CALORIMETRIC STUDY OF THE THERMODYNAMIC PROPERTIES

OF THE

NICKEL-CADMIUM CELL

FINAL REPORT: Project SC-MGR-33-006-015

TO: National Aeronautics and Space Administration
Goddard Space Flight Center

PERIOD: October 1, 1964 - December 31, 1965

BY

Professor Paul F. Bruins

Stanley M. Caulder

Adj. Prof. Alvin J. Salkind

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POLYTECHNIC INSTITUTE OF BROOKLYN
Department of Chemical Engineering

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ABSTRACT

An adiabatic calorimeter was designed and constructed, and a calorimetric technique developed to determine thermal characteristics of electrochemical cells. The validity of the apparatus and method was confirmed by the excellent agreement obtained between the experimentally determined heat of reaction for the nickel-cadmium (KOH) cell, 33.15 Kcal/equiv., and the theoretically accepted value obtained from the literature by voltage measurements 33.15 Kcal/equiv.

The heat of reaction for a nickel-cadmium (LiOH) cell was measured and determined to be 37.7 Kcal/equiv. This corresponds to a heat of formation of 157.55 Kcal/mole for the NiOOH·LiOH compound if it is assumed that the change in the heat of reaction was due solely to the heat of formation of the charged nickel hydroxide compound. This change in heat of reaction with variation of electrolyte type indicates that the previously believed independence of the electrochemical system on electrolyte is not completely valid.

In addition, a short series of tests were made, using a didymium hydroxide additive to the nickel hydroxide electrode.

Author

I. PURPOSE

The purpose of this study was to investigate and identify the thermal and thermodynamic characteristics of alkaline electrolyte secondary nickel-cadmium cells by means of an adiabatic calorimeter.

In view of the extensive use of the nickel hydroxide electrode in certain batteries used in satellites and missiles, and because of the difficulties encountered in attempts to improve the quality of the electrodes (even though the electrode processes are not well understood), it was thought worthwhile to investigate certain parameters that may participate in the electrode reaction.

The first year of this program was devoted to the design and construction of the adiabatic calorimeter.

Initial studies of nickel-cadmium cells were made with electrolytes either of potassium hydroxide or lithium hydroxide.

II. INTRODUCTION

The electrode reactions taking place within the nickel-cadmium electrochemical cell have been extensively investigated and several reaction mechanisms have been proposed[2,13,14]. Nevertheless, there are still many uncertainties associated with these electrode reactions which have yet to be resolved. The reaction mechanism of the nickel hydroxide electrode, and the compounds which exist on the electrode in the charged and discharged condition, is still subject to controversy. It is apparent from several publications and communications [1-5,13] that our knowledge concerning the possibility of the electrolyte participation in the nickel electrode reaction is vague with respect to the potassium (or other alkali metals) content in the reaction products; participation of water in forming hydrates, and the structures produced when these substituents are incorporated in the nickel hydroxide lattice. There are also discrepancies in the thermodynamic data for the Ni-Cd cell reaction. The values reported by different authors[4,6,7,8] for the heat of reaction, free energy and entropy change, exhibit appreciable difference.

The enthalpy change accompanying a cell reaction is generally calculated from the Gibbs-Helmholtz equation. This is accomplished by determining the emf of the cell at various temperatures, and thus ascertaining its temperature coefficient. The value obtained by this method is related to the equilibrium reactions of the cell, and the treatment is only valid if the system exhibits a stable emf when there is no current passing through the cell, and when pressure-volume work is done at constant pressure. It is not valid when there is a change

in pressure at constant volume; for example, when there is gas evolution in a sealed cell. This method does not give any information about the reactions occurring during the charging or discharging of a cell and cannot be applied to a system, such as the nickel-cadmium alkaline cell in which the open circuit voltage varies with time. To overcome these limitations a calorimeter was developed by which the enthalpy change of an electrochemical system undergoing irreversible thermodynamics could be ascertained. Thus, from thermal measurements made during the charge-discharge cycle of the Ni-Cd cell, one can calculate heats of reaction and from this calculate other thermodynamic properties. Calorimetric measurements have previously been used in the study of electrochemical cells[7,8,15,16,17]. These calorimeters were developed to perform specific functions, and therefore varied in size, sensitivity, complexity, and difficulty of operation. All the calorimeters, except one[17], were of the adiabatic type; the other being isothermal.

This report describes the design of an adiabatic calorimeter and its use for the measurement of thermal characteristics of Ni-Cd cells having various alkaline electrolytes and Ni electrode additives.

III. APPARATUS DESIGN

A) Calorimeter (Fig. 1)

The outside box of the calorimeter (A) was constructed from 3/4"
marine plywood, with the front of the box being made of 1" thermopane (B).
This allowed the cells under test to be viewed continuously. The inside
of the five remaining sides of the box were then insulated with 1"
Styrofoam (C). The Styrofoam was then covered with 1/4" plywood (D),
thus forming another box within a box, with the Styrofoam separating
them. The volume of this inner box was approximately 26 liters. The
back of the box was not sealed, thus enabling it to serve as a door
for placing the cells in the calorimeter. The Styrofoam and plywood
were placed on the back (door) with very close tolerance, thereby in-
suring that, when the back was in place, it formed a tight seal, with
the other four sides, thus minimizing heat transfer with the outside
environment.

Three holes were drilled in the top of the calorimeter. The middle
hole housed the fan (E), while the other two holes functioned as air
inlets into the calorimeter. Above and along each side of these three
openings were placed two 1/2" strips of asbestos board (F). These
boards served as holders for the nichrome heater wire. The heater and
openings were then covered with a wooden box (G), thereby insuring that
the calorimeter was completely sealed.

When the calorimeter is in operation, the fan draws air up through
the heater coils, where it is heated as required and then passes through
the two openings leading back into the calorimeter.

B) Thermometry

All of the experiments entail the periodic measurement of the tem-

perature of the calorimeter (which will be the same as the cell). One junction of a copper-constantan thermocouple was placed inside the cell under test, and the other junction was placed in a dewar flask containing ice water. The difference in potential of the thermocouple was read on a Leeds & Northrup millivolt potentiometer. From this potential the temperature rise of the cell with time was obtained.

