1-1-1935

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Recommended Citation

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A Thesis
Submitted to the Department of Chemistry
in Partial Fulfillment of the
Requirements for the Degree of
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MONTANA SCHOOL OF MINES

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TABLE OF CONTENTS

THE EFFECTS OF ZINC SULPHATE, MANGANESE SULPHATE, AND IRON SULPHATE ON THE LEAD STORAGE CELL

The lead storage battery as it is used today is made up of the pasted type plates of lead dioxide, the anode, and sponge lead, the cathode, and wooden or hard rubber separators, which serve to insulate these from one another. In manufacturing these, it is desirable to keep them free from impurities. This is impossible for small amounts will get in with the water, acid or even from the steel tools which contact the cell during its construction or repair. The most common impurities entering a cell in this manner would be iron and manganese. It is evident that these, each with the possibility of having more than one valence, would be oxidized at the anode and reduced at the cathode. This results in sulphating both plates and producing a loss of capacity. Another impurity which might also get into a cell is zinc; it is not exactly known how this would react on a cell. In order to study the definite effects of these impurities on a battery, this investigation was made. The voltage characteristics on charge and discharge, the self discharge, and the capacity of the lead storage cell were studied with reference to the effects of the presence of zinc, manganese and iron in the electrolyte.

APPARATUS AND REAGENTS

For the investigation, it was necessary to use at least two cells to study the effects of each impurity, so that the

results of one could be checked against the other. Seven
cell, in all, were used, each one being composed of two
negative plates, one positive plate, and inserted between
these were cedar separators. The plates used were manufactured
by The Henderson Battery Company of Spokane, Washington.
The exact composition of the materials used to prepare these
is not known, but "Arendt" (Bibliography 1) says that, in
general, one part of litharge (PbO) and one part of 1.10
to 1.15 specific gravity, sulphuric acid, whereas, that of
the cathode is made up of five parts of litharge (PbO) and
one part of 1.10 to 1.15 specific gravity, sulphuric acid.
They also contain some filler, such as magnesium or barium
sulphate, or wood flour, to increase the porosity, for this
is an essential of a good plate since it allows acid to pene-
trate the plates easily, thereby exposing a maximum of sur-
face to the electrolyte. The plates, after being thoroughly
dried, are placed in weak sulphuric acid (specific gravity
1.15) and formed into a positive plate of lead dioxide (PbO_2)
and a negative of sponge lead. The negative plates, as used
in this work, were thoroughly formed but the positive required
about ten or twelve hours to insure complete conversion to
PbO_2.

The electrolyte was a solution of chemically pure
sulphuric acid and distilled water mixed in the proper
proportions to give a specific gravity of 1.275. The level
of the solution in the cell was maintained above the top of
the plates to prevent exposure to the air for sponge lead

is very susceptible to oxidation and will take up carbon dioxide; this has a tendency to harden and thus reduce the capacity of the plate by clogging up its pores. The rapidity with which this oxidation takes place was observed in one case during this work when a set of plates upon removal of the electrolyte immediately developed a large amount of heat at their surfaces.

Enough material was available to prepare seven of these cells, which were placed in an old (12-volt) battery box, since this contained compartments that were of the size desired. Tests were made to be sure there were no breaks in the partitions between cells.

A copper coulometer, used to determine the capacities of the cells, was composed of three electrodes, two of which were anodes, and a solution of 150 grams of copper sulphate and 50 grams of alcohol per liter of water. The set-up is shown in Figure 2.

For ordinary voltage readings a common Weston voltmeter functioned well, but for measuring potentials of a reference electrode against each plate it could not be used, due to the fact that it contains only a low resistance and this allows current to flow through, thus introducing an error. Therefore, a potentiometer was more suitable. All the current readings were ascertained with a common Weston ammeter.

