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Report
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Committee on Thesis

The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by Marshall A. Peterson for the degree of Chemical Engineer.

They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Chemical Engineer.

Charles A. Mann
Chairman

L. F. Miller

Oscar E. Harder

Date _____

THE INTER-INFLUENCE OF THE INDIVIDUAL
METALS ON THE DEPOSITION OF AN ALLOY

A Thesis

Submitted to the Graduate Faculty

of the

University of Minnesota

by

Marshall A. Peterson

In partial fulfillment of the requirements

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INTRODUCTION

The purpose of this thesis is to show what effect one metal has on another on the deposition of an alloy of the two where both metals are used as anodes in a bath of their mixed salts. Quoting from Allmand, in connection with the deposition of nickel and zinc as an alloy, he says: "Although zinc is more strongly electro-positive than nickel and should therefore not deposit as easily, and although the nickel salts may be present in excess the cathode deposit will nevertheless principally consist of zinc, so strongly has the nickel depolarized the discharge of the zinc ions."

This statement is not followed by any discussion or data. The purpose of this thesis, then, was to test the correctness of this statement.

If this were true, it should be possible to note the depolarizing effect, if the polarization curve of one of the metals in a bath of its salt was compared with a polarization curve of this same metal as obtained from a bath of mixed salts of two metals. If the polarization

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curve under the second conditions does not coincide with the curve obtained from the first method, of a metal in a bath of its salt, then Allmand's statement is not valid.

HISTORICAL

Very little work has been done on this problem, in attacking it in this manner. The work by Shoch and Hirsch² is perhaps all that has been reported which takes into consideration the polarization of this alloy. The values obtained by them, however, were taken with constant voltage and not with a steady increasing voltage as is done by the writer. Their work which covers a period of several years had not been finished as far as shown by the literature. Ferguson³ worked on brass deposition after the same manner as Schodh and Hirsch.

THEORY

The alloy which was deposited in the following experiments was composed of nickel and zinc. An anode of each of the metals was used, while a lead cathode was used. Lead was used as it was the only metal that would not dissolve to a large extent with the alloy in making analysis, or be permanently effected by it.

As no data was available as to in what bath the single potentials of nickel and zinc would be most nearly equal, a sulphate solution was used. This was also used so as to check some of the results obtained by C. Shoch and A. Hirsch.

There are many factors which must be taken into consideration, as each has a definite effect on the alloy deposition. The factors considered by the writer are:

- a. Metal content in the bath
- b. Metal ratio in the bath
- c. Current density.
- d. Neutrality of the solution.

- e. Single potentials and the polarization during the whole time of deposition.
- f. The effect of additions agents.

As in all plating the concentration of the bath has a definite effect on the deposition, the higher concentration gives a rapid deposition but one which is not very smooth or firm. There is also a greater tendency for the deposit to burn. If too dilute a great deal of time is required but better results are obtained.

The ratio of the metal ions has a peculiar effect altho theoretically it should be simple for, contrary to the belief the metal in greates concentration will not always be deposited out in the larger amounts. Therefore it is difficult to control definitely the composition of the deposit. No one has as yet been able to give a definite reason for this, but it is the cause of the statement by Allmand, referred to above.

The current density is considered as controlling the rate of deposition, which in turn, controls the quality of the plate. The lower the current density,

as a rule, the better the plate. Where an alloy is deposited out, the two metals should be deposited out according to Faraday's Laws of Electrolysis, so that if two anodes, one of nickel and one of zinc be placed in a bath, and an equal amount of current is sent thru each for the same length of time, the alloy should consist of nickel and zinc in the ratio of their equivalent weights. This might hold true by the introduction of an addition agent or by some means by which the nickel will enter the solution as readily as the zinc. Experiments 23 and 24 show that nickel has a far higher solution contact resistance than the zinc. Therefore, if nickel and zinc are connected to the same line and no other means is taken to adjust the current which flows into each, the amount flowing into the bath thru the zinc electrode will be far greater in amount than that flowing in thru the nickel electrode.

The neutrality of the nickel and zinc solutions has been an important factor to electroplaters ever since plating was first attempted. The gases which are freed at the electrodes are dependent for their liberation on

the neutrality to a great extent. As a better plate is obtained with a lower liberation of gas, the neutrality of the bath is watched closely by the electroplaters. As a rule, neutral solutions will give off less gas than an acid or alkaline bath. The most satisfactory results are obtained from a very weakly acid solution. Therefore, a bath is used which is slightly acid, made so by the addition of dilute sulphuric, boric, or some organic acid.

Addition agents are added for the purpose of improving the quality of the plate and to increase the tendency of the anode to go into solution. In the following experiments it was not necessary to add any substance to the zinc bath, but with the nickel bath several different agents were added.

The single potential of an electrode may be regarded as the measure of its tendency to go into solution. For if we allow (M) to stand for any metal we can write the reaction; $M - (-) M$. It is this tendency which is called the single potential and is measured by means of a standard electrode. As stated by Washburn; "The characteristic electrode potential of a given electro-

chemical reaction under a given set of conditions is the potential difference which exist between the electrode and the solution when the two are in equilibrium with each other with respect to the reaction in question.⁴"

If two electrodes are placed in the same bath, it is possible, to measure the difference of the potential between them. The farther apart they are in the electro-motive series, the greater will be their difference of potential or E.M.F. From these two electrodes immersed in a bath we can draw a current or impress a current, thereby increasing the original E.M.F. This should be polarization for Allmand defines it as, "When current is passed in this way into a cell from the outside raising the voltage of the system, the cell is said to be polarized, and the phenomena observed are those of polarization. Similarly when a primary cell discharges in such a way that the voltage falls below its static value (the E.M.F.) the cell is polarized".⁵

The causes of polarization can be said to be an attempt of the cell to bring itself back to equilibrium between the electrode and solution. But it is not only

that, for polarization can be said to be due to concentration in the bath, gas evolution, temperature, the electrode material, or the character of the electrode.

The one phenomena which is difficult to understand is overvoltage, but which is explained in a single sentence briefly and clearly by Watts as, "The difference in volts between the discharge potential of hydrogen on platinized platinum and on any other metal is called the overvoltage of hydrogen on that metal." The overvoltage of oxygen upon anodes is similar to hydrogen overvoltage.

Impressed		Polarization				Impressed		Results
Volts	Amps.	Total	Cathode	Anode	Amps.	Time	Cathode Pol.	Anode Pol.
0.	.0022	.45	.08	.17	.0	0	.48	.39
0.	.0024	.30	.08	.17	.0015	20	.48	.39
.17	.0030	.17	.08	.17	.001	25	.48	.39
.20	.0032	.15	.09	.18	.0008	18	.47	.39
.22	.0040	.13	.16	.17	.0007	15	.40	.39
.32	.0088	.01	.17	.17	.0002	20	.39	.39
.48	.018		.17	.17		22	.39	.39
.41	.012		.17	.17		30	.39	.39
.60	.021		.17	.17		120	.39	.39
.67	.0225		.17	.17		120	.39	.39

These results were not complete and are not of any value due to the change of the time intervals, through which the current was impressed. The method then used was that used by Watts in determining the polarization.⁶ The set up will first be explained from the diagram.

1. The electrolyzing circuit comprising a source of E.M.F., a line switch S_6 , a rheostat R, milliammeter MA, switch-key K, and electrolytic cell.

2. The potentiometer circuit, consisting of battery B, reversing switch S_4 , potentiometer, key K, galvanometer, cell, and switch S_2 .

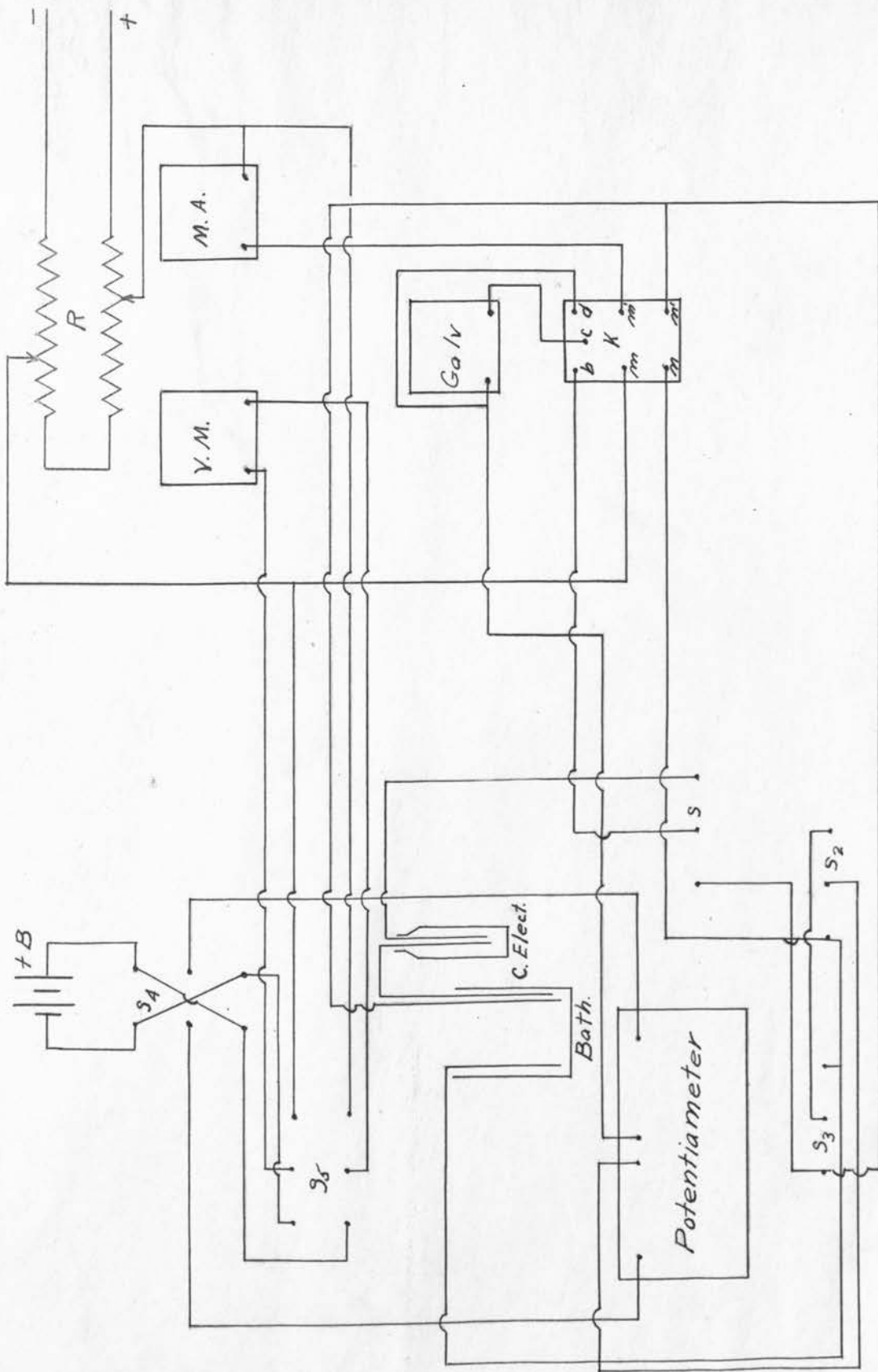
3. Switches S_2 and S_3 for substituting in the potentiometer circuit the calomel electrode in place of either anode and cathode.

EXPERIMENTAL

In carrying out the experiments there were two methods used. The first method was only used for the first experiment with zinc, as it was not accurate enough. Therefore only a description of the general method used and the results obtained will be given.