C) Electrical System

Temperature Control Circuit: A temperature sensitive thermistor (T_1) was immersed about 3 cm. below the level of the electrolyte in the cell, and another thermistor (T_2) was placed against the cell in the surrounding atmosphere of the calorimeter. These thermistors were wired into two arms of a Wheatstone-bridge circuit, as shown in Fig. 1. During the course of an experiment, the temperature of the cell increased, thereby causing an imbalance in the bridge due to the changes in the resistance of the thermistors. The off-balance voltage from the bridge was fed into a control amplifier (Fig. 2). The output of the amplifier was then fed into the silicon-controlled rectifier (SCR) circuit (Fig. 3). The magnitude of the off-balance voltage from the amplifier controlled the magnitude of the current through R_1, which charged capacitor C_1. When the potential across capacitor C_1 reached the emitter peak-point voltage of the unijunction transistor Q_1, C_1 was discharged through Q_1 and the primary of the transformer T_1 created a pulse to turn on whichever SCR was forward-biased. When the SCR turned on, the circuit of the air heater in the calorimeter was completed. As a result, the air temperature surrounding the cell was increased until it was equal to the cell temperature, thus balancing the bridge circuit. This caused the SCR to turn off, thereby opening the heater circuit.

The power supply circuits for the amplifier and Wheatstone-bridge are shown in Figs. 4 and 5.

Electrolysis Circuit: The electrolysis circuit consisted of a Kepco (Model KS-36-30M) power supply, automatic battery cycling device (Fig. 6), and recorders for the measurement of the current through and the potential across the cell. The power supply was remotely programmed through the automatic cycling device. This allowed the cell to be charged at constant current, or constant potential, and discharged at constant current or constant load. The cell potential was recorded with a Sargent MR recorder, and the current through the cell was re-corded (Bausch & Lomb VOM-5) indirectly as the potential drop across a .002 ohm shunt, which was incorporated in the cycling device.