The reference electrode (Bibliography 2) was a stick of cadmium, three-eighths of an inch in diameter, immersed in a solution of sulphuric acid of a specific gravity of 1.275. These were contained in a bottle that was sealed by a rubber stopper. The cadmium stick, and a long glass tubing, that was shaped in such a way that it could be immersed in the electrolyte of the battery cells, projected from the bottle and through the stopper. The glass tubing served to join the electrolyte of the half cell with that of the battery cells. In all cases, the end of this connection tube was placed against the plate in order to have the same position for each reading. This procedure is necessary because a reading taken with the tube placed away from the plate is different from that where it is set against the plate. Potentials of both plates were always positive to the cadmium cell. The potential of the lead dioxide, as measured against this half cell, decreases on discharge but it is at all times higher than that of the cell, and the sponge lead potential will rise from 0.1 to about 0.3 volts on completion of the discharge. The difference between the cadmium-sponge lead and the cadmium-lead dioxide potential at any moment equals the cell voltage for the corresponding instant. All readings of Electromotiveforce were taken on open circuit. The advantages gained in employing the half cell as described here are the insolubility of cadmium in sulphuric acid, thus insuring against any
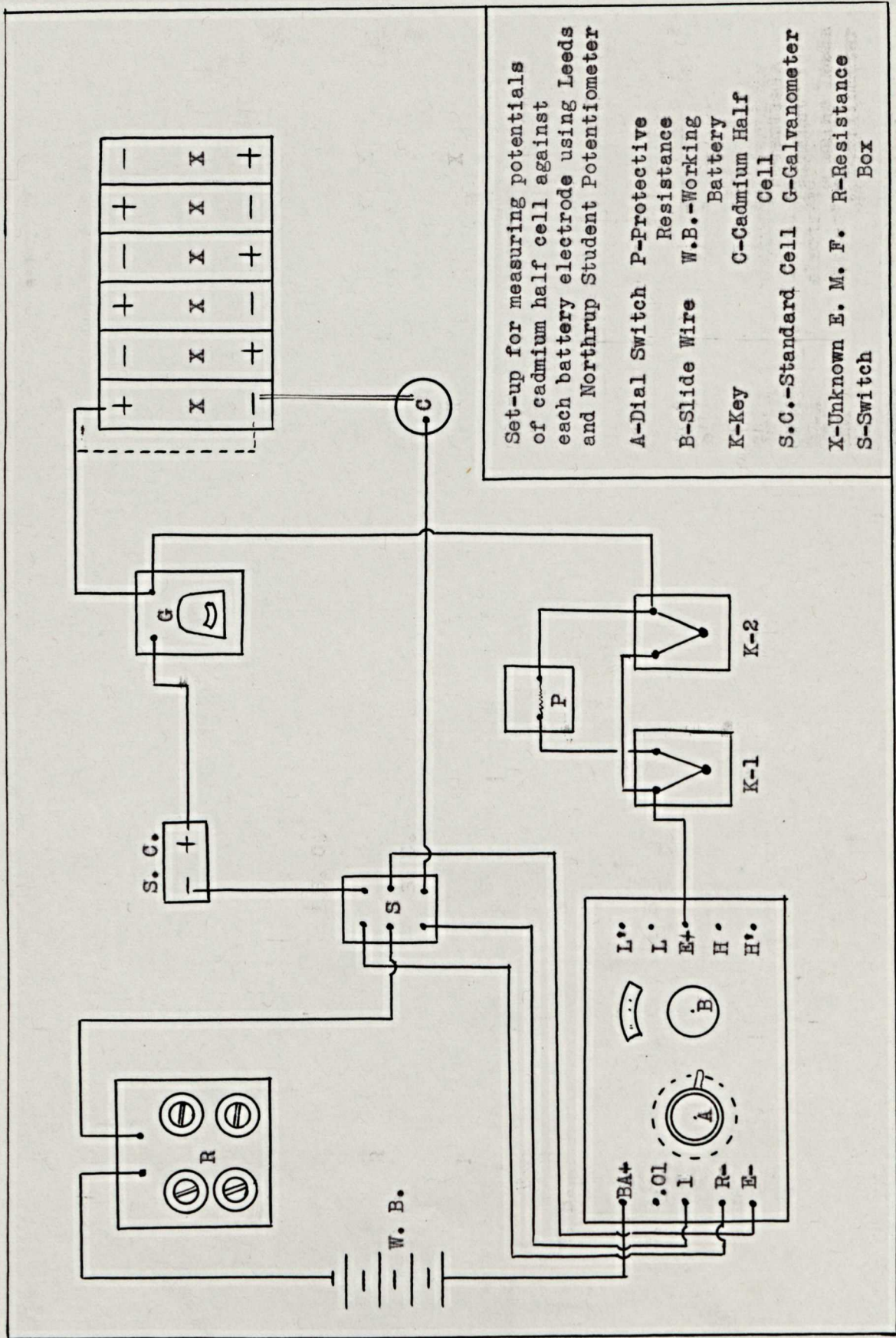
Set-up for measuring potentials
of cadmium half cell against
each battery electrode using Leeds
and Northrup Student Potentiometer