Using a zinc anode and a lead cathode in a bath of normal $ZnSO_4$, the polarization readings were taken at as regular intervals as possible. The electrodes were cut to the required size, cleaned by mechanical means, then treated with conc. hydrochloric acid, washed with water, alcohol and dried with ether. They were then immersed in the bath and the run started.

The results obtained are listed below.



4. Switch S_5 by which either the E.M.F. of the electrolytic cell or of the battery B may be read on the voltmeter.

The key K is a combination of a short-circuit galvanometer key (binding posts b, c, d,) and a double-pole line switch (binding posts mh and m'n') operated by a single lever. Normally the line circuit is closed, the galvanometer is short-circuited, and the potentiometer circuit is open. On depressing the key, the line is opened and then the potentiometer circuit is closed.

The above directions were taken from Watts' Electro-chemistry.

In the actual work, the first readings taken upon immersing the electrodes in the bath are the potentials of the electrodes. The circuit with a voltage of .2 volts is then impressed. This circuit is switched off after a period of two minutes. Then, as quickly as possible the polarization readings are taken. Then the voltage is increased by .2 volts and allowed to run for two minutes and the process repeated. This is continued until the cathode deposit is burned.

The two minute periods were chosen as it was just enough time for the writer to take readings and to see what reactions were taking place. The polarization readings were taken as quickly as poss-

ible to prevent a decrease in the values.

The electrodes were treated as in the experiment using the first method. A number of electrodes of each kind were made of the same size so that in the future experiments, no preparation but the cleaning would be necessary.

Experiments I & II

Bath: 150 cc of N ZnSO₄. Electrodes 7½ cm apart.

Area of surface exposed: 2x.15 x 2.6 - Zn - .78 sq.cm.

2x2.87x.1 - Pb - .574 " "

E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pb.	Anode Zn	Pol. of Pb.	Pol. of Zn.
.0	.0	1.5	.475	.25	.725	.185	.527
.0	.023	1.5	.335	.388	.725	.0225	.527
.2	.018	1.5	.335	.392	.727	.022	.53
.3	.017	1.5	.335	.392	.727	.022	.53
.4	.018	1.5	.335	.392	.728	.022	.532
.5	.024	1.5	.335	.392	.725	.022	.527
.6	.0368	1.5	.335	.395	.726	.032	.529
.8	.051	1.5	.095	.795	.725	.632	.527

At .8 volts the circuit broke causing the experiment to end without definite results.

The results obtained were not so very far off but they were not complete enough.

II

Conditions the same as in experiment I

E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pb	Pol. Pb	Pol. Zn	Pol. Total	Anode Zn
.0	.0	1.5	.355	.375	.002	.527	.532	.725
.0	.0082	1.5	.345	.380	.01	.529	.517	.726
.2	.034	1.5	.015	.733	.439	.529	.0225	.726
.4	.081	1.5	.005	.746	.559	.53	.0075	.727
.6	.122	1.5	.001	.726	.529	.53	.0015	.727
.8	.178	1.5	-.005	.726	.529	.53	-.0075	.727
1.0	.22	1.5	-.005	.727	.530	.53	-.0075	.727
1.2	.26	1.5	-.005	.726	.539	.53	-.0075	.727
1.4	.30	1.5	.0	.727	.530	.53	.0	.727
1.6	.33	1.5	.0	.727	.530	.53	.0	.2727
1.8	.41	1.5	-.015	.727	.530	.53	-.0225	.727
2.0	.422	1.5	-.025	.732	.538	.53	-.0375	.727
2.2	.48	1.5	-.015	.736	.544	.532	-.0225	.727
2.4	.535	1.5	-.2	.736	.544	.532	-.030	.728
2.6	.59	1.5	.0	.739	.548	.532	.0	.728
2.8	.69	1.5	-.015	.738	.547	.532	-.0225	.728
3.0	.755	1.5	-.015	.736	.544	.532	-.0225	.728

These values are a little high if the values in Watt's Manual for the potentials of metals in their normal salts are taken as a standard. The total polarization values were also irregular.

As the results were of no value a third experiment was run under the same conditions.

The values given for zinc in a sulphate solution is usually $-.529$, while for lead a value between $.022$ and $.258$ is used. The potentials of lead should be obtained for the first polarization reading, then it should approach the value of zinc as the run is continued and the zinc plated out on the cathode.

III

Potentials of Zn in its normal salt. (Watts) = .524
 For Pb no values are given.

C.E.M.F.	C Amps	Battery E.M.F.	Total	Cathode Pb	Anode Zn	Pot. Total	Pot. Cathode	Pot. Anode.
0.0	.007	1.48	.353	.376	.725	.529	.004	.527
0.2	.008	1.5	.175	.528	.695	.262	.232	.482
0.4	.014	1.5	.025	.681	.715	.0375	.462	.512
0.6	.023	1.5	.005	.716	.726	.0075	.514	.529
0.8	.032	1.5	.004	.715	.725	.006	.512	.527
1.0	.044	1.5	.004	.717	.725	.005	.516	.527
1.2	.055	1.5	.004	.718	.725	.006	.518	.527
1.4	.065	1.5	.003	.718	.726	.0045	.518	.529
1.6	.076	1.5	.0	.720	.726	.0	.522	.529
1.8	.087	1.5	.003	.723	.727	.0045	.525	.531
2.0	.095	1.5	.003	.725	.727	.0045	.527	.531
2.2	.105	1.5	.003	.726	.728	.0045	.529	.533
2.4	.120	1.5	.003	.727	.728	.0045	.531	.533
2.6	.128	1.5	.003	.728	.728	.0045	.533	.533
2.8	.135	1.5	.005	.728	.728	.0075	.533	.533
3.0	.15	1.5	.005	.728	.728	.0075	.533	.533
4.0	.18	1.5	.005	.727	.727	.0075	.531	.531
5.0	.24	1.5	.005	.726	.726	.0075	.529	.529
		1.5	.005	.726	.773	.0075	.529	.599

This solution was neutralized and then acidified with one drop of dilute Sulphuric Acid.

The time required for the first four volts was 40 minutes, with an interval of one-half hour before the 5 volts reading was taken.

Area of Zn electrode is $2 \times .15 \times 2.6 = 11.39 \text{ cm}^3$

Area of Pb electrode is $2 \times 2.87 \times .1 = 11.88 \text{ cm}^3$

The values for the anode and cathode are very nearly equal towards the end of the run.

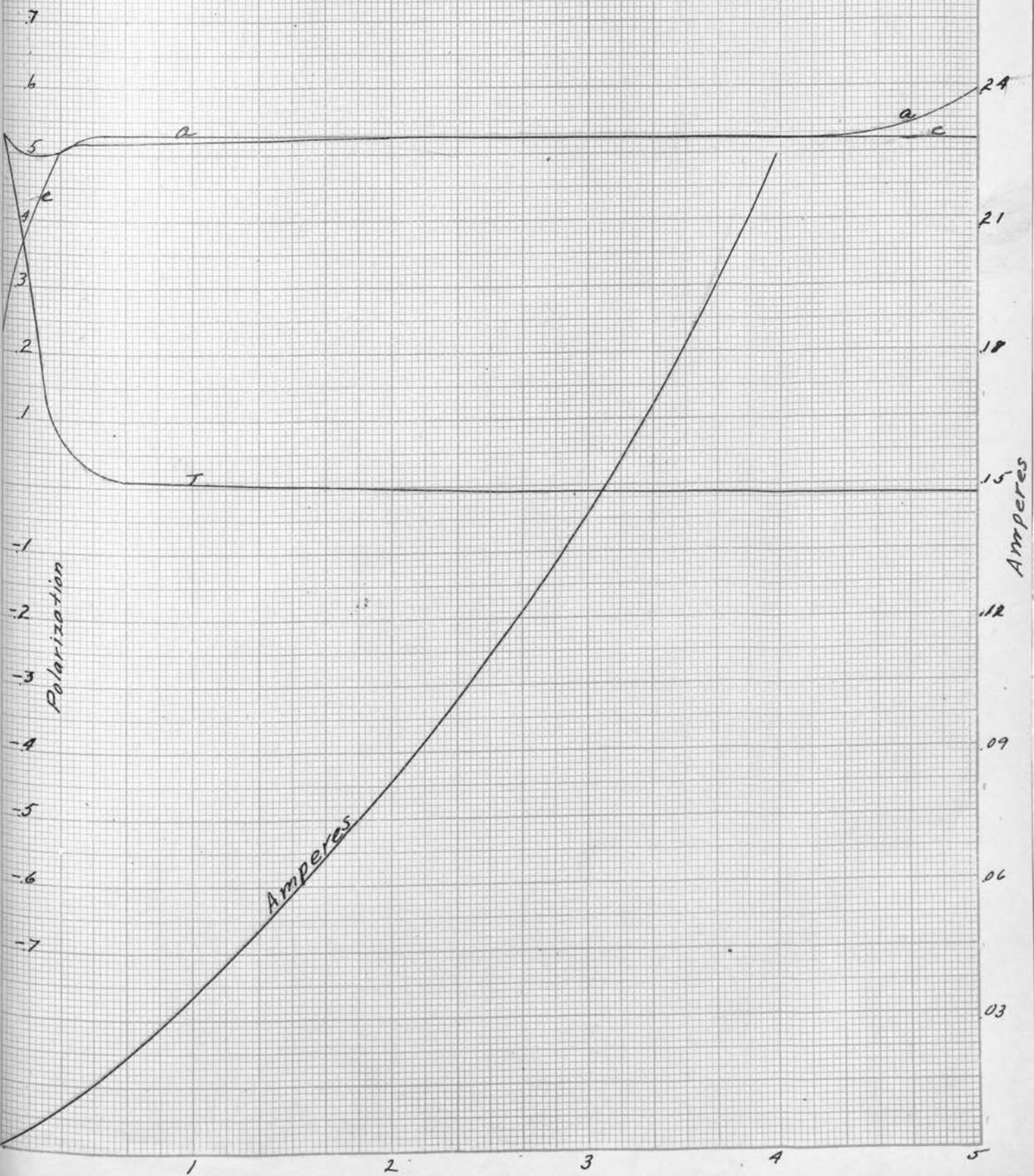
The curves obtained from these results are very satisfactory. They show quite plainly that before gas evolution and after the lead is covered with Zn that the polarization is nearly the same at both

electrodes. But one thing is noticeable, the decomposition voltage of ZnSO_4 is not shown by the curve until perhaps at the very end where the anode polarization curve rises quickly, at this point gas was observed to be liberated.

As these curves are satisfactory for the purpose the writer decided to begin work on the nickel polarization.

Experiment III

A - Anode Curve.
C - Cathode Curve.
T - Total Polarization Curve.



Experiment IV

Using a Nickel anode.

The solution is made up of an equivalent weight of NiSO_4 . This bath did not contain any addition agents to overcome the passivity of the nickel anode, as the results were wanted on a straight run of the solution. Different additions agents will be used to overcome this passivity in the next experiments.