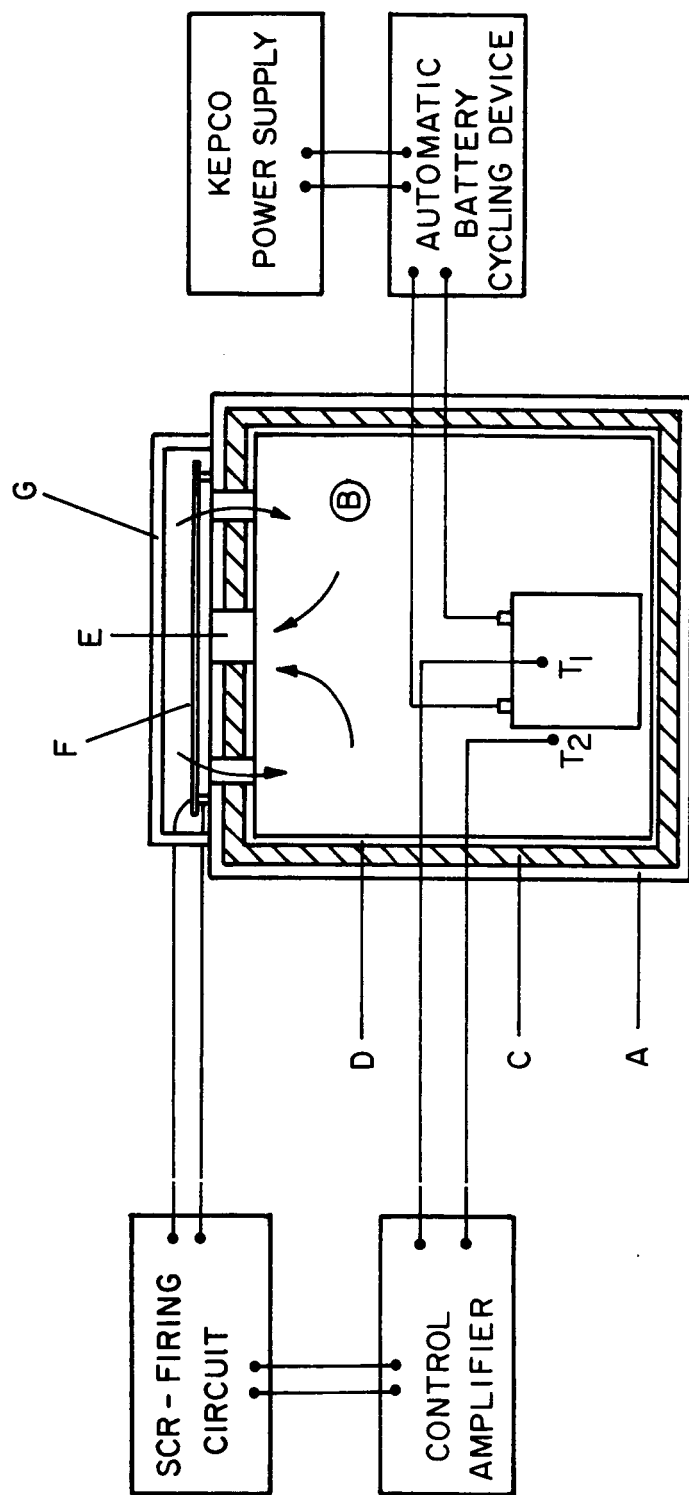FIGURE 1

ADIABATIC CALORIMETER
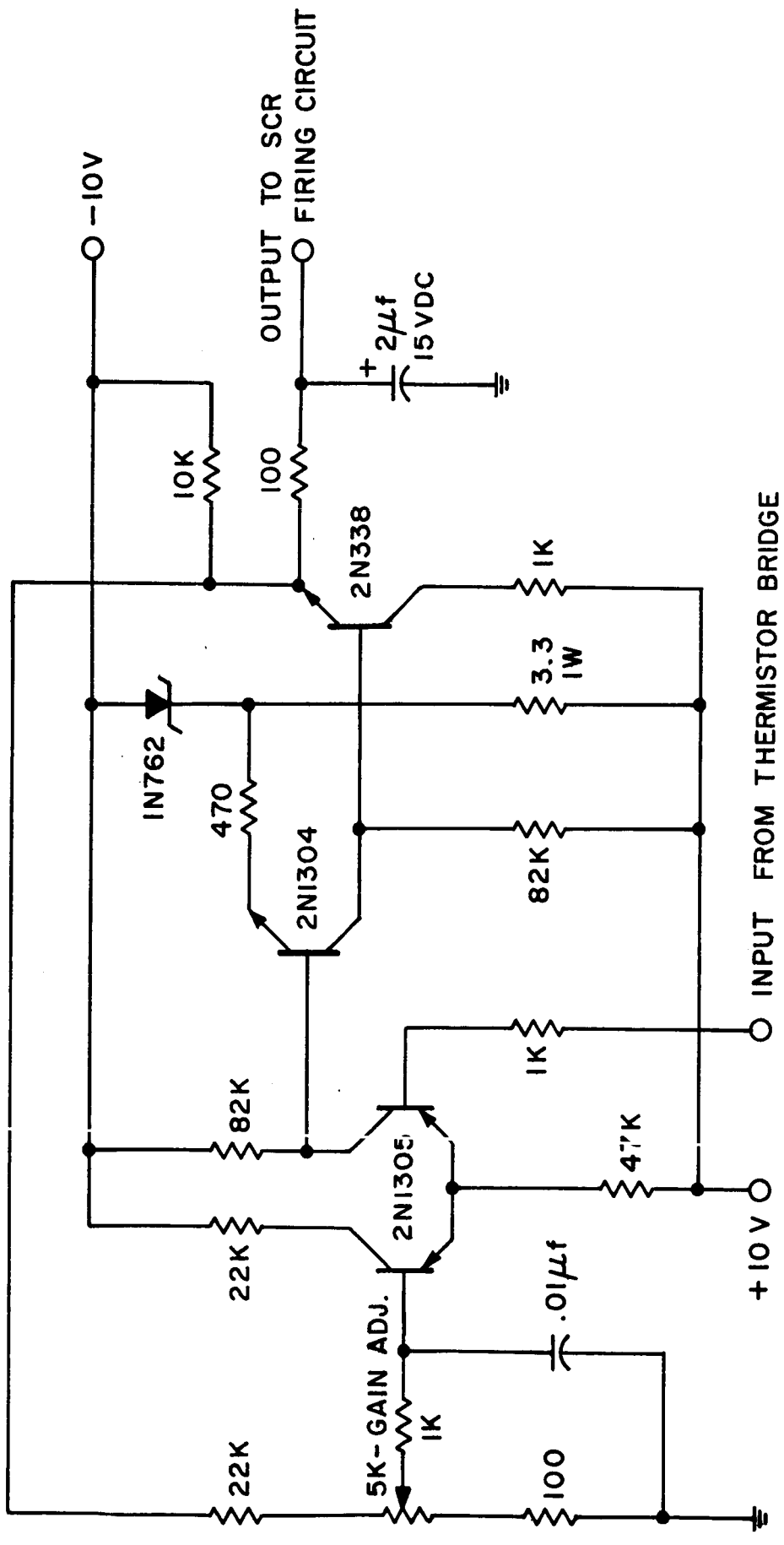
FIGURE 2

CONTROL AMPLIFIER

FIGURE 3

SCR—FIRING CIRCUIT

H-51 SECONDARY (FROM SCR-FIRING CIRCUIT)