A—Dial Switch   P—Protective
                   Resistance
B—Slide Wire   W.B.—Working
                   Battery
K—Key   C—Cadmium Half
                   Cell
S.C.—Standard Cell   G—Galvanometer

X—Unknown E. M. F.   R—Resistance
S—Switch   Box

FIGURE 1

RHEOSTAT

BATTERY OF CELLS

COULOMETER

AMMETER

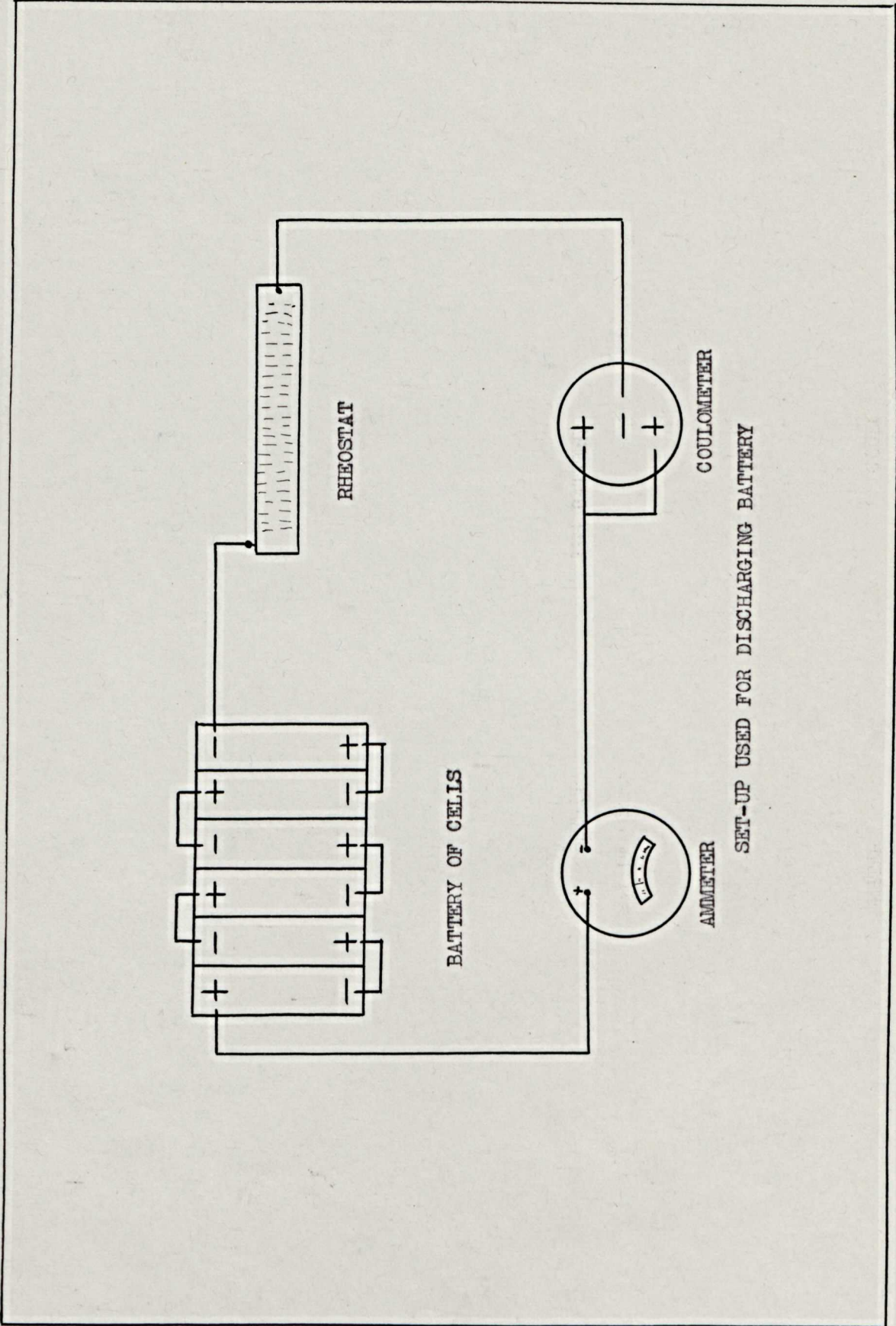SET-UP USED FOR DISCHARGING BATTERY

FIGURE 2

contamination of the battery, and the absence of a differ-
ence of potential that would exist if the acid of the battery
cell and half cell were not practically of the same concen-
tration. The set-up used to read these potentials is
illustrated in Figure 1.

The solutions of zinc sulphate, iron sulphate, and
manganese sulphate were made from chemically pure materials.
The first two of these were somewhat deprived of their water
of hydration, thereby making it necessary to determine the
concentration of the solutions by a volumetric analysis;
the zinc was titrated against a standard solution of potassium
ferrocyanide and the iron against a standard solution of
potassium permanganate. The manganese sulphate was only
slightly effloresced so that it was only necessary to make
the solution up of a definite amount of water and the salt.

EXPERIMENTAL PROCEDURE

In this work impurities were added to the cells in
definite concentrations and their effects on the voltage
of the cell, when on charge and discharge; on the self
discharge; and on the capacity, were noted.

At first it was necessary to make a study of the
characteristics of an uncontaminated cell to determine the
rate of charge and discharge to be used, and also to ascertain
the capacity of the normal cell at this rate of discharge.

Keeping the results of this investigation in mind, the other work was carried out as follows. Six more cells were put into service, five of which contained the impurity to be studied, the other being left as a normal cell. With this arrangement the effects of the iron sulphate, manganese sulphate, and zinc sulphate could be noted by comparison with the uncontaminated cell.

The effects of impurities were studied in the concentrations as tabulated below:

Impurity	Impurity added as a water solution of	Concentration in grams of metal per liter of Electrolyte
Zinc	$Zn\ SO_4\ 7H_2O$	.07395
