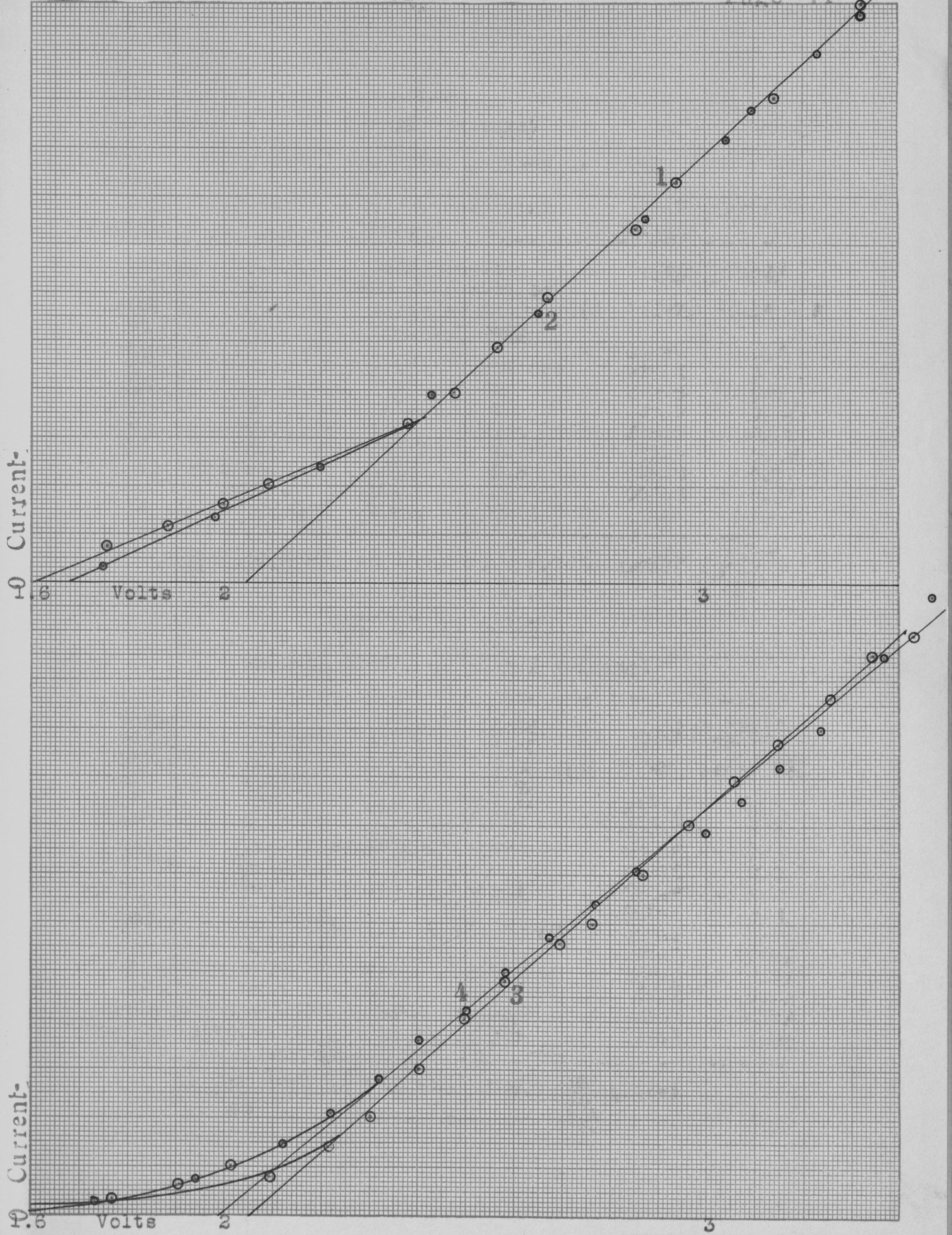


TABLE NUMBER XXXII.

Summary of Decomposition and Overvoltages.