Area of nickel anode - $2 \times .08 \times 3.08 = 12.89 \text{ cm}^2$

Area of lead cathode - $2 \times 2.87 \times .1 = 11.88 \text{ cm}^2$

E.M.F.	Amp.	Battery E.M.F.	Pol. Total	Cathode Pb	Anode Ni	Pol. Total	Pol. Pb	Pol. Ni.
0.0	.0	1.48	.013	.21	.23	.0192	.245	.215
0.0	.0	1.5	.005	.227	.235	.0075	.22	.208
0.2	.001	1.5	.005	.23	.235	.0075	.215	.208
0.4	.003	1.5	.003	.23	.235	.0045	.215	.208
0.6	.0085	1.5	.015	.245	.235	.0025	.193	.208
0.8	.282	1.5	.015	.25	.24	.00225	.193	.200
1.0	.031	1.5	.015	.245	.235	.0025	.190	.208
1.2	.0417	1.5	.015	.245 ^b	.235	.0025	.193	.208
1.4	.0562	1.5	.015	.25	.24	.0025	.190	.200
1.6	.071	1.5	.025	.26	.245	.0375	.170	.193
1.8	.086	1.5	.035	.275	.252	.0525	.148	.182
2.0	.10	1.5	.032	.273	.252	.048	.151	.182
2.2	.12	1.5	.030	.27	.250	.045	.155	.185
2.6	.135	1.5	.030	.275	.255	.022	.148	.178
2.8	.150	1.5	.045	.26	.215	.067	.17	.238
3.0	.060	1.5	.045	.26	.215	.072	.17	.238
3.25	.06	1.5	.048	.26	.215	.067	.17	.238
3.5	.07	1.5	.045	.264	.21	.067	.164	.245
4.0	.085	1.5	.045	.26	.208	.069	.17	.248
5.0	.125	1.5	.046	.258	.208	.069	.173	.248

Both the anode and the cathode were dark in color, the deposit was burned on the cathode at the end of the run.

These results were of little value as they were not regular in increasing or decreasing values and

this irregularity cannot be explained except through experimental error.

The decomposition voltage is obvious at 2.8 volts, where the current takes a sudden drop from .15 to .06 amperes.

The value of the potential of nickel is .022, therefore the values of both electrodes should be near to that value at the end of the run or just before gas evolution.

V.

25 c.c. of NH_4Cl (approx 12.5 gms) was added to this bath as an addition agent.

E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pb	Anode Ni	Pol. Total	Pol. Pb	Pol. Ni
0.0	.0	1.49	.023	.378	.363	.0343	.003	.015
0.001	.0	1.49	.015	.379	.363	.0224	.008	.015
0.2	.001	1.49	.016	.388	.363	.0238	.022	.015
0.4	.081	1.49	.023	.381	.363	.0343	.0115	.015
0.6	.037	1.49	.027	.384	.363	.0402	.016	.015
0.8	.048	1.5	.035	.388	.362	.0525	.022	.017
1.0	.059	1.5	.035	.385	.358	.0525	.017	.017
1.2	.097	1.5	.035	.379	.355	.0525	.008	.023
1.4	.127	1.5	.045	.379	.355	.0675	.008	.028
1.6	.172	1.5	.045	.379	.348	.0675	.008	.028
1.8	.218	1.5	.045	.378	.348	.0675	.007	.048
2.0	.268	1.5	.035	.378	.343	.0525	.007	.048
2.2	.311	1.5	.15	.381	.348	.225	.0115	.046
2.4	.362	1.5	.056	.378	.348	.084	.007	.048
2.6	.41	1.5	.055	.378	.348	.0835	.007	.048
2.8	.465	1.5	.055	.378	.348	.0835	.005	.047

The same results were obtained here, both the anode and cathode were dark.

The chloride ion was added as NH_4Cl to overcome the passivity of the nickel anode. It was added to such an extent that it would make a large difference

from the preceding experiment, giving the writer an idea as to the limits of the concentration that could possibly be used. The values of the nickel electrode polarization are far worse than the values obtained from the experiment IV. The fact that the anode and cathode both turn black can easily be explained on the bases that the anode was oxidized by the gas liberated while the cathode was burned.

VI

Since the results obtained in V did not agree with single potential as ordinarily given and the anode and cathode were dark, it was decided to try the NiSO_4 bath which was used for nickel plating in the lab. This was made up according to Watt's.

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 50 gms.

NH_4Cl 25 gms.

Made up to one liter.

E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pb.	Anode Ni.	Pol. Total	Pol. Pb	Pol. Ni.
0.0	.0	1.48	.123	.38	.26	.162	.01	.17
0.005	.0	1.5	.12	.384	.263	.18	.016	.166
0.2	.001	1.5	.046	.38	.343	.069	.01	.044
0.4	.004	1.5	.045	.374	.337	.068	.001	.055
0.6	.008	1.5	.045	.374	.337	.068	.001	.055
0.8	.028	1.5	.035	.372	.347	.052	.002	.04
1.0	.0585	1.5	.055	.373	.348	.082	.001	.038
1.2	.093	1.5	.072	.373	.315	.109	.001	.088
1.4	.13	1.5	.075	.373	.315	.112	.001	.088
1.6	.185	1.5	.07	.373	.317	.105	.001	.083
1.8	.215	1.5	.065	.373	.318	.097	.013	.083
2.0	.255	1.5	.065	.365	.318	.097	.011	.083
2.2	.30	1.5	.065	.366	.318	.097	.011	.083
2.4	.355	1.5	.065	.366	.318	.097	.011	.083

The results were the same, both the anode and cathode were dark and the potentials did not approach .002, the potential of nickel.

Experiment VII

To see what effect the area would have on the potentials each electrode was covered with paraffin and only one side of each electrode was cleaned, so as to expose equal surfaces of metal.

9 grams of NH_4Cl was added to 100 c.c. of NiSO_4 solution.

E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pot.	Anode Pot.	Total	Pb Pot.	Ni Pot.
0.0	.0	1.48	.0055	.385	.380	.00814	.009	.002
0.2	.001	1.5	.0055	.385	.380	.00825	.017	.010
0.4	.002	1.52	.005	.385	.380	.0076	.025	.018
0.6	.01	1.52	.015	.39	.383	.0228	.033	.023
0.8	.006	1.52	.015	.385	.380	.0228	.025	.018
1.0	.012	1.52	.015	.382	.375	.0228	.020	.010
1.2	.0255	1.52	.025	.380	.370	.038	.018	.004
1.4	.0442	1.52	.032	.378	.370	.0457	.015	.005
1.6	.067	1.52	.040	.375	.360	.0680	.010	.013
1.8	.083	1.52	.050	.375	.360	.0760	.010	.013
2.0	.10	1.52	.060	.375	.360	.0912	.010	.005
2.2	.12	1.52	.060	.370	.350	.0912	.003	.02
2.4	.105	1.52	.070	.375	.355	.1065	.010	.02
2.6	.17	1.52	.075	.375	.350	.114	.010	.028
2.8	.19	1.52	.090	.375	.345	.1369	.010	.036
3.0	.22	1.52	.095	.375	.350	.1445	.010	.068
4.0	.31	1.52	.100	.380	.340	.1520	.018	.043
5.0	.45	1.52	.11	.375	.355	.1671	.010	.050

At 2.2 - 2.4 volts the anode darkened.

While the results were of a fairly constant value, they did not come to any value which could be used.

Experiment VIII

3½ grams of NH₄Cl were added to this bath of 100cc of NiSO₄. The results were not any better.

At 1.6 volts the anode began to darken a little, which increased steadily. At 3.0 volts, approximately, the cathode deposit became dark and burned.

E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pbl.	Anode Ni.	Total Pol.	Pb. Pol.	Ni. Pol.
0.0	.0	1.52	.05	.378	.335	.072	.015	.051
0.05	.0	1.52	.04	.379	.344	.0608	.016	.037
0.2	.0005	1.48	.035	.379	.345	.0518	.010	.035
0.4	.006	1.51	.045	.383	.347	.068	.022	.032
0.6	.005	1.52	.048	.377	.337	.073	.014	.048
0.8	.0095	1.52	.034	.369	.343	.0516	.001	.039
1.0	.023	1.52	.055	.369	.327	.0836	.001	.064
1.2	.0455	1.52	.055	.367	.330	.0836	.002	.059
1.4	.075	1.52	.078	.37	.298	.1185	.002	.107
1.6	.105	1.52	.09	.366	.292	.1368	.004	.116
1.8	.14	1.52	.095	.366	.287	.1445	.004	.124
2.0	.17	1.52	.067	.365	.215	.1020	.005	.080
2.2	.205	1.52	.089	.370	.289	.1352	.002	.121
2.4	.24	1.52	.085	.370	.288	.1292	.002	.122
2.6	.27	1.52	.09	.370	.288	.1368	.002	.122
2.8	.305	1.52	.067	.357	.320	.1020	.002	.074
3.0	.33	1.52	.10	.366	.282	.1520	.004	.131
4.0	.48	1.52	.095	.366	.287	.1480	.004	.024
5.0	.66	1.52	.15	.366	.285	.2280	.004	.126

So far it has appeared that with a change in the composition of a bath, we have a corresponding value at which the anode darkens. This value is always fairly close to the decomposition voltage of NiSO₄.

Experiment IX

5 grams of $\text{Al}_2(\text{SO}_4)_3$ were added to 100 c.c. of NiSO_4 . 2 drops of H_2SO_4 and 2 drops of conc. HCl were used. The acid was used to cause more complete solution of the $\text{Al}_2(\text{SO}_4)_3$.

At 2.4 volts the electrode darkened.

E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pb	Anode Ni.	Total Pol.	Pb. Pol.	Ni. Pol.
0.0	.00	1.49	.035	.372	.342	.052	.005	.05
0.003	.0	1.49	.028	.378	.350	.0417	.004	.039
0.2	.001	1.5	.035	.378	.352	.0525	.004	.031
0.4	.002	1.52	.04	.380	.358	.0608	.016	.032
0.6	.008	1.52	.05	.386	.35	.076	.026	.039
0.8	.007	1.52	.05	.385	.348	.076	.025	.032
1.0	.012	1.52	.05	.385	.346	.076	.025	.034
1.2	.018	1.52	.054	.383	.346	.082	.023	.034
1.4	.030	1.52	.058	.383	.340	.0865	.023	.054
1.6	.05	1.52	.060	.383	.336	.0912	.023	.049
1.8	.064	1.52	.080	.383	.318	.1217	.023	.076
2.0	.081	1.52	.10	.383	.315	.152	.023	.081
2.2	.048	1.52	.10	.383	.305	.152	.023	.096
2.4	.11	1.52	.11	.383	.300	.167	.023	.104
2.6	.125	1.52	.115	.383	.305	.175	.023	.096
2.8	.143	1.52	.08	.382	.315	.1218	.021	.082
3.0	.145	1.52	.12	.382	.305	.183	.021	.096
4.0	.218	1.52	.13	.382	.286	.1978	.021	.125
5.0	.220	1.52	.20	.375	.215	.304	.010	.233

Experiment X

From an article in the Chem & Met.³, a bath of the following composition was suggested.

NiSO₄ - 3 Lbs. MgSO₄ - 6 - 8 oz.

Powdered Boric Acid 1 - 4 Oz.

Water 1 gallon.