25Ω
HEATER
400-500WATTS

SCR-1

SCR-2

H-51 SECONDARY

110 V. A.C.
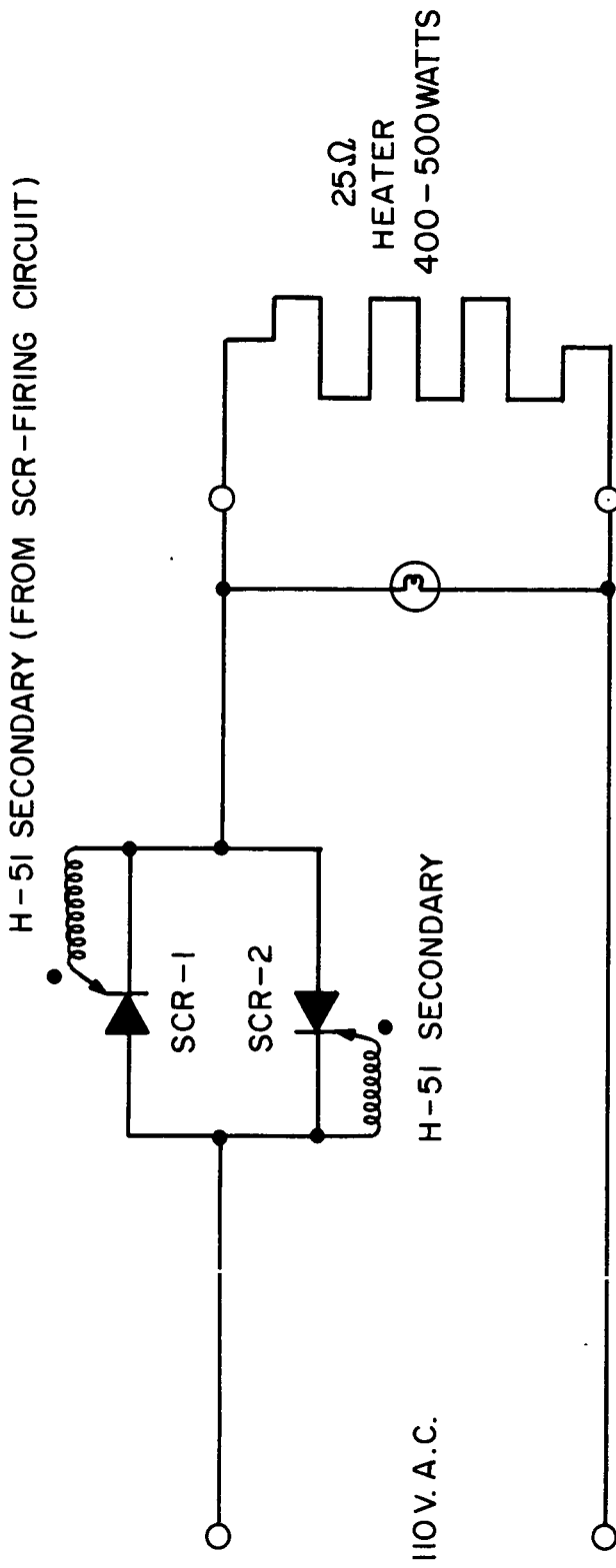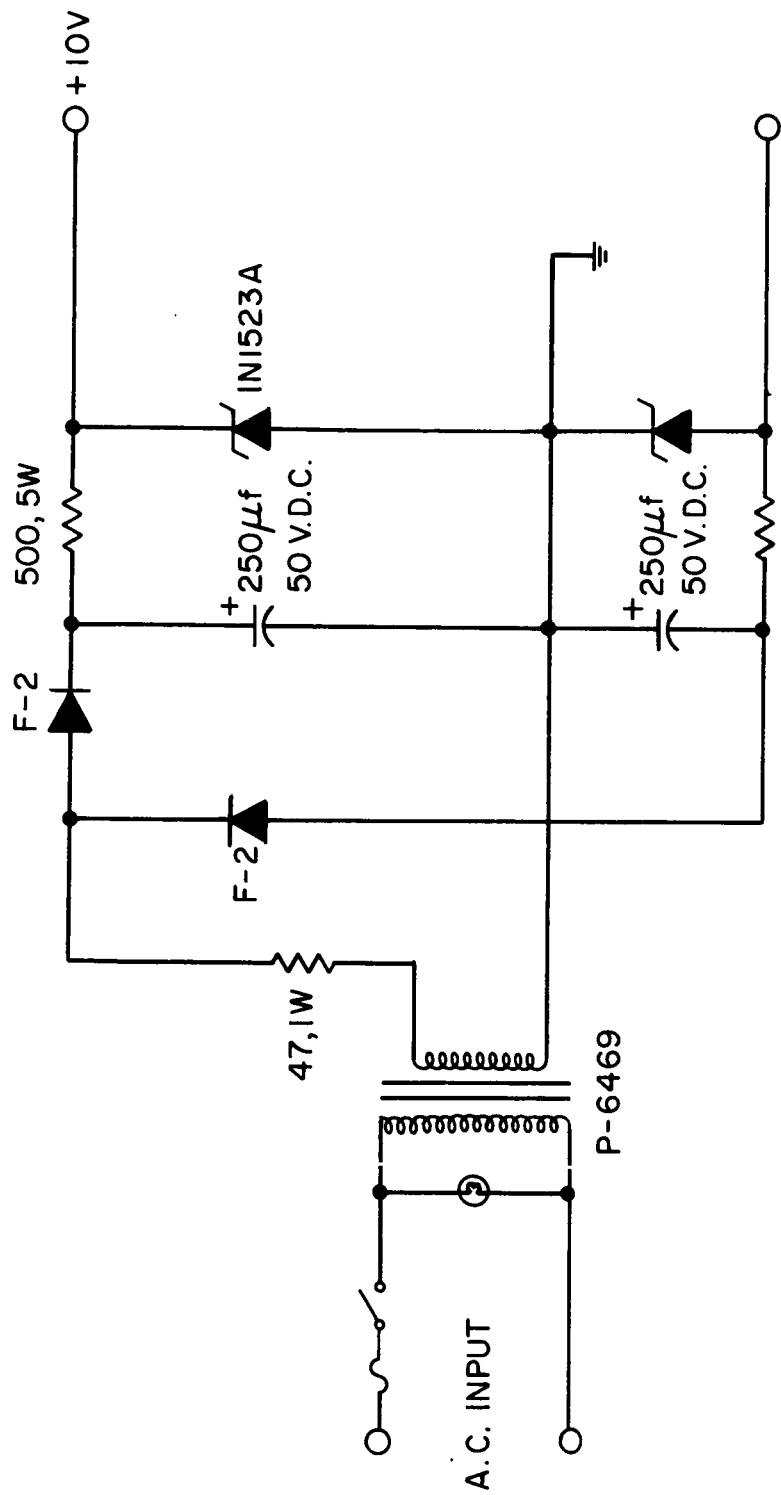
FIGURE 3A

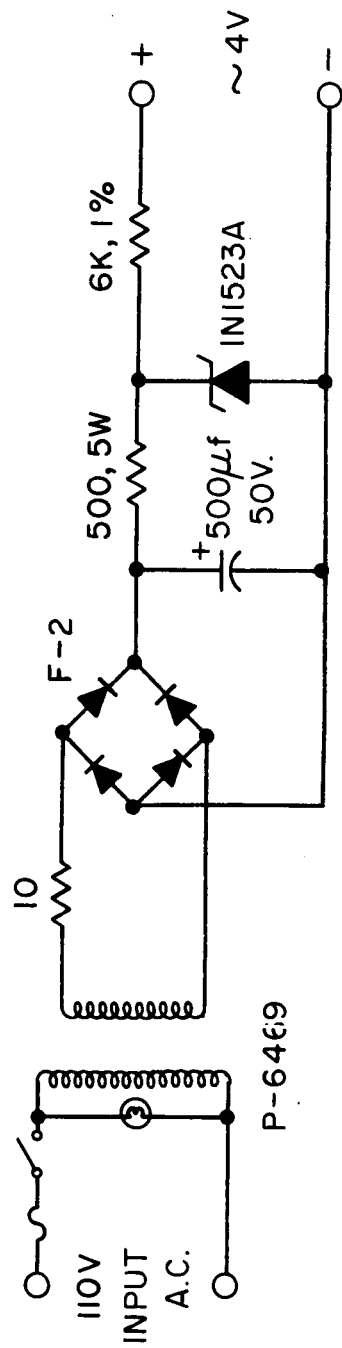HEATER CIRCUIT

FIGURE 4 POWER SUPPLY – AMPLIFIER

FIGURE 5

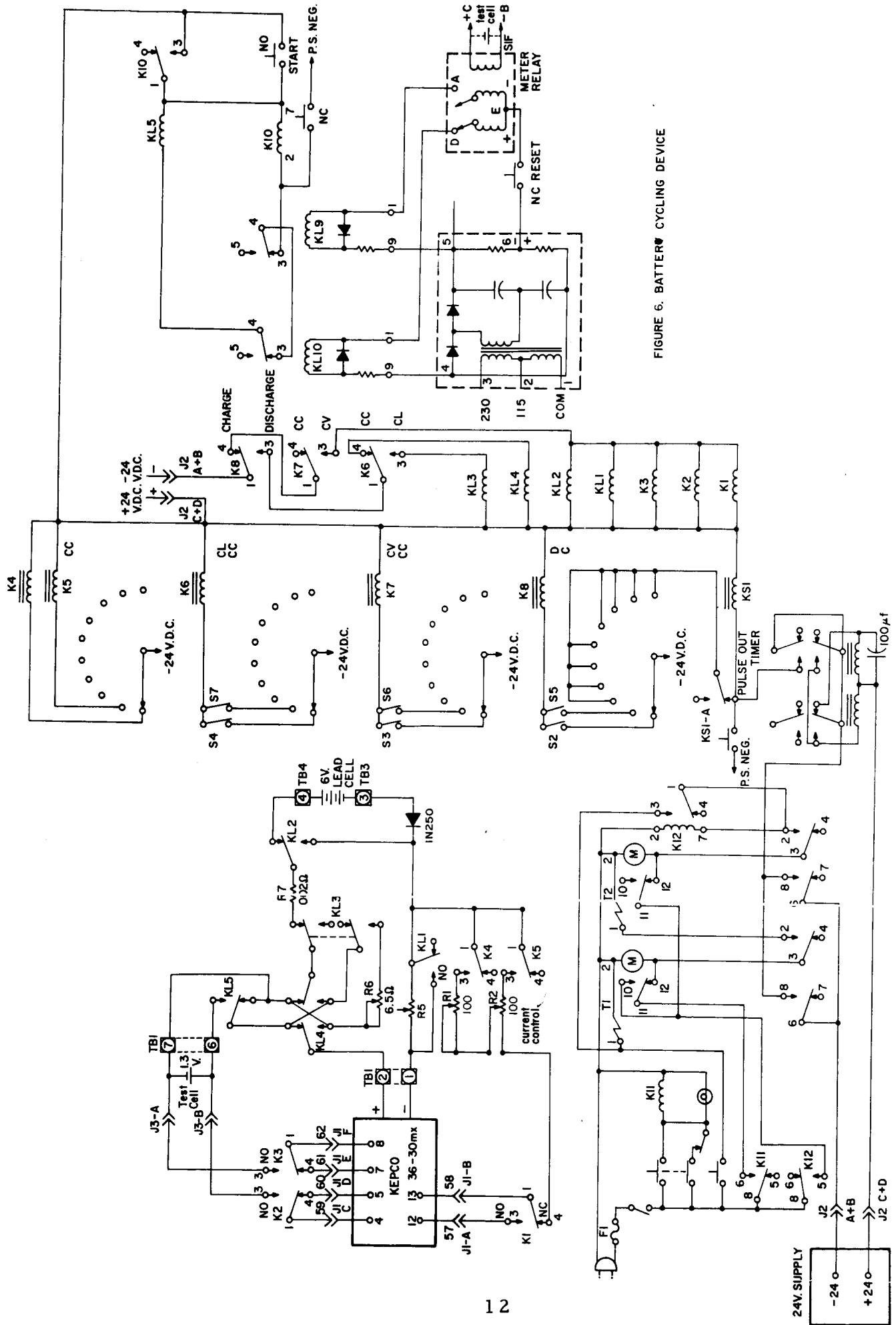POWER SUPPLY – THERMISTOR BRIDGE

FIGURE 6. BATTERY CYCLING DEVICE

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IV. CELL DESIGN

The sintered electrode nickel-cadmium cells utilized in this study were previously constructed as part of the Sandia Research Project "SAND", as reported by A. J. Salkind and P. F. Bruins[19].

The electrodes (manufactured by the Sonatone Corp.) were prepared using normal aqueous methods of impregnation, and their characteristics are given in the following table.

TABLE I.

NICKEL-CADMIUM CELL ELECTRODE CHARACTERISTICS

		Positives	Negatives
1.	Size - Full	2-3/8" x 2-11/16"	2-3/8" x 2-11/16"
	Uncoined area	6.18 sq.in.	6.18 sq.in.
2.	Thickness (Av.)	.02372"	.02392"
	Range	.0221 - .0251"	.0221 - .0261"
	Mean Deviation	.00052"	.00093"
	Standard Deviation	.00065"	.00116"
3.	Weight gain active material	3.0 grams $Ni(OH)_2$	4.8 grams $Cd(OH)_2$
	Faraday equivalent	.86 A.H.	1.76 A.H.
	Theoretical cell capacity	6.9 A.H.	12.3 A.H.

The cells used in these studies had the characteristics shown in Table II.

TABLE II.

DISCHARGE CHARACTERISTICS OF NICKEL-CADMIUM CELLS AT ROOM TEMPERATURE

	Cell Groups	
	F	G
1 Amp. Disch. Rate		
Init. Volt.	1.28	1.29
Mid-Volt.	1.25	1.25
Cap. AH to 0.6V/cell	5.67	5.57
Cap. AH to 1.0V/cell	5.64	5.56
7 Amp. Disch. Rate		
Init. Volt.	1.23	1.23
Mid-Volt.	1.18	1.20
Cap. AH to 0.6V/cell	5.50	5.55
Cap. AH to 1.0V	5.37	5.50
Total Cap. with supps.	5.86	5.90
28 Amp. Disch. Rate (av. 3 cycles)		
Init. Volt.	1.16	1.17
Mid-Volt.	1.12	1.14
Cap. AH to 0.6V/cell	4.73	5.05
Cap. AH to 1.0V	4.23	4.60
Total Cap. with supps.	5.47	5.74

Code

F group cells = Nylon-cellophane-nylon separators,
total thickness 12.5 mils

G group cells = Polypor PVA separators, 5 mils thick

The cells were conditioned before utilization in the present study, as described under "Experimental Procedure".