Substances.	Decomposition volts			Overvoltages.		
	in ammonia	in water	in difference	in ammonia	in water	in difference
AgNO ₃	1.09	0.87	0.22	0.29	0.02	0.27
AgNO ₂	1.02	0.32	0.70	0.28	0.06	0.22
Ni(NO ₃) ₂	2.19	2.36	-0.17	1.25	0.89	0.36
Cd(NO ₃) ₂	1.87	2.36	-0.49	0.23	0.16	0.07
DdI ₂	1.67	1.10	0.57	0.02	0.02	0.00
Hg(NO ₃) ₂	0.79	1.37	-0.58	0.07	0.03	0.04
Other Hg salts	0.88	1.37	-0.49	0.04	0.03	0.01
Pb(NO ₃) ₂	1.61	1.84	-0.23	0.15	0.03	0.12
Zn(NO ₃) ₂	2.09	2.86	-0.77	0.03	0.48	-0.45
ZnI ₂	2.23	1.36	0.87	0.08	0.04	0.04
Cu(NO ₃) ₂ xNH ₃	0.94	1.08 1.25	-0.14	0.02	0.01 0.01	0.01
Cu(NO ₃) ₂ ·xH ₂ O	0.88 1.04	1.80	-0.92	-0.04 0.05	0.09	-0.13
Fe(NO ₃) ₃	1.02 2.02	1.19 1.78	-0.17 0.24	0.15 1.32	-0.8 -0.2	0.23 0.44 1.52
AgI	0.85			0.05		
HgI ₂	0.82			0.02		
CuSO ₄	1.	1.63			0.09	
" - NH ₄ OH		1.06			-0.16	
NH ₄ I	2.03					
NH ₄ Cl	2.11					
" at -60 C.	2.17					
NH ₄ Br	1.64 & 2.05					
NH ₄ NO ₃	1.53, 1.65, 1.88 and 2.01					

When the value in ammonia is smaller then there is a minus (-) sign before the difference. The same sign before a number under overvoltage indicates an undervoltage. All values taken from Plates I to XXVIII.

RESULTS.

Table No. XXXII page 75 is a summary of the results obtained in this investigation. The third column has the difference between the decomposition voltages in ammonia and water. The last column has the difference between the metal overvoltages in ammonia and water. A minus (-) sign before these differences indicates that the value in ammonia is less than in water.

SILVER NITRATE (Tables I and II) was composed of pure white crystals which readily dissolved in ammonia and water.

SILVER NITRITE (Tables III and IV) was only slightly soluble in ammonia but readily dissolved in water. It is interesting to note that in ammonia the decomposition voltage of the silver nitrite is nearly that of the silver nitrate, in water, however, it is much lower. The metal overvoltage^{for} silver nitrate and silver nitrite is considerably larger in ammonia than it is in water.

SILVER IODIDE (Table V) is rather soluble in ammonia but insoluble in water. When this salt was electrolysed in ammonia, a gas was liberated at the anode but there was no indication that free iodine was formed. Its metal overvoltages are considerably less than those of the nitrate and the nitrite.

NICKEL NITRATE (Tables VI and VII) formed a bright red solution in liquid ammonia. The deposit of nickel

on the cathode was smooth and the metal overvoltage rather high, being again greater in ammonia.

CADMIUM NITRATE (Tables VIII and IX) readily dissolved in ammonia but formed a basic salt to some extent in water.

CADMIUM IODIDE (Tables X and XI) is not sufficiently soluble to form a N/10 solution in ammonia. There was no indication of free iodine at the anode in ammonia while in water the solution turned brown due to its liberation.

The MERCURIC SALTS (Tables XII, XIII, XIV and XV) give very similar results in both ammonia and in water. The mercuric nitrate and the acetate are not sufficiently soluble to give a N/10 solution in ammonia and the mercuric chloride is even less soluble. Mercurous salts give a black deposit of free mercury when dissolved in ammonia. Their decomposition voltages and also their metal overvoltages were very nearly the same as those of the mercuric salts, probably, due to the fact that they changed into mercuric salts. The data for the mercurous salts is not included in this paper.