Calculating the amounts of each of the above for 77.4 grams per liter, we have:-

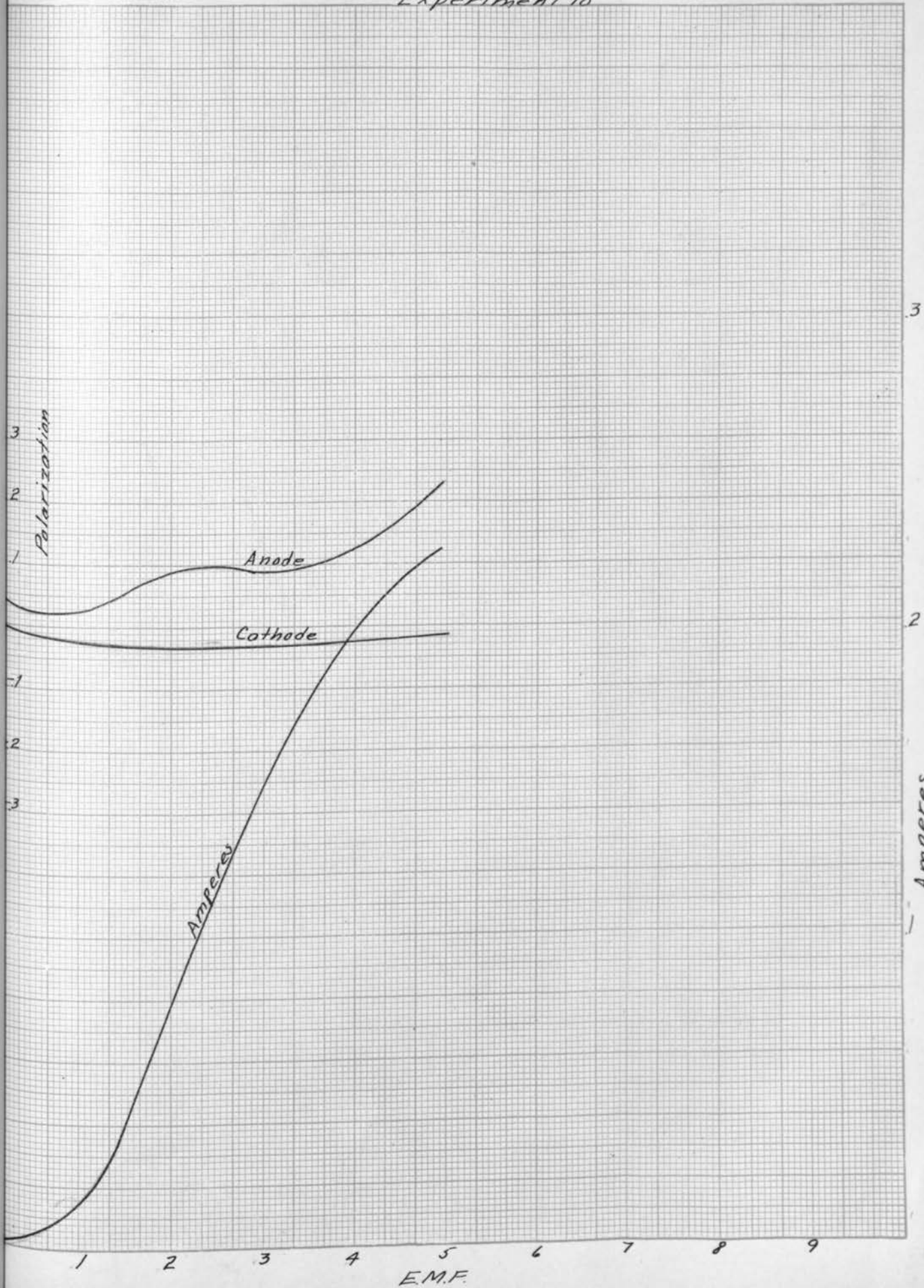
MgSO₄ 1.201 grams

Powdered Boric acid .428 - .45 grams

NiSO₄ 100 c.c. (77.4 grams/l)

This is 1/4.36 times as strong as the original solution. Conditions otherwise were the same as in the former experiments.

C.C.	E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pb	Anode Ni	Total Pol.	CNi Pol.	CPb Pol.
0.004	0.0	0.0	1.49	.035	.372	.344	.0516	.027	.009
0.2	.0005	1.49	1.49	.025	.382	.358	.0373	.020	.012
0.4	.0035	1.49	1.49	.025	.384	.362	.0373	.020	.018
0.6	.005	1.49	1.49	.030	.388	.362	.0447	.020	.018
0.8	.006	1.49	1.49	.040	.388	.360	.0556	.024	.018
1.0	.009	1.49	1.49	.035	.388	.358	.0522	.026	.018
1.2	.015	1.49	1.49	.040	.388	.356	.0556	.029	.018
1.4	.024	1.49	1.49	.050	.385	.350	.0795	.038	.014
1.6	.035	1.49	1.49	.055	.384	.347	.0875	.044	.022
1.8	.044	1.49	1.49	.060	.382	.346	.0894	.045	.009
2.0	.056	1.49	1.49	.065	.382	.335	.0974	.060	.009
2.2	.065	1.49	1.49	.080	.382	.325	.1192	.076	.009
2.4	.0745	1.49	1.49	.085	.381	.319	.1267	.084	.008
2.6	.0845	1.49	1.49	.085	.381	.313	.1267	.094	.008
2.8	.0893	1.49	1.49	.085	.381	.313	.1267	.094	.008
3.0	.070	1.49	1.49	.10	.379	.300	.149	.013	.005
4.0	.075	1.49	1.49	.10	.376	.215	.149	.240	.000
5.0	.105	1.49	1.49	.135	.373	.205	.2022	.254	.006
				.135	.373	.208	.2022	.250	.006



Up to 5 volts, the Ni was gray (light Ni color). The cathode slightly darker. After 5 volts was reached the voltage was raised to $9\frac{1}{2}$ volts for one-half hour. There then was a thick green salt of Ni deposited on the cathode. This deposit was soft.

The deposit up to 5 volts was of good appearance, being solid and uniform.

The green deposit on the cathode was nickel hydroxide.

Experiment XI

This solution was made up the same as for experiment X. Only 90 c.c. of NiSO_4 were used.

E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pb	Anode Ni.	Total Pol.	Cathode Pol.	Anode Pol.
0.0	.0	1.48	.035	.395	.388	.0518	.025	.002
0.2	.0065	1.48	.025	.396	.373	.0373	.026	.008
0.4	.002	1.48	.035	.382	.355	.0518	.006	.034
0.6	.005	1.48	.04	.384	.353	.0592	.009	.037
0.8	.0065	1.48	.045	.386	.351	.0666	.000	.031
1.0	.008	1.48	.045	.384	.353	.0666	.009	.037
1.2	.0115	1.48	.055	.382	.345	.0814	.006	.049
1.4	.016	1.48	.060	.380	.342	.0888	.002	.054
1.6	.024	1.48	.075	.377	.346	.1110	.002	.049
1.8	.0305	1.48	.085	.375	.326	.1260	.005	.0478
2.0	.0375	1.49	.085	.374	.320	.1260	.006	.086
2.2	.013	1.49	.055	.372	.321	.1814	.009	.085
2.4	.016	1.49	.085	.373	.327	.1260	.008	.002
2.6	.021	1.49	.06	.373	.390	.0888	.008	.103
2.8	.0265	1.49	.08	.373	.274	.1185	.009	.052
3.0	.0195	1.49	.075	.366	.255	.1110	.018	.018
4.0	.0475	1.49	.09	.369	.260	.1330	.014	.162
5.0	.082	1.49	.11	.367	.255	.1630	.016	.180

The potentials of the cathod and anode do not come near to what they should be, the cathode decreases while the anode increases, Altho they both became minus in value.

At 2.2 volts, the vcurrent took a drop from .0375 to .013 amperes. This is the decomposition voltage of NiSO_4 , and accured in a number of the experiments carried out.

Experiment XII

This is the third experiment using boric acid and MgSO_4 .

The size of the cathode this time was only two thirds the size used in the former experiments.

C.C.	Amps.	Battery E.M.F.	Total	Cathode Pb	Anode Ni.	Total Pol.	Cathode Pol.	Anode Pol.
0.0	.0	1.48	.100	.377	.285	.148	.002	.139
0.2	.0005	1.48	.035	.375	.332	.0518	.005	.069
0.4	.004	1.48	.040	.365	.332	.0592	.020	.069
0.6	.0095	1.48	.060	.380	.335	.0890	.003	.065
0.8	.012	1.48	.075	.385	.334	.1110	.010	.066
1.0	.012	1.48	.070	.385	.336	.1035	.010	.062
1.2	.205	1.48	.073	.383	.328	.1080	.007	.075
1.4	.305	1.48	.085	.382	.315	.1260	.005	.094
1.6	.040	1.48	.085	.378	.312	.1260	.000	.098
1.8	.052	1.48	.105	.375	.283	.1555	.005	.141
2.0	.013	1.48	.060	.375	.303	.0890	.005	.111
2.2	.0165	1.48	.060	.373	.300	.0890	.008	.116
2.4	.0225	1.48	.080	.370	.357	.1180	.012	.180
2.6	.0295	1.48	.115	.365	.223	.1690	.020	.230
2.8	.0375	1.48	.125	.363	.208	.1850	.203	.252
3.0	.048	1.48	.185	.360	.183	.2740	.027	.289
4.0	.077	1.48	.160	.365	.200	.2360	.020	.264
5.0	.012	1.48	.160	.358	.205	.2360	.030	.256

The peculiar results in experiment XI again show up. The values in no cases showing a constant increase or dedcrease.

Experiment XIII

The same conditions and solution as in exp. XI.

E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pb.	Anode Ni	Total Pol.	Cathode Pol.	Anode Pol.
0.0	.0	1.49	.025	.373	.355	.0372	.004	.032
0.2	.0005	1.49	.023	.378	.358	.0343	.004	.026
0.4	.0025	1.49	.025	.383	.361	.0372	.011	.022
0.6	.004	1.49	.025	.383	.360	.0372	.011	.024
0.8	.006	1.49	.025	.382	.358	.0372	.009	.026
1.0	.009	1.49	.027	.380	.354	.0402	.006	.033
1.2	.0159	1.49	.038	.378	.348	.0566	.004	.041
1.4	.0295	1.49	.055	.376	.338	.0820	.000	.056
1.6	.034	1.49	.065	.375	.332	.0969	.001	.065
1.8	.043	1.49	.075	.375	.326	.113	.001	.074
2.0	.0555	1.49	.075	.373	.315	.113	.004	.099
2.2	.0650	1.49	.075	.371	.313	.113	.006	.094
2.4	.0750	1.49	.085	.370	.309	.127	.004	.100
2.6	.0830	1.49	.085	.368	.305	.127	.011	.105
2.8	.0915	1.49	.155	.363	.248	.231	.020	.190
3.0	.0300	1.49	.165	.361	.230	.246	.022	.218
4.0	.0685	1.49	.165	.363	.225	.246	.020	.212
5.0	.104	1.49	.160	.363	.200	.268	.020	.262

As the method used did not turn out as expected and as the bubbles on the electrodes formed by the gas evolved, were thought to cause the difficulty, it was decided to try a run with a vacuum. This would require that the whole bath, electrodes and calomel electrode should be placed in a vacuum.

Experiment XIV

This run was carried on in a vacuum. The mixture in the bath was used as in experiment XII.

E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pb.	Anode Ni.	Total Polarization	Cathode Pol.	Anode Pol.
0.0	.0	1.48	.033	.379	.350	.0489	-.001	.042
0.2	.005	1.49	.035	.381	.351	.0521	-.009	.028
0.4	.0025	1.49	.033	.388	.362	.0489	-.019	.021
0.6	.007	1.49	.045	.385	.348	.067	-.014	.041
0.8	.009	1.49	.047	.385	.346	.070	-.019	.044
1.0	.010	1.49	.053	.383	.335	.082	-.011	.060
1.2	.0185	1.49	.065	.382	.324	.0969	-.009	.077
1.4	.024	1.49	.090	.380	.315	.134	-.006	.090
1.6	.034	1.49	.090	.380	.309	.134	-.005	.107
1.8	.044	1.49	.095	.379	.304	.1415	-.005	.104
2.0	.053	1.49	.095	.378	.306	.1415	-.004	.108
2.2	.0625	1.49	.100	.377	.303	.149	-.001	.110
2.4	.072	1.49	.100	.377	.302	.149	-.001	.108
2.6	.077	1.49	.090	.377	.299	.134	-.001	.114
2.8	.085	1.49	.090	.374	.222	.134	.003	.224
3.0	.070	1.49	.155	.367	.270	.251	.013	.158
4.0	.080	1.49	.105	.370	.270	.156	.009	.169
5.0	.120	1.49	.160	.368	.362	.246	.011	.169

At 2.6 volts, a drop in total polarization occurred, but the amperage increased steadily to 3.0 volts where it dropped, with a drop also in total polarization.