V. EXPERIMENTAL PROCEDURE

A) THERMAL CAPACITY OF THE CELLS

The thermal capacities of the nickel-cadmium cells used in this study were determined by the water equivalent method[22]. The cells were heated in an oven at 80°C for 16 hours, and then quickly transferred to a calorimeter containing a known amount of water. The temperature rise of the water was plotted against time. By extrapolation of the heating and cooling curves, Fig. 7, and knowing that the heat lost by the cell equaled the heat gained by the water, the thermal capacity of the cell could be calculated.

B) CELL CONDITIONING

Prior to experimentation the cells were conditioned as follows: the cells were discharged at one amp. until the voltage fell to 1.0V. They were then charged at 0.5 amp. for 16 to 18 hours. The cells were then discharged again in the above manner. The above charge-discharge cycle was repeated. Following this capacity test, the cell was shorted for 14 hours. The short was removed and the cell charged at 0.5 amp. for 10 minutes. The cell was then open-circuited for 24 hours, during which time, if its voltage remained above 1.16V, the cell was considered acceptable.

C) CYCLING OF Ni-Cd CELL IN CALORIMETER

The previously conditioned cell was placed in the calorimeter and charged at 1.5 amps. for 2 hrs., then 0.5 amp. for 1 hr. Upon completion of charge, the cell was allowed to cool to about 25°C and it was then discharged at 1.5 amps. until the voltage fell to 1.0V.

D) FABRICATION OF NEW ELECTRODES FOR SPECIAL TESTS

Certain experiments required special nickel hydroxide electrodes. One such experiment was the thermal characterization of a nickel-hydroxide electrode impregnated with didymium hydroxide. This electrode

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was prepared in accordance with a technique described in NASA Tech. Brief 65-10083. Upon fabrication, the electrodes were subjected to analysis by x-ray fluorescence and x-ray diffraction to ascertain the presence of the didymium compounds. The x-ray fluorescence showed strong lines for Ni, Nd, La, and also some Pr.