LEAD NITRATE (Tables XVI and XVII) is readily soluble and forms clear solutions. To avoid the formation of an alloy between the lead and the platinum, the cathode was silver plated. Unless this was done, the lead was removed with great difficulty from the electrodes.

ZINC NITRATE (Tables XVIII and XIX) has a lower decomposition voltage in ammonia than in water. The metal overvoltage, however, is much greater in water. This might be due ^{to} some impurity in the zinc nitrate. This was at least thought to be the case and in order to prove or disprove it four different samples of zinc nitrate and also the salt formed by dissolving pure zinc in nitric acid were used and they all gave the same overvoltage. This shows that it was not caused by an impurity but is the true metal overvoltage.

ZINC IODIDE (Tables XX and XXI) is not very soluble in liquid ammonia and forms a milky solution. This may in part be due to its high decomposition voltage in ammonia. In water it has a much lower metal overvoltage than zinc nitrate.

COPPER NITRATE (Table XXII, first and second trials and Table XXIII, third and fourth trials) with ammonia of crystallization gives only one decomposition voltage in ammonia, (the decomposition voltage of the cupric ion changing to metallic copper not having been reached under the conditions of the experiment), while in water there are two as shown by the break in the curve (see Plate XXI page 60). Evidently the cupric ion was changed to the cuprous ion under the conditions represented by the lower part of the curves and metallic copper was deposited at the higher voltages.

COPPER NITRATE (Table XXII, third and fourth trials and Table XXIII, first and second trials) with water of crystallization gives two decomposition voltages in ammonia and only one in water. The reason is the same as in the above case only the water and ammonia have exchanged places.

COPPER SULPHATE (Table XXIV) was run in water with and without ammonia, in order to determine the effect of the ammonia added. Copper sulphate without ammonia has a lower decomposition voltage than the copper nitrate. When ammonia is present then the decomposition voltages are the same for the sulphate and the nitrate but both are considerably lower than in the case where no ammonia was present. The cathode overvoltages do not show any characteristic relations except that they are all very similar and that there is a very distinct undervoltage when water is present in the liquid ammonia solution and also when ammonia is present in the water solution.

FERRIC NITRATE (Tables XXV and XXVI) could not be completely dehydrated and the dried product was only slightly soluble in both ammonia and water, possibly due to the formation of basic salts in both cases. In the first trial in liquid ammonia there is only one decomposition voltage while in the other cases there are two. This is due to the fact that the cathode was first plated with iron in the first trial while

in the other trials plain platinum cathodes were used. The difference in the overvoltages is respectively equal to the differences in decomposition voltages.

AMMONIUM NITRATE (Table XXVII and Plate XXV page 68) shows a number of breaks in the current-voltage curves. This then gives several decomposition voltages and each, possibly, representing a certain set of electrode processes taking place on the electrodes. Although all these points are easily reproducible only two trials are given, in all six runs were made with this salt. It was impossible to get reproducible resultsⁱⁿ overvoltage when using an ammonium-amalgam reference electrode.

The decomposition voltages of AMMONIUM CHLORIDE at the boiling point of ammonia (Table XXVIII) and also at -60 C. have been determined. The temperature has a very small effect. Table XXIX contains this latter data.

The current-voltage curve for AMMONIUM BROMIDE (Table XXX and Plate XXVIII page 74) shows a break and hence has two decomposition voltages. There was, however, no indication of free bromine being liberated at the anode.

AMMONIUM IODIDE (Table XXXI) has only one decomposition voltage. It is very nearly equal to the decomposition voltages of ammonium chloride and to the maximum values for the nitrate and the bromide.

Whenever we have a galvanic cell with the products on its electrodes in stable form and the solution at definite concentration, a definite difference of potential will be set up. If the processes are reversible, then the application of a slightly greater external potential will cause electrolysis. This potential then represents the static²⁰ decomposition voltage. When the voltage is increased and thereby also the current density, then, in general, the potential necessary to continue electrolysis will be greater. This increase may be due to changes in concentration in the immediate vicinity of the electrodes and to irreversible processes taking place on them.