Experiment XV.

This experiment was run in a vacuum, using a bath containing .8 grams of Boric acid, 2.4 grams of $MgSO_4$, 200 c.c. of $NiSO_4$ solution.

E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pb.	Anode Ni.	Total Pol.	Cathode Pol.	Anode Pol.
0.0	.000	1.48	.055	.42	.41	.0222	.061	.046
0.2	.001	1.48	.015	.395	.383	.0222	.025	.006
0.4	.0035	1.48	.023	.395	.375	.0330	.025	.005
0.6	.008	1.48	.035	.395	.375	.0519	.025	.012
0.8	.008	1.48	.035	.400	.370	.0519	.032	.012
1.0	.010	1.48	.037	.400	.370	.0549	.032	.012
1.2	.0145	1.48	.055	.410	.370	.0814	.046	.012
1.4	.020	1.48	.075	.440	.370	.1110	.091	.012
1.6	.026	1.48	.095	.450	.370	.1405	.021	.016
1.8	.0315	1.48	.075	.460	.390	.1700	.021	.016
2.0	.0375	1.48	.095	.463	.390	.2000	.026	.024
2.2	.044	1.48	.115	.466	.395	.2140	.030	.020
2.4	.0515	1.48	.135	.463	.392	.1850	.126	.006
2.6	.058	1.48	.145	.460	.3825	.2000	.121	.009
2.8	.059	1.48	.125	.460	.3725	.1700	.121	.112
3.0	.070	1.48	.135	.460	.370	.1630	.121	.015
4.0	.083	1.48	.115	.460	.368	.1630	.121	.012
5.0	.115	1.48	.110	.460	.370	.1630	.12.	.012

The calomel became green during the run, a Ni salt must have forced its way into the cell. Towards, the end of the run the liquid was drained from the cell, leaving the cell useless altho readings were taken as usually, these readings are worthless.

When the vacuum was removed the solution rushed back into the electroded.

Practically no deposit could be noticed on the cathode. What there was, was soft and muddy. It could be wiped off with a towel.

The values obtained in this experiment have a more constant value, than any values so far obtained.

The amperage increased steadily without any serious breaks.

Experiment XVI

This experiment was carried out under a vacuum with a bath diluted to twice its original volume. It consisted of 150 c.c. of water, 150c.c. NiSO_4 , 18 grams Boric acid and 2.4 grams MgSO_4 .

E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pb	Anode Ni.	Total Pol.	Cathode Pol.	Anode Pol.
0.0	.0	1.48	.015	.380	.370	.0222	.002	.012
0.2	.001	1.48	.015	.382	.370	.0222	.005	.012
0.4	.003	1.48	.020	.388	.375	.0296	.014	.005
0.6	.005	1.48	.025	.388	.373	.037	.014	.008
0.8	.0062	1.48	.015	.388	.375	.0222	.014	.005
1.0	.010	1.48	.025	.387	.372	.037	.013	.010
1.2	.017	1.48	.035	.375	.365	.0519	.005	.020
1.4	.024	1.48	.045	.385	.360	.0666	.006	.027
1.6	.030	1.48	.065	.350	.342	.0962	.002	.054
1.8	.032	1.48	.055	.375	.335	.0814	.005	.164
2.0	.012	1.48	.035	.378	.350	.0519	.001	.141
2.2	.015	1.48	.045	.373	.330	.0666	.005	.171
2.4	.019	1.48	.050	.371	.310	.0814	.001	.101
2.6	.026	1.48	.083	.367	.259	.0223	.017	.176
2.8	.032	1.48	.100	.365	.230	.1480	.020	.220
3.0	.0405	1.48	.145	.365	.216	.2150	.020	.230

At .8 volts a wire broke causing all readings in that row to be uncertain.

When the voltage was 2 volts, it jumped to 2.6 volts. Here it remained and had to be brought down by use of the rheostat. This again was due to the decomposition voltage of nickel sulphate.

Experiment XVII

In this experiment the suction was not turned on until 1.0 volts was reached.

E.M.F.	Amperage	Battery E.M.F.	Total	Cathode Pb.	Anode Ni.	Total Pol.	Cathode Pol.	Anode Pol.
0.0	.0	1.48	.015	.371	.360	.0222	.011	.026
0.2	.001	1.48	.015	.371	.359	.0222	.011	.028
0.4	.0015	1.48	.018	.375	.360	.0268	.005	.026
0.6	.0035	1.48	.023	.377	.353	.0341	.002	.038
0.8	.0035	1.48	.025	.375	.352	.0370	.005	.019
1.0	.008	1.48	.040	.373	.340	.0592	.008	.056
1.2	.014	1.48	.043	.370	.338	.0621	.012	.060
1.4	.0185	1.48	.045	.367	.338	.0666	.012	.069
1.6	.025	1.48	.055	.362	.331	.0814	.016	.060
1.8	.033	1.48	.055	.368	.334	.0814	.024	.066
2.0	.040	1.48	.065	.366	.330	.0962	.016	.071
2.2	.048	1.48	.065	.366	.327	.0962	.019	.076
2.4	.055	1.48	.075	.365	.320	.0962	.019	.086
2.6	.063	1.48	.075	.365	.312	.1110	.020	.098
2.8	.068	1.48	.085	.360	.315	.1258	.019	.094
3.0	.077	1.48	.085	.360	.310	.1258	.020	.101
4.0	.085	1.48	.085	.363	.308	.1258	.027	.104
5.0	.120	1.48	.085	.363	.307	.1405	.023	.106

The amperage increases uniformly as also does the total polarization. The potential of the cathode is irregular, while the anode potential, while not as bad, is not very good.

Experiment XVIII

This attempt was carried on without using any change in pressure. The bath used consisted of 60 c.c. of NiSO_4 , and 2.5 grams of Boric Acid. This was made up to 100 c.c.

E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pb.	Anode Ni.	Total Pol.	Cathode Pol.	Anode Pol.
0.0	.000	1.49	.025	.37	.35	.037	.012	.042
0.2	.001	1.48	.025	.376	.356	.037	.004	.34
0.4	.003	1.48	.027	.383	.357	.0399	.006	.031
0.6	.0045	1.48	.035	.383	.355	.0814	.006	.034
0.8	.006	1.48	.038	.383	.355	.0562	.006	.034
1.0	.0095	1.48	.045	.382	.346	.0666	.005	.048
1.2	.0145	1.48	.055	.378	.338	.0814	.000	.060
1.4	.0205	1.48	.065	.375	.327	.0961	.005	.076
1.6	.0275	1.48	.075	.373	.312	.111	.008	.098
1.8	.0345	1.48	.085	.373	.310	.125	.011	.101
2.0	.0415	1.48	.095	.3705	.310	.1405	.0105	.101
2.2	.0480	1.48	.095	.371	.300	.148	.015	.116
2.4	.0560	1.48	.100	.368	.294	.148	.016	.125
2.6	.0645	1.48	.105	.367	.292	.155	.020	.128
2.8	.068	1.48	.105	.365	.290	.155	.024	.131
3.0	.0745	1.48	.105	.362	.295	.155	.024	.124
4.0	.0830	1.48	.105	.362	.300	.155	.026	.116
5.0	.0950	1.48	.165	.361	.262	.244	.034	.172
6.0	.1200	1.48	.205	.355	.252	.304	.054	.187
7.0	.1550	1.48	.245	.342	.215	.362	.019	.242
9.5	.235	1.48	.255	.345	.205	.377		.257

A good smooth, firm deposit, slightly gray was obtained.

The anode was corroded very slightly and smoothly, and perfect in color. i.e. had a Ni color.

At 2.0 volts, gas appeared at the cathode.

At 3.0 volts, gas appeared at the anode.

Experiment XIX

The bath consisted of 1.9 grams of Boric acid,
50 c.c. of NiSO_4 solution 154.8 grams per liter,
and 50 c.c. of water.

E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pb.	Anode Pb.	Total Pol.	Cathode Pol.	Anode Pol.
0.0	.000	1.49	.0035	.400	.3775	.0052	.036	.002
0.2	.0005	1.49	.035	.4125	.3825	.0521	.355	.010
0.4	.004	1.49	.045	.416	.3773	.067	.060	.002
0.6	.008	1.49	.055	.415	.3725	.082	.051	.005
0.8	.007	1.49	.052	.415	.375	.0775	.051	.001
1.0	.0095	1.49	.055	.4125	.3725	.082	.055	.005
1.2	.0155	1.49	.055	.410	.265	.097	.051	.016
1.4	.023	1.49	.075	.4075	.358	.112	.0475	.026
1.6	.030	1.49	.080	.405	.350	.119	.044	.039
1.8	.0375	1.49	.095	.405	.349	.143	.040	.040
2.0	.046	1.49	.105	.402	.332	.1565	.039	.065
2.2	.055	1.49	.055	.400	.355	.082	.036	.031
2.4	.0165	1.49	.055	.398	.360	.082	.034	.024
2.6	.025	1.49	.085	.3975	.3025	.1266	.032	.095
2.8	.030	1.49	.100	.398	.265	.148	.034	.165
3.0	.038	1.49	.120	.398	.245	.179	.034	.195
4.0	.0665	1.49	.155	.395	.250	.231	.029	.1875
5.0	.1000	1.49	.175	.393	.258	.261	.026	.176

At 2.2 volts, the voltage would not remain constant, but jumped to 3 volts, this it seems was due to the decomposition of the NiSO_4 . The drop of resistance of the solution can be noticed from the change in amperage.

There was no deposition on the front of the cathode, but on the back there was a very poor one.

The anode was slightly corroded and was of a good color.

At 2.2 volts, there was gas at the cathode.

At 2.8 volts, there was gas at the anode.

Experiment XX

In this experiment, the method of taking readings was changed slightly, so as to eliminate as much as possible the time factor. The readings were taken first in the following order, Total, Cathode, Anode, then the next time Anode, Cathode, Total, etc.

Those series marked with R were taken in the reverse method.

	E.M.F.	Amps.	Battery E.M.F.	Total	Cathode Pb.	Anode Ni.	Total Pol.	Cathode Pol.	Anode Pol.
	0.0	.000	1.41	.035	.395	.363	.0494	.002	.049
R	0.2	.0005	1.41	.035	.397	.365	.0494	.00	.045
	0.4	.0035	1.41	.045	.402	.3675	.0635	.007	.043
R	0.6	.005	1.41	.045	.4025	.3675	.0635	.0075	.043
	0.8	.006	1.41	.035	.402	.3675	.0494	.007	.043
R	1.0	.010	1.41	.045	.4012	.366	.0635	.006	.044
	1.2	.018	1.41	.065	.4016	.357	.0916	.001	.056
R	1.4	.0265	1.41	.055	.399	.335	.0775	.006	.088
	1.6	.036	1.41	.085	.395	.332	.1195	.006	.092
R	1.8	.044	1.41	.065	.395	.313	.1195	.008	.119
	2.0	.055	1.41	.105	.392	.312	.148	.008	.120
R	2.2	.0165	1.41	.065	.392	.313	.0916	.010	.119
	2.4	.017	1.41	.065	.390	.312	.0916	.017	.120
R	2.6	.028	1.41	.105	.385	.250	.148	.017	.118
	2.8	.035	1.41	.145	.385	.247	.2021	.021	.212
R	3.0	.042	1.41	.130	.382	.230	.1692	.017	.236
	4.0	.0805	1.41	.145	.382	.230	.2021	.021	.236
R	5.0	.120	1.41	.150	.382	.232	.2109	.021	.233
	6.0	.160	1.41	.170	.382	.2325	.240	.021	.234
R	7.0	.200	1.41	.145	.378	.232	.2021	.0275	.234

At 2.4 volts, gas appeared on the cathode.