E) DETERMINATION OF E FOR Ni-Cd(KOH) and Ni-Cd(LiOH) CELLS[4]
In order to obtain a voltage representative of the main Ni-Cd cell reaction, a fully charged cell was placed in a constant temperature bath at 110°F (43.3°C), and the open-circuit voltage measured with time. The voltage-time plot was then extrapolated back to a common time of 1000 minutes. This was done with both the Ni-Cd(KOH) cell and the Ni-Cd(LiOH) cell.
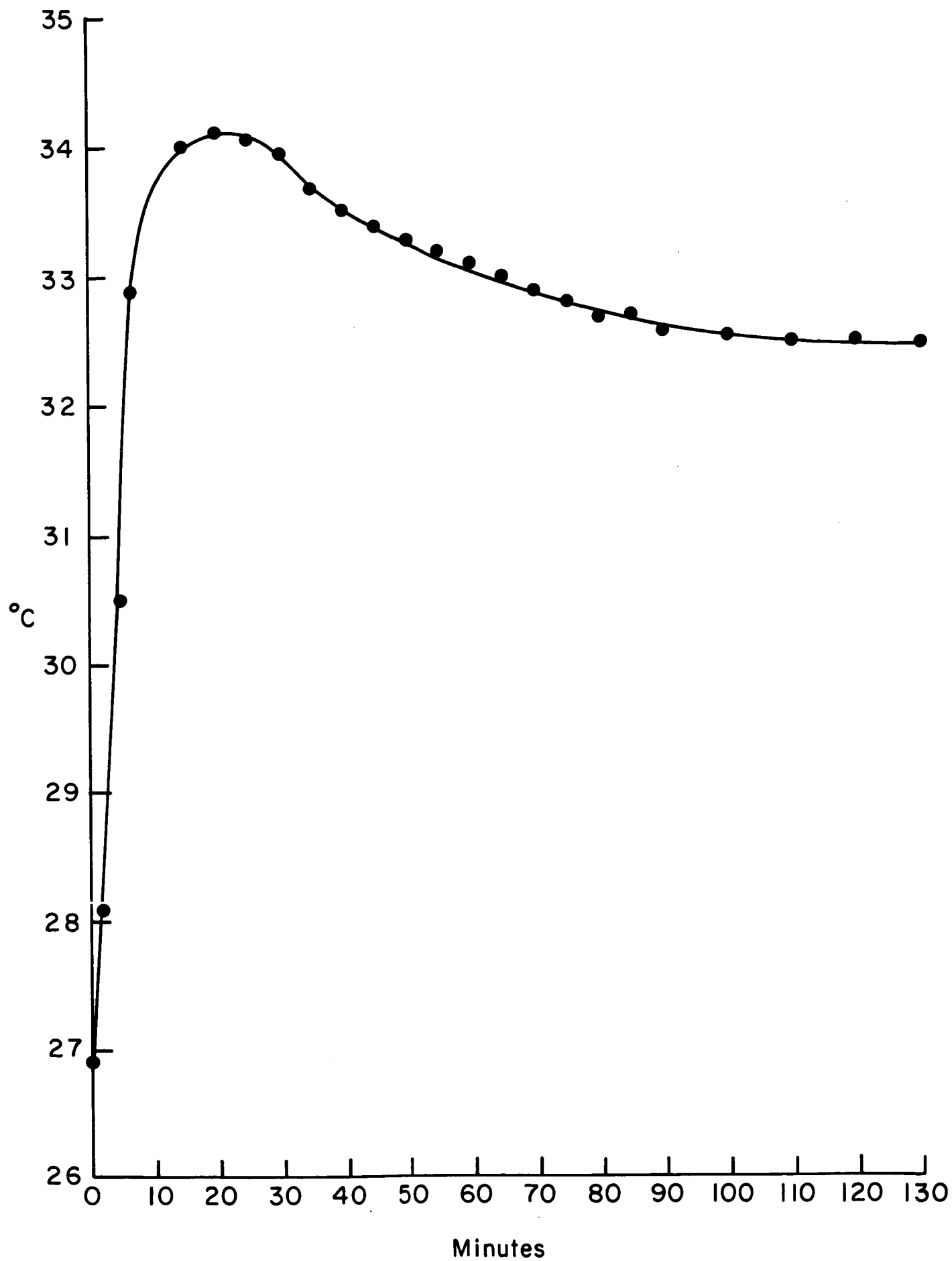
Minutes

FIG. 7 COOLING CURVE

VI. RESULTS

A) TYPICAL DISCHARGE CURVES

The rise in temperature of a 5 AH Nickel-Cadmium cell containing
7.9NKOH, which occurred when it was discharged at 1.5A in the adiabatic
calorimeter, is shown in Fig. 8. The corresponding changes in cell
voltage are shown in Fig. 9. Similar plots were made when the nickel-
cadmium cell 6.3N LiOH was discharged at the 1.5 amp. rate. These
results are shown in Figs. 10 and 11.

The results of the nickel-cadmium cell constructed, using didymium
hydroxide in the nickel electrode, are shown in Figs. 12 and 13. This
cell contained 7.9NKOH.

The thermal capacities of the cells utilized in the above mentioned
experiments were approximately the same, and varied from .077 Kcal/°C
to .079 Kcal/°C.

B) OPEN-CIRCUIT VOLTAGE DECAY OF THE Ni-Cd(KOH) and Ni-Cd(LiOH) CELLS

The open-circuit voltage decay of the Ni-Cd (KOH) cell and Ni-Cd
(LiOH) cell at 110°F (43.3°C) are shown in Figs. 15 and 16, respectively.
By extrapolation of these curves we obtained a reversible potential of
1.270V for the Ni-Cd(KOH) cell, and 1.293V for the Ni-Cd(LiOH) cell.
However, the closed circuit potential of the Ni-Cd cells in lithium
hydroxide electrolyte (6.3N) is not higher than cells with potassium
hydroxide electrolyte (7.9N). This is accounted for by the lesser con-
ductivity of the lithium hydroxide which we found to be 0.310 ohm^{-1} cm^{-1}
at room temperature, compared to 0.590 ohm^{-1} cm^{-1} for potassium hydroxide.

C) ENERGY BALANCE OF THE Ni-Cd CELL

The enthalpy change (ΔH) for the reaction taking place in an elec-
trochemical cell equals the work done on the cell, less the heat evolved
by the cell. This derives from the first law of thermodynamics, and is

true regardless of the thermodynamic reversibility of the process. It is also true when pressure-volume work is done at constant pressure. It is not valid when there is a change in pressure at constant volume; e.g., oxygen evolution in a sealed cell.

The energy balance can be represented by the equation:

$$\text{Electrical Energy} = \text{Chemical Energy} - \text{Heat Energy} \tag{1}$$

Similarly, for a steady state situation, the rate of increase of the enthalpy of the cell equals the rate at which work is being done on the cell, less the rate at which it is evolving heat, provided oxygen is not being evolved. The rate of a stoichiometric electrochemical reaction is fixed by the current. Knowing both the rate of the reaction and the rate of enthalpy increase, one can calculate the reaction ΔH on an equivalent or molar basis. In order to do this, however, two conditions must be met. First, due to the thermal lag of the system, the measurements must be based on a steady state condition; and, second, the reaction must be stoichiometric.

In practice, these conditions required (a) that ΔH values be calculated using slopes from only those parts of the time-temperature curve which were essentially straight lines; and (b) that the data used was taken over a time interval during which the cell reaction involved neither tetravalent nickel or oxygen gas evolution.

Since a ΔH computation must be based on a steady state, it is obvious that the particular time and temperature selected for the computation was more or less arbitrary. For the same reason, the corresponding voltage was also arbitrary, and thus introduced a second uncertainty in the determination. It was also true, however, that if a steady state prevailed, the voltage changed slowly with time, and the particular voltage

chosen did not materially influence the value of ΔH.