Zinc	"	.14790
Zinc	"	.29580
Zinc	"	.36975
Zinc	"	7.39500
Iron	$Fe\ SO_4\ 7H_2O$	.014
Iron	"	.028
Manganese	$Mn\ SO_4\ 2H_2O$	.020
Manganese	"	.040

The cells contaminated with these various concentrations of impurities were put through a number of cycles of charging and discharging at a constant current rate of two amperes. Before drawing the energy from the charged cell, it was left idle for a period of ten or twelve days. The cells, when on

the charging line, were assumed to contain a maximum of energy when a voltage of 2.5 was reached.

When the cells were standing idle, the rate of self discharge of each plate was determined by noting its potential drop from day to day, the potential being measured against a cadmium half cell. These readings were taken with a potentiometer, set-up, as illustrated in Figure 1.

After remaining idle for a definite length of time, a discharge was made, using the arrangement as shown in Figure 2. The ampere hours obtained from each cell were utilized to produce a deposit of copper in the coulometer. From this, the capacity was determined by calculation. A cell on the discharge circuit was considered to be depleted of its energy when a voltage of 1.8 was reached.

RESULTS AND DISCUSSIONS

In the case of charging voltages, cells containing iron and manganese were expected to have potentials which differed from that of a normal cell. This expectation arose from the fact that these salts, being so easily oxidized and reduced, would tend to dissipate of the energy being delivered to the cells, but on the contrary, no differences could be detected. All cells were charged up to a line voltage of 2.5 volts in the same length of time.

The cell potentials and single potential of the plates did not deviate much from those of a normal cell, even after

remaining idle for eight or ten days, The data taken during such periods is recorded in the following table. In reading this, it must be kept in mind that the cadmium half cell was always negative to the plates. Also, the "minus" sign as placed before a figure indicates that the potential of the lead-cadmium or the lead dioxide-cadmium is becoming more negative by this value. The "plus" sign applied in the same manner, except that the change denotes the potential as one becoming more negative.