Since the decomposition voltage was the cause of the results not being reliable, it was decided that it was best to go on with the decomposition

of the allow, as more time could not be spent working with the nickel salt.

Experiment XXI

The bath was made up of 91.25 c.c. of $ZnSO_4$, 100.00 c.c. of $NiSO_4$, (Ni : Zn :: 1 : 1), 1.16 grams of Boric acid. 15 % of weight of Ni.

As an beginning experiment the bath was made up with a ratio of 1:1 of the Ni and Zn ions. From previous experiments and from the literature it was decided to try Boric acid of such weight so as to be 15 % of the weight of the Ni.

E.M.F.	Amps.	Battery E.M.F. Total	Cathode	Anode both	Zn	Ni	Total	Cathode	Anode both	Zn	Ni
0.0	.00	1.4 .15	.665	.73	.76	.388	.21	.306	.461	.503	.016
0.2	.0025	1.4 .045	.692	.745	.76	.405	.063	.409	.481	.503	.006
0.4	.008	1.4 .005	.745	.752	.77	.630	.007	.482	.492	.519	.322
0.6	.0135	1.4 .015	.748	.758	.773	.655	.021	.488	.50	.521	.356
0.8	.021	1.4 .005	.540	.750	.76	.625	.007	.196	.49	.503	.315
1.0	.029	1.4 .025	.750	.755	.772	.642	.035	.49	.499	.521	.339
1.2	.0375	1.4 .005	.755	.757	.383	.607	.0075	.498	.50	.524	.290
1.4	.045	1.4 .025	.757	.750	.770	.618	.0375	.490	.49	.519	.305
1.6	.053	1.4 .015	.750	.750	.775	.593	.0225	.502	.453	.525	.220
1.8	.061	1.4 .015	.760	.754	.774	.612	.0225	.502	.48	.525	.096
2.0	.0685	1.4 .035	.762	.745	.774	.590	.049	.508	.475	.522	.266
2.2	.078	1.4 .015	.760	.740	.774	.583	.0225	.502	.508	.525	.256
2.4	.085	1.4 .035	.763	.762	.775	.581	.049	.509	.479	.529	.254
2.6	.095	1.4 .00	.751	.742	.776	.580	.0	.491	.49	.525	.252
2.8	.10	1.4 .045	.754	.750	.775	.578	.0030	.492	.461	.529	.250
3.0	.105	1.4 .005	.750	.730	.777	.578	.0075	.490	.449	.522	.250
4.0	.130	1.4 .055	.750	.720	.774	.572	.0770	.49	.391	.521	.240
5.0	.165	1.4 .045	.740	.680	.772	.522	.063	.475	.426	.520	.171
6.0	.200	1.4 .085	.743	.705	.771	.540	.119	.48	.49	.519	.196
9.0	.335	1.4 .045	.756	.750	.769	.490	.063	.499	.490	.517	.126

At the beginning, there was a counter E.M.F. of approximately .3 volts.

At .6 volts, there was gas on both anodes, and

at .8 volts, gas appeared on the cathode.

At 4.0 volts black spots appeared on the Zn, which became black entirely at 6 volts.

Between 6 and 9 volts, black spots appeared on the cathode.

The nickel anode was in fine condition.

Experiment XXII

Bath composition:- 100 c.c. of NiSO_4 , 100 c.c. of ZnSO_4 , 2 grams of Boric Acid.

The readings are given on the next page.

The back E.M.F. was again .3 volts, and at .6 volts there was gas at the anodes.

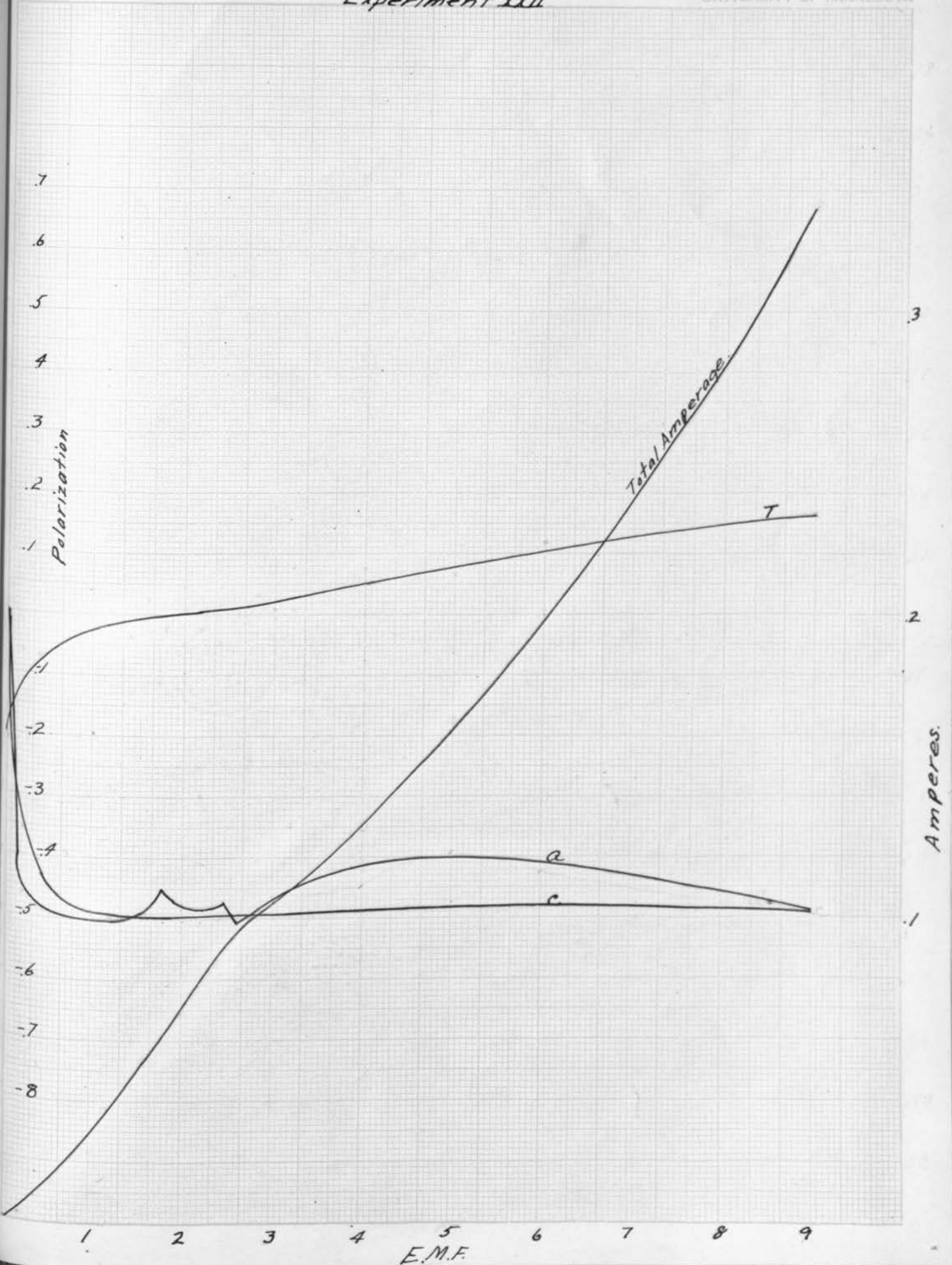
At 4.0 volts the Zinc became black.

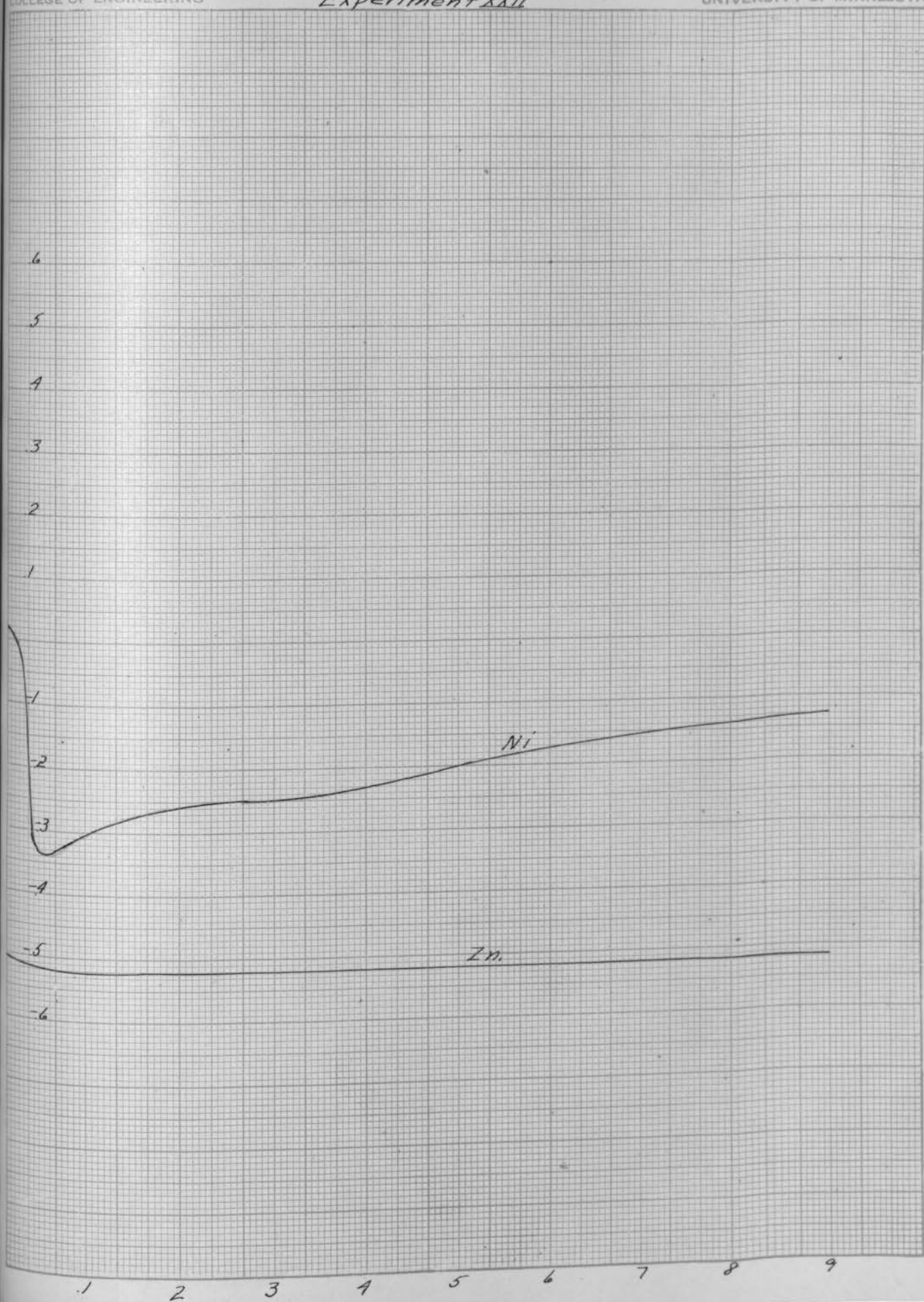
The total back E.M.F. was divided in amperage as follows, total reading -.03 amperes, Zn .06, and Ni -.03 amperage.

Readings of the portions of the total current which passed through the Zinc anode and that which passed through the nickel anode were taken. As is shown by the readings the greater part of the current passed through the zinc anode.

The total time that the current was passing was 40 minutes.