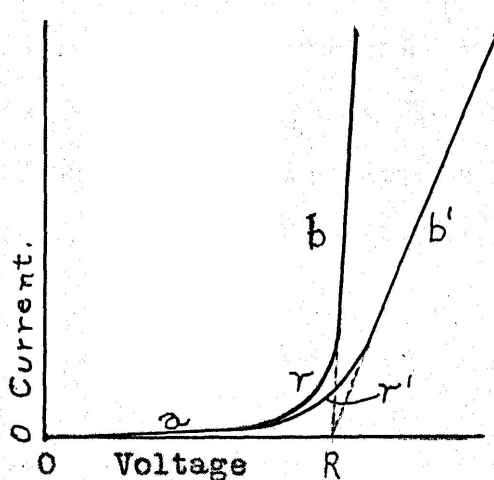
In this investigation the change in concentration near the electrodes was reduced to a minimum by rapidly rotating them. The irreversibility at the cathode was measured by determining the potential existing, during electrolysis, between the cathode and a reference electrode of the same metal as the cation under investigation, all in the same solution. This is generally known as the metal overvoltage. An overvoltage of this kind would of necessity be meaningless unless the

²⁰ The term "static" decomposition potential, obtained only at the beginning electrolysis, is used to differentiate it from the dynamic decomposition potential that would be obtained when considerable electrolysis was taking place.

current density were also given.

Le Blanc¹² has determined many static decomposition voltages. He applied a gradually increasing potential and then noticed the potential at which there was a sudden increase in current. This voltage he then called the decomposition voltage.

Moeller²¹, in plotting the current against the voltage applied, found a relation as shown in Figure 4.



The portion a is a straight line which then gradually changes into the curved portion r. Later this again becomes straight as is shown by b. Le Blanc called the voltage at the beginning of r the decomposition voltage. This we would call the

Figure 4.

static decomposition voltage.

In this investigation, it was found very difficult and often impossible to successively reproduce the static decomposition voltage. The interval of time between successive readings of the ammeter greatly affected the results. The following illustrates this point. N/10 silver nitrate in liquid ammonia gave 0.2 milliamperes of current one-half minute after applying a potential of 0.4 volts. Three minutes later the current had dropped to zero. Again, one-half minute

²¹ Z. phys. Chem., 65, 232, (1909).

after applying 0.5 volts the milliammeter read 0.5 and in three minute dropped to 0.1. It would seem that increasing the interval of time until the current remained stationary would give the desired results. The portion r of figure 4 is not only dependent on the time interval as will be presently shown.

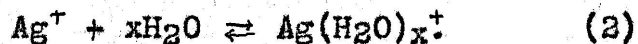
When a salt like silver nitrate is dissolved in water and a silver electrode immersed into this solution, then some of the silver will go into solution to form silver ions. This process will continue until the silver has acquired a potential just sufficient to maintain the equilibrium represented by the equation



If the above were in a galvanic cell then there would be a similar state of affairs at the anode. On applying an external potential, slightly greater than the potential of the cell, the equilibrium of (1) will be upset, electrolysis will take place and silver will be deposited on the cathode. If equation (1) represented all that was going on, then the current should increase directly with the increase in voltage instead of as represented by r Figure 4. The current would rise sharply from the start and a and b (Figure 4) would meet in a point and then show only a break.

What then is the cause for this gradual increase in the current when the potential is also gradually increased?

Suppose that in addition to the equilibrium of equation (1) there were another equilibrium between silver ion and the water, like,



Suppose also that the concentration of the silver ion were small and that the rate of the above reaction were slow but increased by an increase in the potential. Then whenever electrolysis is begun the silver ions in the immediate vicinity of the cathode will be deposited. This is represented by a considerable current which would of necessity decrease since all the free silver ions would soon be used up. Rotating the electrodes will supply these ions to some extent but will not be able to supply them in sufficient quantity continuously. Increasing the applied potential still further, will increase the current for two reasons. In the first place the field from which silver ions are drawn is increased. This would increase the current proportionally to the increase in potential. This would mean that part r of Figure 4 would not be curved but be a straight portion like part b for example. The second reason for the increase in current is the increase in the rate of reaction (2) producing more silver ions. This readily explains the shape of r. When this increase in the rate is a maximum then a further increase in the potential will have a proportional

increase in the current. This would be represented by part b of Figure 4 and is the condition that generally exists in electrolysis.