Impurity	Concentration in grams of metal per liter of electrolyte	Cell Voltage first day after charge	Average drop in cell potential per day	Variation of potential of cadmium to: PbO_2 Plate	Pb Plate
None		2.1460	.0035	-.0043	-.0008
Zinc	.07395	2.1478	.0035	-.0043	-.0008
Zinc	.14790	2.1486	.0036	-.0045	-.0009
Zinc	.29580	2.1471	.0033	-.0039	-.0006
Zinc	.36975	2.1443	.0030	-.0034	-.0004
Zinc	7.3950	2.1112	.0039	-.0032	+.0007
Iron	.014	2.1116	.0036	-.0030	+.0006
Iron	.028	2.1042	.0037	-.0033	+.0004
Manganese	.020	2.1082	.0042	-.0036	+.0006
Manganese	.040	2.1030	.0042	-.0035	+.0007

The potential change per day is slight, but it is interesting to note that this figure, with the first additions of zinc, became smaller, and, then when the concentration reached something near 0.5 grams of zinc per liter of electrolyte, it begins to increase. The potentials, that were taken each day, of the cadmium-sulphuric acid half cell against each plate indicates the effects of the different concentrations on the cell electrodes. With increasing concentrations of zinc, the lead dioxide potential shows a decreasing tendency to become more negative with each succeeding day of idleness. The sponge lead potential, on the other hand, moves in a more negative direction with the small concentrations, but, as the concentration increases, the change per day in this direction diminishes until a concentration of about 0.5 grams of zinc per liter of electrolyte is reached, after which the potential of the sponge lead becomes more positive with each day of idleness. Iron and manganese present in any concentrations accelerated the natural tendency of the cathode to become more positive and the anode less positive with each succeeding day of idleness. Therefore, these increased the average potential drop per day of their cells as compared with that of a normal cell.

The capacities of the cells were rather drastically affected by iron, manganese and the high concentration of zinc. From statements made by "Arendt" (Bibliography 3) the loss of

capacity was not expected to be so great. The cells, from which the capacities recorded here were taken, remained idle for twelve days; following this, they were discharged (set-up as in Figure 2). The ampere hours obtained from each cell was noted by the amount of copper they deposited in a coulometer. The percentage loss of capacity of any cell was determined by comparison with a normal cell, the capacity of which was assumed to be one hundred per cent.

Impurity	Concentration in grams of metal per liter of electrolyte	Capacity in amperes per hour	Percentage of loss as compared with normal cell
None		5.6	0
Manganese	.04	1.37	75.5
Manganese	.02	2.30	58.9
Iron	.028	2.53	54.8
Iron	.014	3.14	43.9
Zinc	7.395	2.52	55.0