	E.M.F.	Total Amps.	Amps. Zn	Amps Ni.	Total	Cathode	Anode Total	Zn	Ni	Battery E.M.F.	Total	Cathode	Anode Total	Zn	Ni
R	0.0	.0	.0	.0	.205	.510	.715	.735	.380	1.41	.289	.16	.449	.475	.022
R	0.1	.0015	.0025	.0015	.035	.690	.720	.753	.400	1.41	.0494	.413	.455	.500	.004
R	0.3	.0055	.0055	.0015	.015	.730	.740	.755	.567	1.41	.0212	.47	.482	.503	.240
R	0.5	.011	.015	.002	.025	.715	.735	.751	.600	1.41	.0352	.449	.478	.499	.286
R	0.7	.018	.016	.001	.020	.530	.725	.745	.580	1.41	.0282	.187	.462	.490	.257
R	0.9	.0255	.0225	.001	.025	.715	.740	.753	.605	1.41	.0352	.449	.482	.500	.292
R	1.1	.033	.029	.0	.0	.505	.730	.750	.573	1.41	.0	.166	.470	.508	.248
R	1.3	.0405	.0355	.0	.025	.715	.740	.760	.600	1.41	.0352	.449	.482	.510	.286
R	1.5	.048	.042	.0	.0	.732	.740	.757	.582	1.41	.0	.471	.488	.497	.260
R	1.7	.058	.048	.0	.025	.730	.740	.760	.540	1.41	.0352	.47	.482	.510	.201
R	1.9	.063	.054	.0	.005	.720	.743	.755	.553	1.41	.007	.453	.488	.503	.220
R	2.1	.071	.062	.0	.015	.732	.735	.750	.532	1.41	.0212	.471	.478	.498	.190
R	2.3	.079	.068	.0005	.015	.745	.749	.760	.560	1.41	.0212	.49	.495	.510	.230
R	2.5	.086	.074	.0005	.013	.740	.731	.762	.527	1.41	.0183	.432	.470	.512	.184
R	2.7	.093	.079	.002	.030	.750	.745	.762	.552	1.41	.0213	.498	.490	.512	.225
R	3.0	.100	.085	.003	.015	.740	.741	.762	.535	1.41	.0212	.482	.484	.512	.195
R	4.0	.135	.120	.014	.015	.745	.743	.760	.553	1.41	.0212	.49	.487	.510	.220
R	5.0	.170	.145	.019	.005	.733	.725	.760	.490	1.41	.007	.473	.461	.510	.130
R	6.0	.195	.180	.011	.050	.740	.718	.759	.545	1.41	.0705	.482	.452	.519	.108
R	8.0	.270	.260	.010	.005	.730	.700	.759	.440	1.41	.005	.470	.427	.509	.060
R	9.0	.305	.285	.025	.065	.732	.710	.755	.490	1.41	.0916	.471	.441	.503	.130





Experiment XXIII Alloy 2.

Bath composition:- 91 c.c. of $ZnSO_4$, 100 c.c. of $NiSO_4$, 2 grams of Boric acid.

As no nickel could be expected in the alloy when a low amperage was used, the experiment was started at 2 volts and .095 amps. for total amperage.

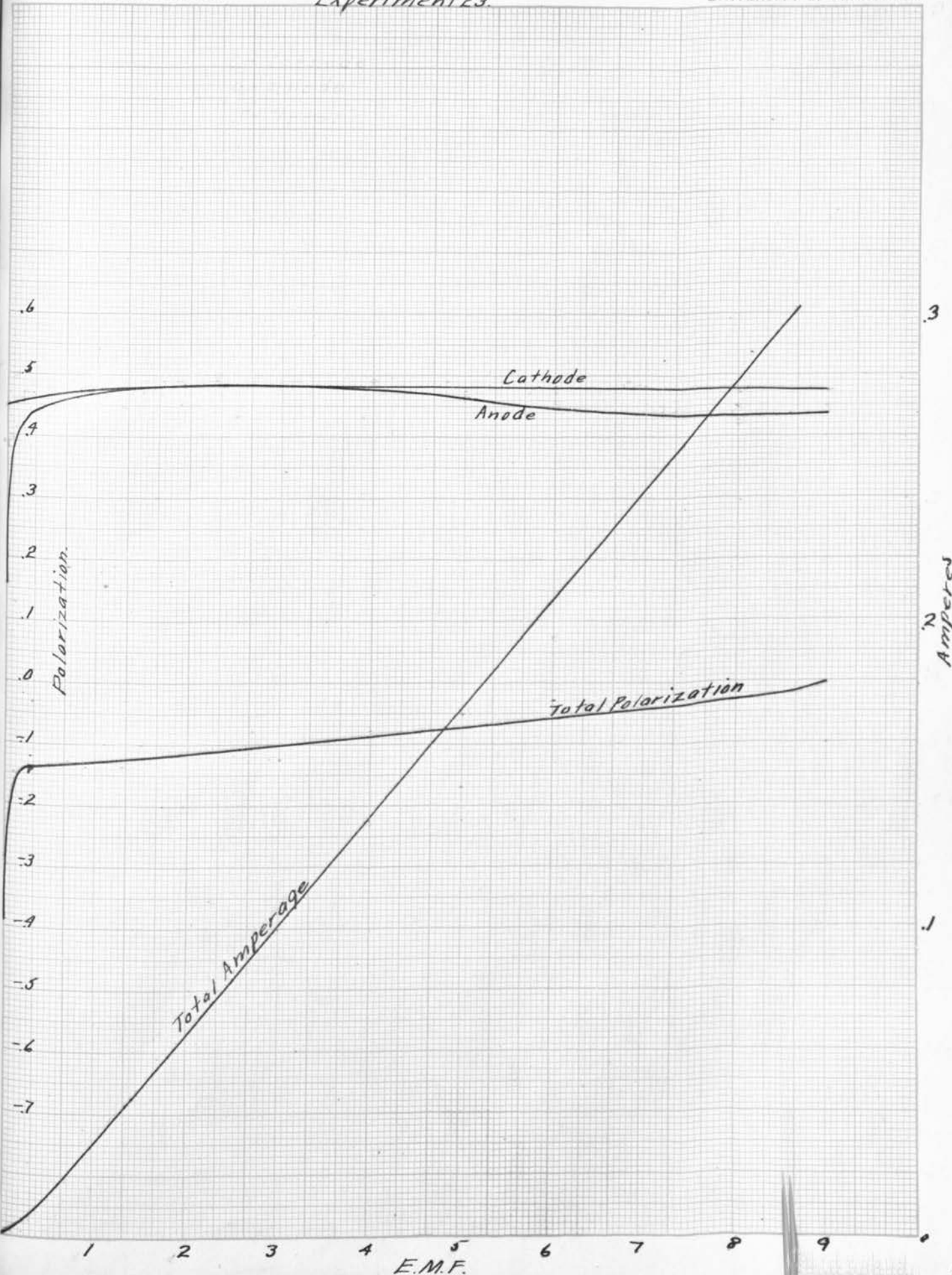
The experiment was continued until the cathode was burned.

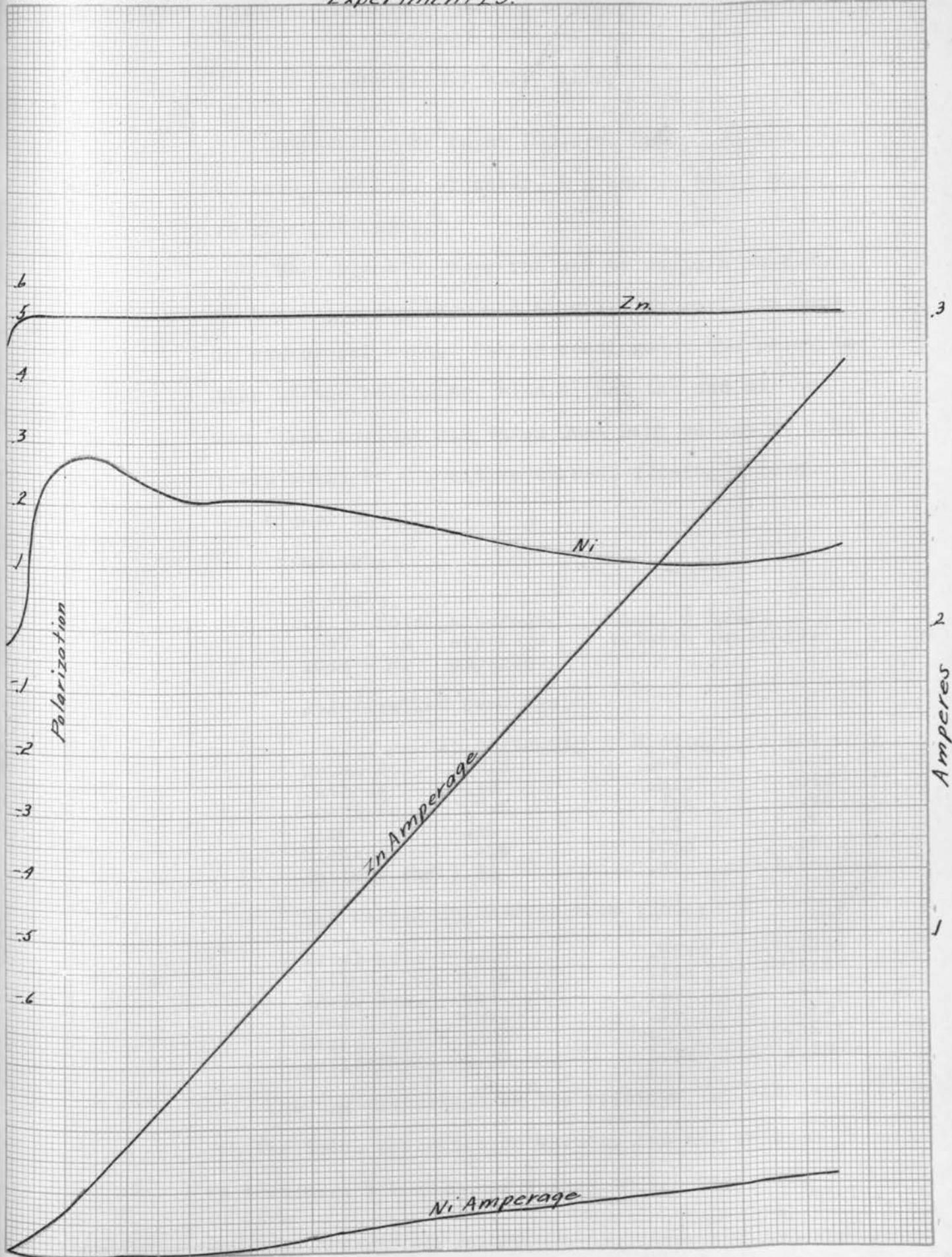
The data taken is given on the next sheet.

The nickel anode was in good shape, but the zinc anode was black.

The deposit had black spots and edges. Gas was produced throughout the whole experiment.

	E.M.F.	Total Amps.	Zn Amps.	Ni Amps	Total Pol.	Cathode Pol.	Anode Pol.	Zn Pol.	Ni Pol.	Battery E.M.F.	Total Pol.	Cathode Pol.	Anode Pol.	Zn Pol.	Ni Pol.
	2.0	.095	.033	.007	.1320	.470	.790	.810	.46	1.4	.448	.099	.549	.573	.084
R	3.0	.130	.110	.013	.1325	.480	.775	.813	.43	1.4	.455	.112	.523	.578	.042
	4.0	.180	.140	.030	.1250	.485	.795	.810	.48	1.4	.350	.120	.552	.573	.112
R	5.0	.225	.180	.024	.1205	.600	.780	.810	.49	1.4	.287	.280	.530	.573	.119
	6.0	.270	.220	.040	.1075	.660	.790	.815	.49	1.4	.105	.365	.548	.580	.139
R	7.0	.315	.270	.010	.135	.655	.785	.815	.50	1.4	.189	.358	.540	.580	.140
	8.0	.360	.320	.019	.0	.715	.782	.815	.48	1.4	.0	.441	.540	.580	.105
R	8.5	.390	.340	.027	.065	.735	.780	.815	.40	1.4	.091	.470	.530	.580	.0





Experiment XXIV Alloy 3.