With the above limitations in mind, the ΔH of the cell reaction could be calculated as follows:

The rate at which work (electrical energy) is done on (or by) the cell equals I·E watts, where E is the voltage across the cell, and I is the current through it. The rate of heat generation by the cell is calculated by dividing the slope of the time-temperature graph by the thermal capacity of the cell (expressed in ^oC/watt-min.). The rate of the reaction is IF^{-1} equiv./sec., where F is the Faraday in amp. seconds equivalent^{-1}. The value of ΔH during discharge is therefore given by

$$\Delta H = \frac{\left[IE + \frac{m}{c} \right] F}{4.185 \times 10^3 \cdot I} \quad \text{Kcal equiv.}^{-1} \tag{2}$$

where m = slope of the time-temperature graph

c = thermal capacity of the cell

Using this equation, a value of 33.15 Kcal equiv.$^{-1}$ for the heat of reaction of the Ni-Cd (KOH) cell was calculated. This corresponded to a heat of formation of 162.1 Kcal mole^{-1} for the active material NiOOH*, where the asterisk stands for water of hydration or physiosorbed electrolyte. A similar calculation for the Ni-Cd (LiOH) cell gave 37.7 Kcal equiv.$^{-1}$ for the heat of reaction. This corresponds to a heat of formation of 157.55 Kcal mole^{-1} for the lithium nickel (III., IV.) oxide hydroxide. Enthalpy calculations for the didymium hydroxide cell gave results similar to the conventional KOH cell used in the tests.
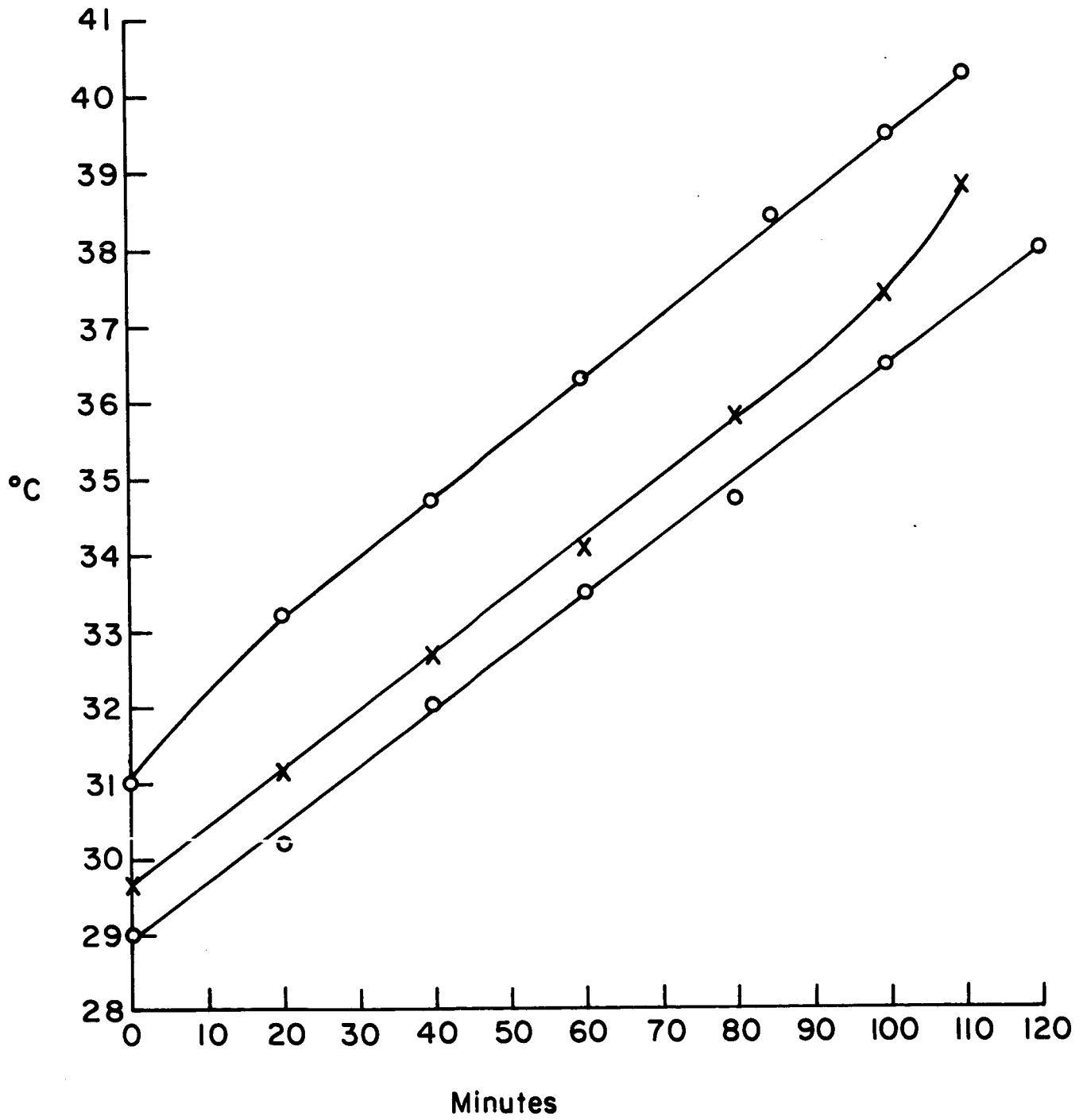
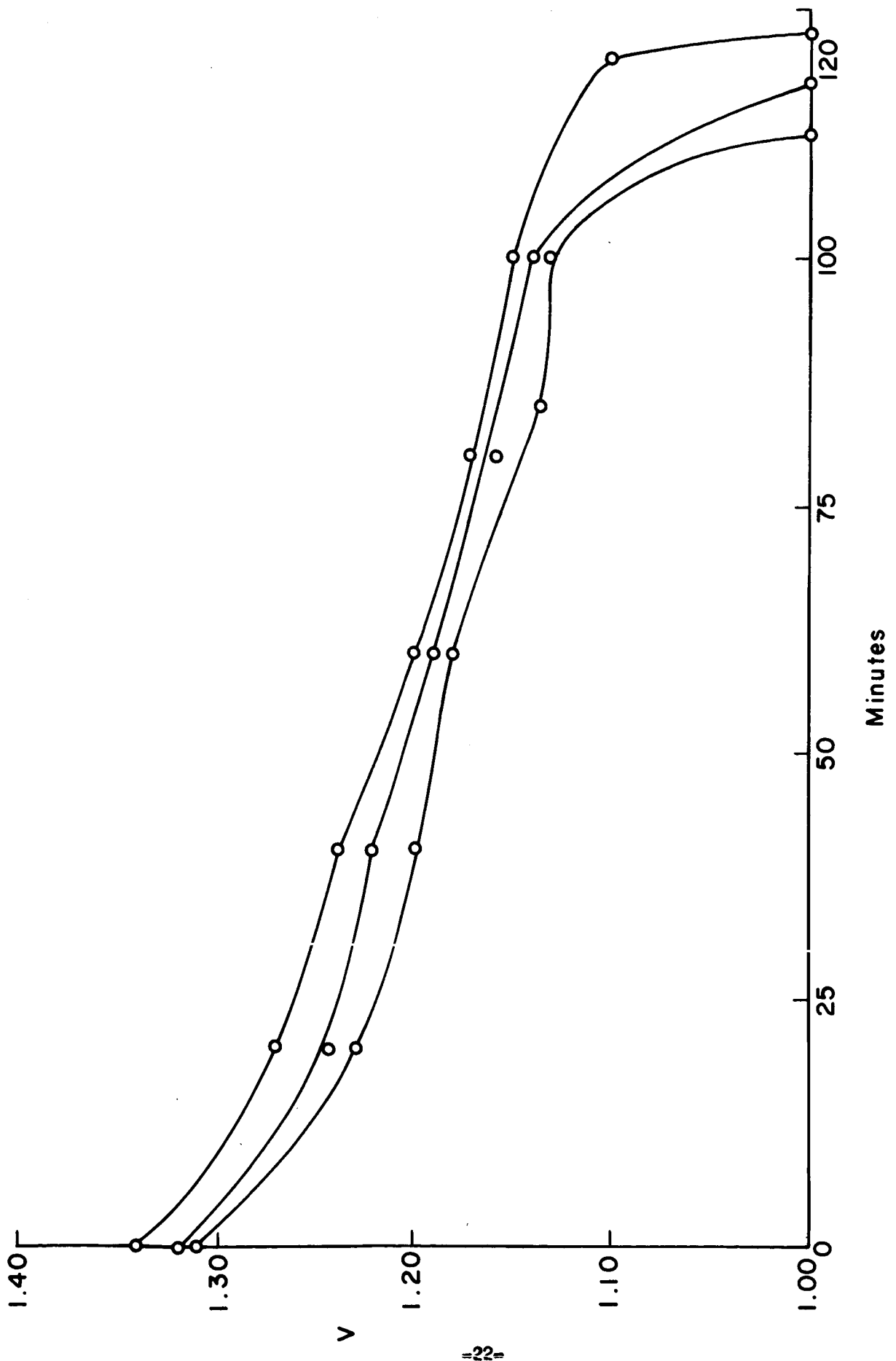FIG.8 HEAT PROFILE Ni—Cd (KOH) CELL