The voltage of these cells on discharge vary somewhat according to their capacities, as shown by the accompanying curves, in which voltage is plotted as the abscissa and the hours of discharge as the ordinate.
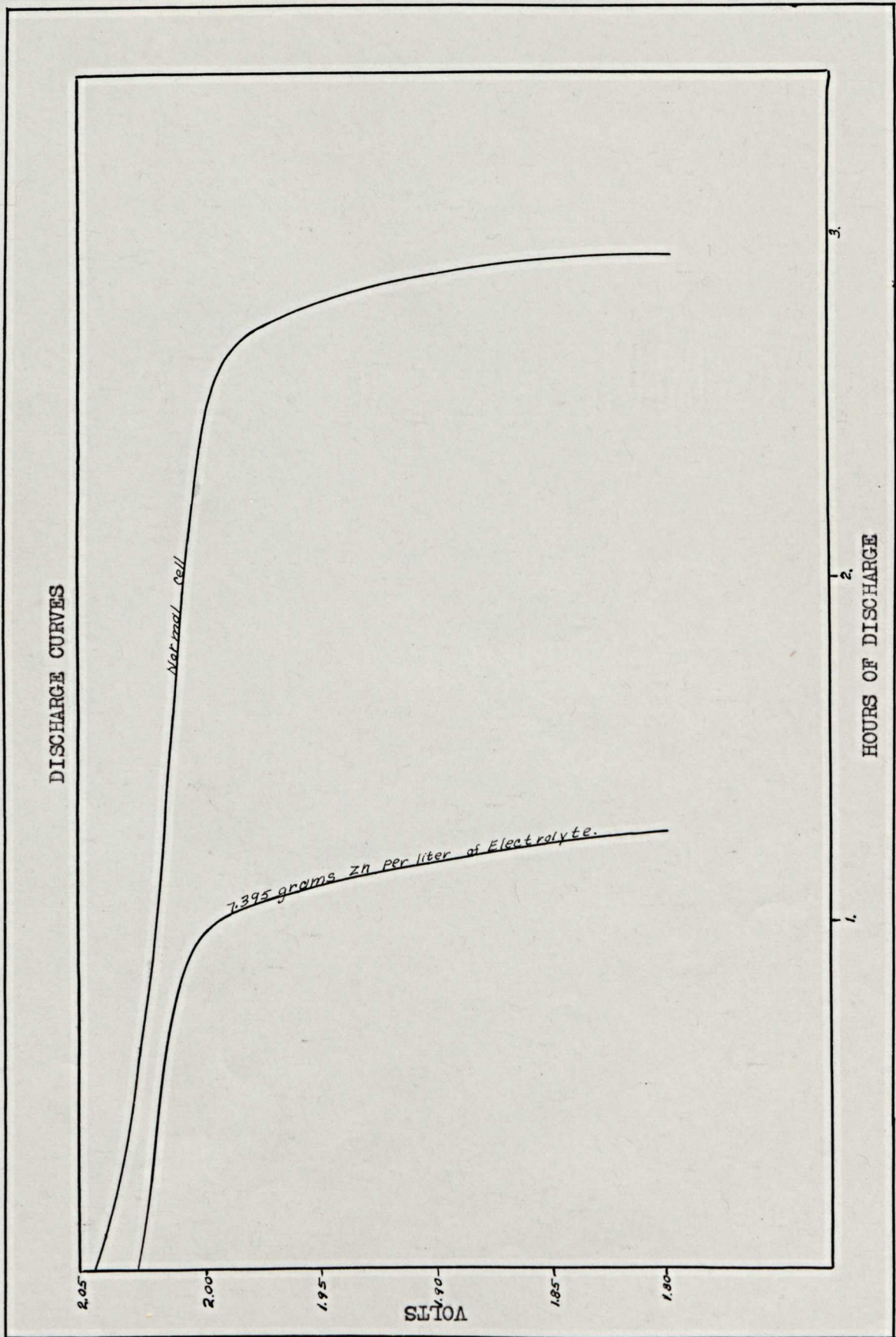
DISCHARGE CURVES

Normal cell

7.395 grams zn per liter of Electrolyte.

VOLTS

2.05
2.00
1.95
1.90
1.85
1.80

HOURS OF DISCHARGE

FIGURE 3

DISCHARGE CURVES

Nermal Cell.

.014 grams of Fe per liter of Electrolyte

.028 gram of Fe per liter of Electrolyte.