Composition of bath; 100 c.c. NiSO_4 , 92 c.c. of ZnSO_4 , 20 c.c. of water, 2 grams of boric acid, .5 grams of MgSO_4 .

The object of this run was to deposit an alloy at a constant voltage and amperage as would be done in commercial work. Taking readings of the polarization at the beginning, middle, and the end of the run. The voltage was taken just high enough so that there would be a positive current flowing through the nickel electrode.

Readings:

2 volts,	
.1 - Total amperage	Time, $\frac{1}{2}$ hours
.097 - Zn amperage	between readings.
.044 - Ni amperage	

Polarization readings,

	At beginning	Middle	End
Total Pol.	.7315	.103	.085
Cathode Pol.	.48	.815	.845
Anode Pol.	.795	.795	.795
Zinc	.81	.82	.820
Nickel	.505	.565	.580
Battery emf	1.32	1.32	1.28

The values calculated from these;

Total Pol.	.7416	.0396	.1088
Cathode Pol.	.7074	.515	.555
Anode Pol.	.49	.492	.49
Zinc Pot.	.51	.522	.522
Nickel Pot.	.106	.185	.182
Battery emf	1.32	1.32	1.28

The big difference in the readings, is noticed in the total polarization values, and the cathode potential. The cathodes values at the beginning

were low, but steadily increased approaching the the zinc anode and going even a little above it. As a check on the values, if the values for the cathode and anode are added together, the sum should be equal to the total polarization. The sum is .1045, an error of 3.96 %.

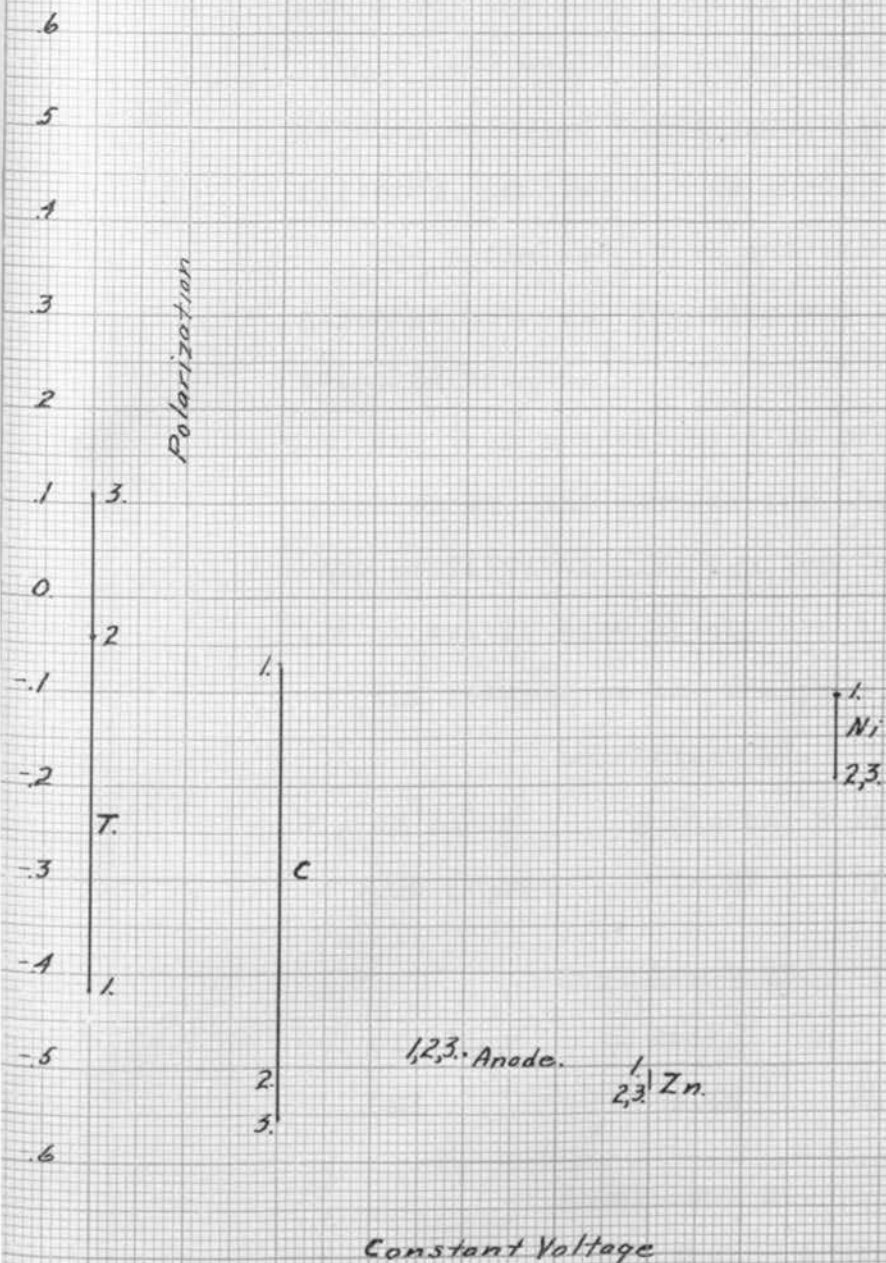
The deposit in this case was very good. The nickel anode was also in good condition, but the zinc was badly burned.

A peculiar feature of this last experiment was the constant value obtained for the anode, while the value for both the nickel and zinc decreased. The cathode potential approached the anode but continued to decrease, going below the anode in value. It is difficult to compare the results obtained for this experiment with those from the former experiments, as they are all obtained with a constant voltage while it varies in all the others.

Numbers 1, 2, 3 indicate readings of the beginning, middle and end

T = Total polarization.

C = Cathode polarization.



ANALYSIS OF ALLOYS.

All alloys deposited were analyzed so as to determine the ratio of the metals to each other. The cathode was cleaned, washed, and weighed. After the deposition of the alloy, the cathode was again weighed. The alloy was dissolved in dilute sulphuric acid. A little lead would be dissolved with the alloy but on further dilution would precipitate out. This was filtered, ignited and weighed.

The nickel was then determined by the dimethyl glyoxime method. The zinc was determined by the sulphide method.

Any iron present will be brought down when the solution is made neutral for the nickel determination. This is filtered off, ignited to the oxide and weighed. the nickel is then determined in the regular way.

The results of the analysis are as follows:

Experiment 21.

Wt. of Alloy	% Nickel	% Zinc	C.D.
.006 grams	16.37	83.65	Increases Steadily

Experiment 22.

Wt. of Alloy	% Nickel	% Zinc	C.D.	% Lead
.021	9.45	80.76	Increases Steadily	9.76

Experiment 24.

Wt. of Alloy	% Nickel	% Zinc	C.D.	% Lead
.1285	20.54	72.81	.776 amps	6.58

The results obtained from the alloy analysis, show that zinc is in the greater amount. With the small amount of data available, the writer was not able to use the analysis of the alloys for any definite result. The steady increasing of the current density also causes it to be difficult.

The percent of theoretical yield was found to be 17.99 % for experiment 24. This agrees fairly well with the results obtained by Shock and Hirsch. This is the only alloy deposited with constant voltage, therefore the only one which can be useful.

The results from

DISCUSSION

The results from the zinc deposition are all very good in experiments three and four, and are perhaps surprising so, since Shock says, "Measurements of the cathode polarization has been attempted during the deposition of nearly all the foregoing alloys", (composed of Ni & Zn) "but the results are of no value, on account of their extreme irregularity". As the curve on the following page show, the cathode polarization curve approaches the anode polarization curve and coincides with it up to approximately 4. volts, where due to gas evolution, the anode curve increases in value. The total polarization curve approaches zero, as theoretically it should, and remains so. This can be said to be due to the fact that the cathode becomes coated with zinc and assumes the value of the zinc anode. The amperage increases steadily with no large breaks.

Considering the nickel deposition it is found that the results are of a peculiar nature. As a polarization curve of nickel was necessary in order to work out this problem by this method every available measure was taken to obtain one. But the two big difficulties encountered were the passivity of the nickel and the evolution of hydrogen. No metal but lead was tried as a cathode for it was known from the literature that the results for other metals were the same, with the exception of mercury which has its

objection as it forms an amalgam lowering the potential.

The means of overcoming the passivity of nickel were partly satisfactory when the chloride ions, sulphate ions, or boric acid were used. It was found that it was difficult to approach the value of nickel .022 no matter what precautions were taken.

The curves obtained were of a peculiar form, increasing or decreasing at random. One thing which is noticeable is that the value of the first readings were seldom the same, even if identical solutions were used. The values obtained from nickel during the deposition of the alloys do not agree very well, but do approach zero potentials. The cathode values approach closer to the zinc curve than to the nickel curve. This is to be expected as all the alloys contained less than 21 % of nickel, which agrees with the theory that they are solutions of nickel in zinc. The values of nickel and zinc are both less when deposited together than when deposited separately.

The passivity of the nickel causes a large contact resistance, this in turn decreased the amount of current flowing into the bath through the nickel anode. This causes the zinc to deposit out more rapidly than the nickel. This is brought out particularly in experiment 22, where the zincamperage curve rises at about 45 degrees from the horizontal but the nickel curve increases but slightly.

The decomposition voltage of nickel sulphate does not show up in the deposition of an alloy as it does in a good number of the nickel deposition experiments from a bath of nickel sulphate.

It may be added that attempts to carry out the deposition in a vacuum was not successful, as the pressure in the calomel electrode will be unbalanced causing the KCl solution in it to be drawn out into the bath.

SUMMARY

The statement in Allmand has not been proved incorrect by this experiment, altho it is not proved to be correct. This was due to the inability in obtaining the polarization curve of nickel in nickel sulphate. The writer has however collected enough data to show that the polarization value of both nickel and zinc as obtained from the deposition of an alloy are lower than that as obtained from the polarization of each in a bath of its salt. This means that nickel lowers the zinc potential and the zinc lowers the potential of the nickel. The writer beleives that if it were known definitely whether nickel could act as a reversible nickel electrode it would aid in solving the problem. Due to the lack of time the alloy was not examined microscopically, altho the writer wished to do so, but knowing that work of this kind must be accurate and thorough, he could not do more in the given time.

BIBLIOGRAPHY

1. Allmand, Applied Electro-Chemistry p. 122.
2. Journal of the American Chemical Society 29,314,(1907)
Transactions of the American Electro-Chemical
Society 135 (1907).
3. Transactions of the American Electro-Chemical
Society (1921).
4. Washburn, Principles of Physical Chemistry.
5. Watt's, Laboratory Course of Electro Chemistry p. 58.
6. Watt's, Laboratory Course of Electro-Chemistry p. 50.
7. Chemical & Metallurgical Engineering, Feb. 8, 1922.
8. LeBlanc, Text Book of Electro-Chemistry.
9. "Nickel Plating Baths", F.C.Mathers and E.G.Sturdevant,
Transactions of American Electro-Chemical Society,
Vol. 30, 1916, p. 135.
10. "The Deposition of Nickel", L.D.Hammond, Transactions
of American Electro-Chemical Society, Vol.30,1916,p.103.
11. "Nickel Plating", F.C.Matners, & E.H.Stuart, &
E.G.Sturdevant, Transactions of American Electro-
Chemical Society, Vol. 29, 1916, p. 383.
12. "Electro Deposition of Zinc", R.S.Snowden, Transactions
of American Electro-Chemical Society, p.121,(1907).