Le Blanc's measurements, and all measurements of decomposition voltages of like nature, represent the electrolysis caused by the discharge of simple ions only. We would call this the static decomposition voltage to distinguish it from determinations, like ours, which we would call dynamic decomposition voltages. For all practical purposes the dynamic decomposition voltages are the more important.

When measuring static decomposition voltage the processes are practically reversible. By carrying electrolysis a little farther the processes become more irreversible and the applied potential must be increased. This irreversibility is the overvoltage, the metal overvoltage when metal is deposited on the cathode and the oxygen overvoltage when oxygen is liberated at the anode. The dynamic decomposition voltage is, therefore, equal to the static decomposition voltage plus the cathode and the anode overvoltages. Knowing any three of the above the fourth can readily be found. This relation will apply only when the reference electrode was composed of the same material as the product deposited.

In this investigation it was often impossible to continue the electrolysis until the current was steady. During electrolysis there was a change in concentra-

tion because of the removal of salt from solution. This would affect the current. Also, the metal seldom deposited in smooth form. Often crystals would grow on the cathode and, due to the resulting decrease in resistance, the current would steadily increase. It was, therefore, necessary to read the ammeter before it had come to complete rest. Definite time intervals were used in making the readings.

If in a pair of runs the interval of time between the application of the voltage and the reading of the current is different, then the current plotted against the voltage will give two curves like a, r, b, and a, r', b' of Figure 4 page 82. The parts b and b' extrapolated to the line of zero current meet at R. This value is easily reproduced and it is what we have called the dynamic decomposition voltage.

Table Number XXXIII gives data to support this

TABLE NUMBER XXXIII.

The Effect of Time on Decomposition Voltage.

Ammonium Chloride in Liquid Ammonia.

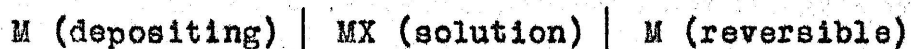
Volts applied. 1st & 2nd trials.	Current, first trial.	Current, second trial.
2.200	5.2	4.0
2.400	8.9	8.2
2.600	13.6	12.6
2.800	17.2	16.8

view. The first trial was taken with one-half minute intervals and the second trial with three minute intervals. In this particular example the current remained constant after the three minute interval.

The dynamic decomposition voltage is the lowest voltage at which, during electrolysis, the electrode processes are the same as they would be when electrolysis with considerable current density were taking place. The dynamic decomposition ^{voltage} cannot be measured directly but is obtained by extrapolating the upper straight part of the current-voltage curve upon the line of zero current.

It is customary to determine the metal overvoltage at definite current densities. There is a simple relation between the current, or what amounts to the same thing in our case the current density, and the overvoltage so that overvoltage at zero current can be determined.

The metal overvoltage, as we have used it, is the voltage, referred to zero current density, between the cathode and a reference electrode, the same as the cation under investigation, all in the same solution, during electrolysis when the metal is being deposited on the cathode. This would then be the potential of the irreversible cell



where M represents the metal under investigation and X the anion of the salt used. The metal overvoltage

can best be determined by extrapolating the upper straight part of the current-voltage (cathode-reference electrode) curve to the line of zero current, for examples of dynamic decomposition voltages and metal overvoltages determined in this way see Plates I to XXVIII.

It was our concern to determine the relation between the decomposition voltages and the metal overvoltages in the two solvents, ammonia and water. The physical nature of the surface of the electrodes was more or less immaterial and, since smooth platinum electrodes are easier to clean, they were used. Any difference in the values that might have been obtained, had platinized electrodes been used, would evidently have been similar in the two solvents and would thus have compensated each other.