VOLTS

2.05 — 2.00 — 1.95 — 1.90 — 1.85 — 1.80
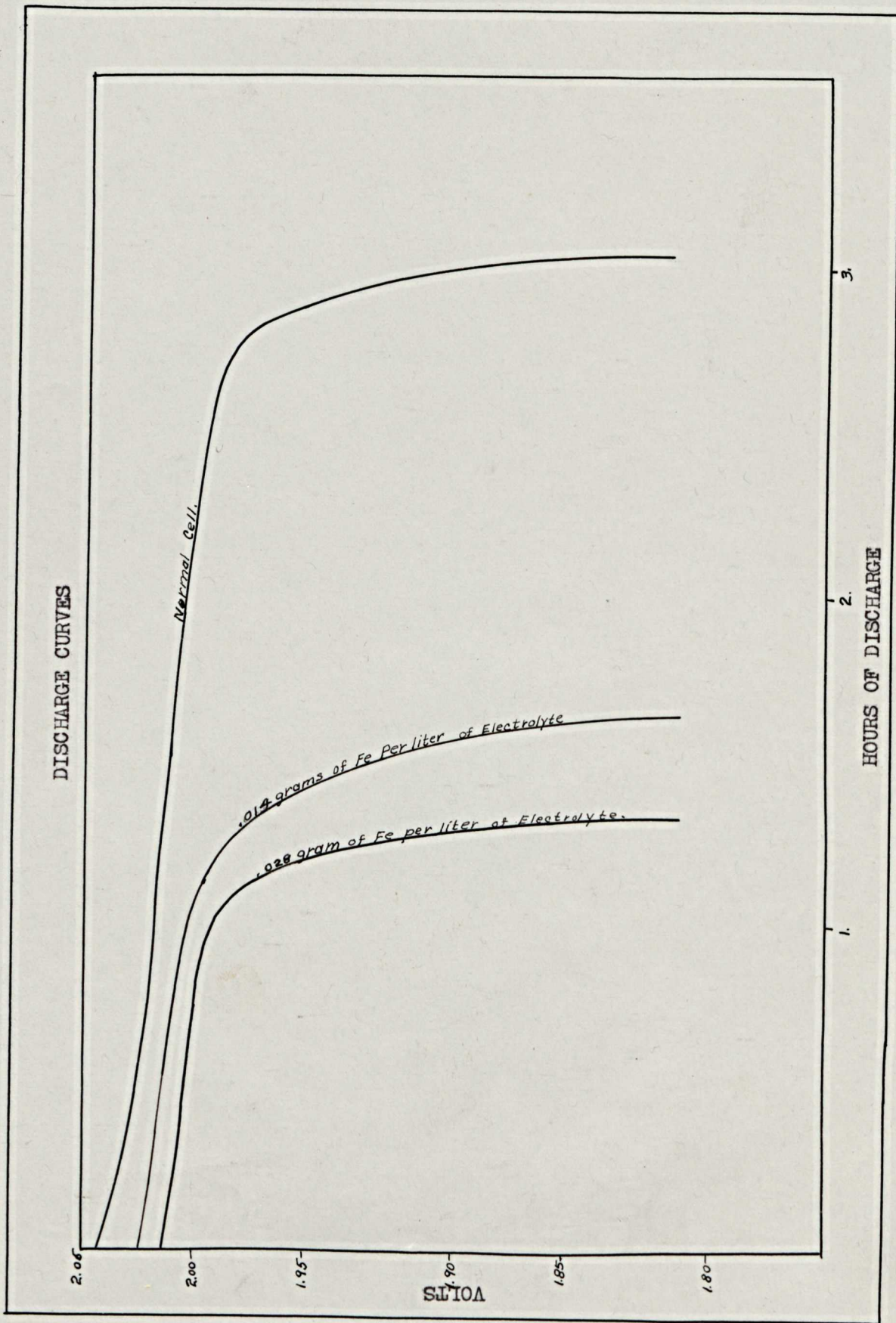
1. 2. 3.

HOURS OF DISCHARGE

FIGURE 4

CONCLUSIONS

From the foregoing discussion of this work, it is evident that every precaution possible was taken to get accurate results. Such being the case, confidence is placed in the data so that the following conclusions may be drawn up:

1. The impurities studied showed no effect on the voltage characteristics of a cell that is being charged.

2. Zinc, added to a normal cell in concentrations smaller than 0.5 grams per liter of electrolyte, is slightly beneficial to it during its idle period, since it decreases its potential drop per day. However, concentrations larger than this are of no advantage. In regard to capacity, there are no effects due to concentrations smaller than 0.5 grams per liter of electrolyte, but, if this is boosted to something near seven grams, the loss of capacity from that of a normal cell is fifty per cent. Evidently, then, this impurity is not desirable in any concentration above 0.5 grams per liter of electrolyte.

3. Iron is definitely injurious to a battery if it is present in any concentration. The data shows that in an idle cell 0.01 grams of iron per liter of electrolyte causes an increase in the potential drop per day. The capacity under

such conditions is lowered as much as forty-five per cent.

4. Manganese is even more detrimental to a battery than is iron. It has an even greater tendency to increase the potential drop per day of an idle cell over that of a normal cell. Also noticeable, is a more pronounced loss of capacity. Therefore, this impurity should never be allowed to enter a battery.

ACKNOWLEDGMENT

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