Table XXXIII page 75 gives us a number of very interesting relations. In only five of the fourteen cases is the decomposition voltage greater in ammonia than in water. Two of these exceptions are iodides and one is a nitrite. In general, this shows that the ions are less firmly held in the ammonia than in water solution.

The metal overvoltages are all higher in ammonia than in water with only two exceptions. These are zinc nitrate, which seems to behave abnormally, and copper nitrate with water of crystallization. One would expect

that the silver ammonia, mercuric ammonia, zinc ammonia and the copper ammonia^{ions} should require more energy to deposit on the cathode in liquid ammonia than when the same ^{metals} ions without ammonia were dissolved in water. This is the case as their greater overvoltage in ammonia would show. In general, a high metal overvoltage in water will also have a corresponding high value when the same salt is dissolved in ammonia.

In Table XXXIV page 90 we have the metal overvoltages subtracted from the respective dynamic decomposition voltage in the same solvent. Here again a minus (-) sign before the difference in these values indicates that the value is the lower in liquid ammonia. There are only three cases where the values are the higher in the ammonia. One of these is silver nitrite and the other two are iodides. The nitrates, without exception, are easier to decompose in ammonia than in water. The apparent exceptions mentioned above were entirely caused by their greater metal overvoltage. Whether this difference in the two solvents is due to a difference in the anode overvoltages or an actual difference in the decomposition voltages we are unable to say at present.

When the nitrites and the iodides are dissolved in ammonia the anions are possibly nearly all in an ammoniated form, like $\text{NO}_2(\text{NH}_3)_x^-$ and $\text{I}(\text{NH}_3)_x^-$. This would then require a much higher potential than it would if they were uncombined.

TABLE NUMBER XXXIV.

Substance.	Decomposition voltage minus metal overvoltage.		Difference (A) -(B).
	(A) in NH ₃ .	(B) in H ₂ O.	
AgNO ₃	0.80	0.85	-0.05
AgNO ₂	0.74	0.26	0.48
Ni(NO ₃) ₂	0.94	1.47	-0.53
Cd(NO ₃) ₂	1.64	2.20	-0.56
CdI ₂	1.65	1.08	0.57
Hg(NO ₃) ₂	0.72	1.34	-0.62
Other Hg salts	0.84	1.34	-0.50
Pb(NO ₃) ₂	1.46	1.81	-0.35
Zn(NO ₃) ₂	2.06	2.36	-0.30
ZnI ₂	2.15	1.32	0.83
Cu(NO ₃) ₂ ·xNH ₃	0.92	1.07	-0.15
Cu(NO ₃) ₂ ·xH ₂ O	0.92	1.71	-0.79
Fe(NO ₃) ₃	0.87 0.70	1.99 1.98	-1.12 -1.28
AgI	0.80		
HgI ₂	0.80		

The difference between the values (Table XXXIV) of the nitrates and the iodides of silver is 0; of Cadmium 0.01; of mercury 0.08 and of zinc 0.09. The difference is unexpectedly small. The values for the iodides are the larger. Making the same comparison for these salts in water solution, we have for cadmium 1.12 and for zinc 1.04. The iodides being the lower here.

It is significant to note the constancy of the differences. In ammonia the decomposition voltages of nitrates would be about the same, while in water the decomposition voltages of the nitrates would be about one volt greater than the respective iodides.

The surety of prediction is of course greatly lessened by the fact that entirely unexpected results may be obtained. This is illustrated by the metal over-voltage of zinc in zinc nitrate in water solution where it is about 0.45 volts greater than in the case of the zinc iodide and the zinc sulphate. One would expect comparable results, at least when the same concentrations were used.

When electrolysing copper nitrate in ammonia the dynamic decomposition voltage is greater when the salt is anhydrous than when it is moist. This difference is however entirely caused by the change in metal over-voltage. The cathode process is less irreversible when the copper nitrate is moist than it is when dry. This simply means that the $\text{Cu}(\text{H}_2\text{O})_x^{++}$ requires a smaller potential for deposition than when the only ions present are $\text{Cu}(\text{NH}_3)_x^{++}$. Copper is plated out with greater difficulty when the ammonia is anhydrous as is shown by the fact that under the conditions of the experiment no copper was deposited when the solution was anhydrous but quite readily when moist.

The dynamic decomposition voltage of copper nitrate in water is affected even more by the presence of ammonia

than the presence of water affected the same values in ammonia. The effect on the metal overvoltages is negligible in this case. The process at the cathode is not changed but the process at the anode must have been. This change in the process may have been due to the formation of complex ions like $\text{NO}_3(\text{NH}_3)_x^-$. The effect on copper sulphate was very similar.

The two values of metal overvoltage and of dynamic decomposition voltage obtained with ferric nitrate were at first thought to be due to the formation of ferrous ion in the one case and deposition of metallic iron in the other. But comparing the results when the metal overvoltages have been subtracted from the decomposition voltages (Table XXXIV page 90) we find that this difference is entirely caused by a change in overvoltage. In the first part of the curve (Plate XXIII page 64 and Plate XXIV page 66) there was only a little metallic iron deposited on the platinum electrode and was then in the active state. Later, either due to the increase in potential or to ^{the} cathode having become completely covered with iron, (having become a true iron electrode), the cathode became passive and it took a greater voltage to deposit the iron upon it. The negative sign before the metal overvoltage is simply caused by the form of the reference electrode being different and hence would have a different potential. The reference electrode was a fine wire while the cathode had the iron in crystalline form.

The ammonium salts have the same general dynamic decomposition voltage of about 2.1 volts. The curve for the nitrate shows several distinct breaks (see Plate XXV page 68). Evidently there are different electrode products represented by the different parts of the curves, but what they are we are unable to say.

The ammonium bromide (Plate XXVIII page 74) also has a distinct break in the current-voltage curve. There was, however, no indication of free bromine being formed during the electrolysis.

The ammonium iodide and the chloride have only one dynamic decomposition voltage in ammonia. It is of interest to note that the dynamic decomposition voltage changes very little with temperature, as would be expected. The ammonium chloride has nearly the same dynamic decomposition voltage at -60° C. as at the boiling point of ammonia. This agrees with results obtained in water.

Overvoltages of ammonium salts measured between an ammonium-amalgam electrode and the cathode were not reproducible even at a temperature as low as -60° C.

SUMMARY.

In this investigation the direct method for determining the dynamic decomposition voltages and metal overvoltages has been used. By rapidly rotating the electrodes, changes in concentration in their immediate

vicinity was avoided.

Most decomposition voltages determined to date have been under very low current density and only at the beginning of electrolysis. This we would call the static decomposition voltage. There is an uncertainty in all values of this kind because the processes are changed with time and the interval used before making readings affects the results. By the method employed in this investigation, it is possible to have electrolysis with considerable current density going on and then, by plotting current against the voltage, obtain a curve which can be extrapolated to the line of zero current and thus get reproducible values. These values we would call dynamic decomposition voltages.

The dynamic decomposition voltages of nineteen salts in liquid ammonia, the metal overvoltages of most of them, and the dynamic decomposition voltages and the metal overvoltages of fourteen salts in water have been determined by the above method.

In general, the dynamic decomposition voltages are lower in ammonia than in water. The exceptions being the iodides and nitrites.

The metal overvoltages are generally higher in ammonia than in water for the same salts.

Water present in ammonia decreases the overvoltages of copper and has an equivalent effect on the dynamic decomposition voltage.

Ammonia present in water very notably decreases the dynamic decomposition voltage but has very little effect on the overvoltage.

Ammonium salts have a general dynamic decomposition voltage of about 2.1 volts when in dry liquid ammonia. Ammonium bromide and nitrate have several additional values that are lower as shown by breaks in the current-voltage curves.

Temperature has a very slight effect on the dynamic decomposition voltage.

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