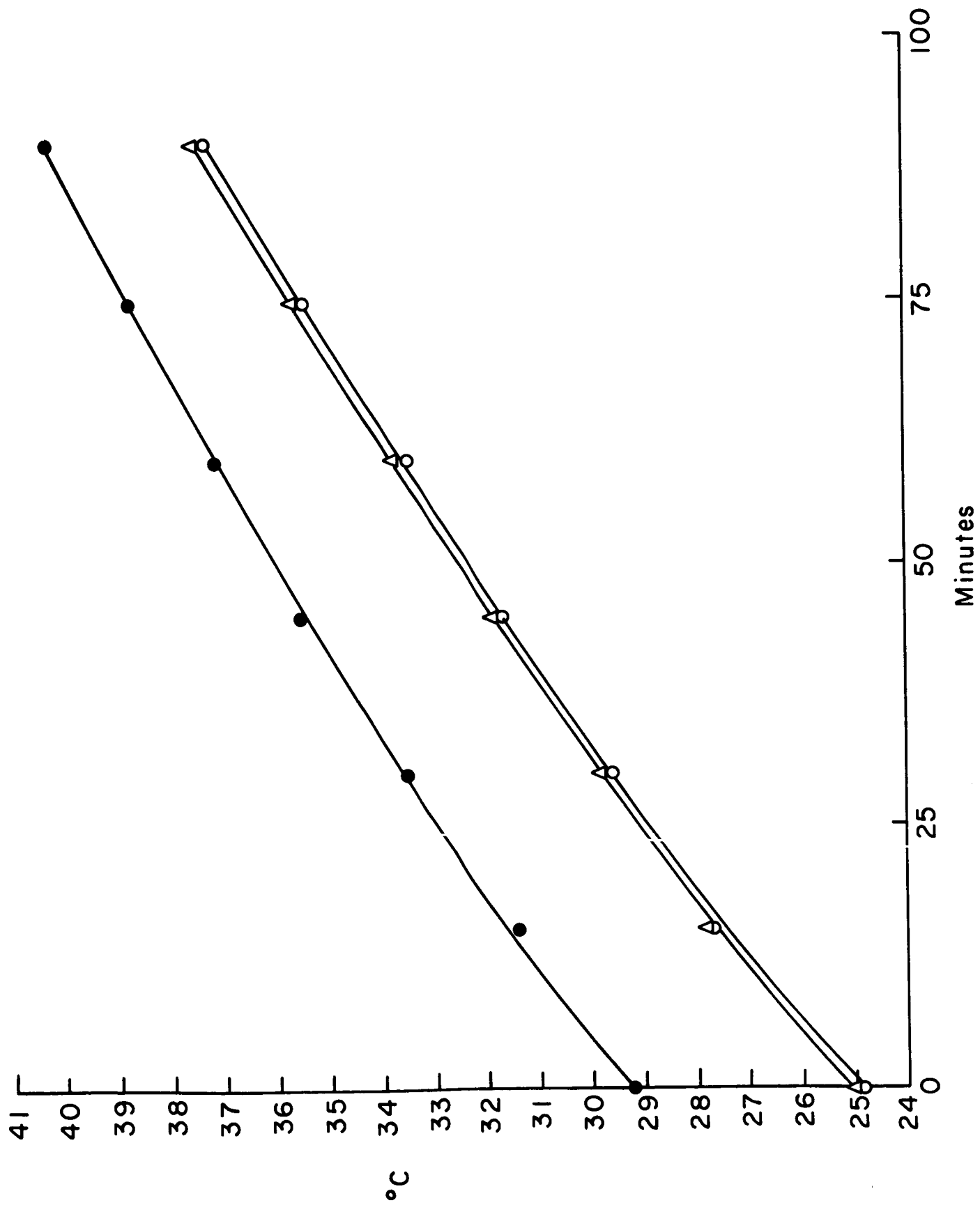FIG. 9. VOLTAGE PROFILE Ni – Cd (KOH) CELL

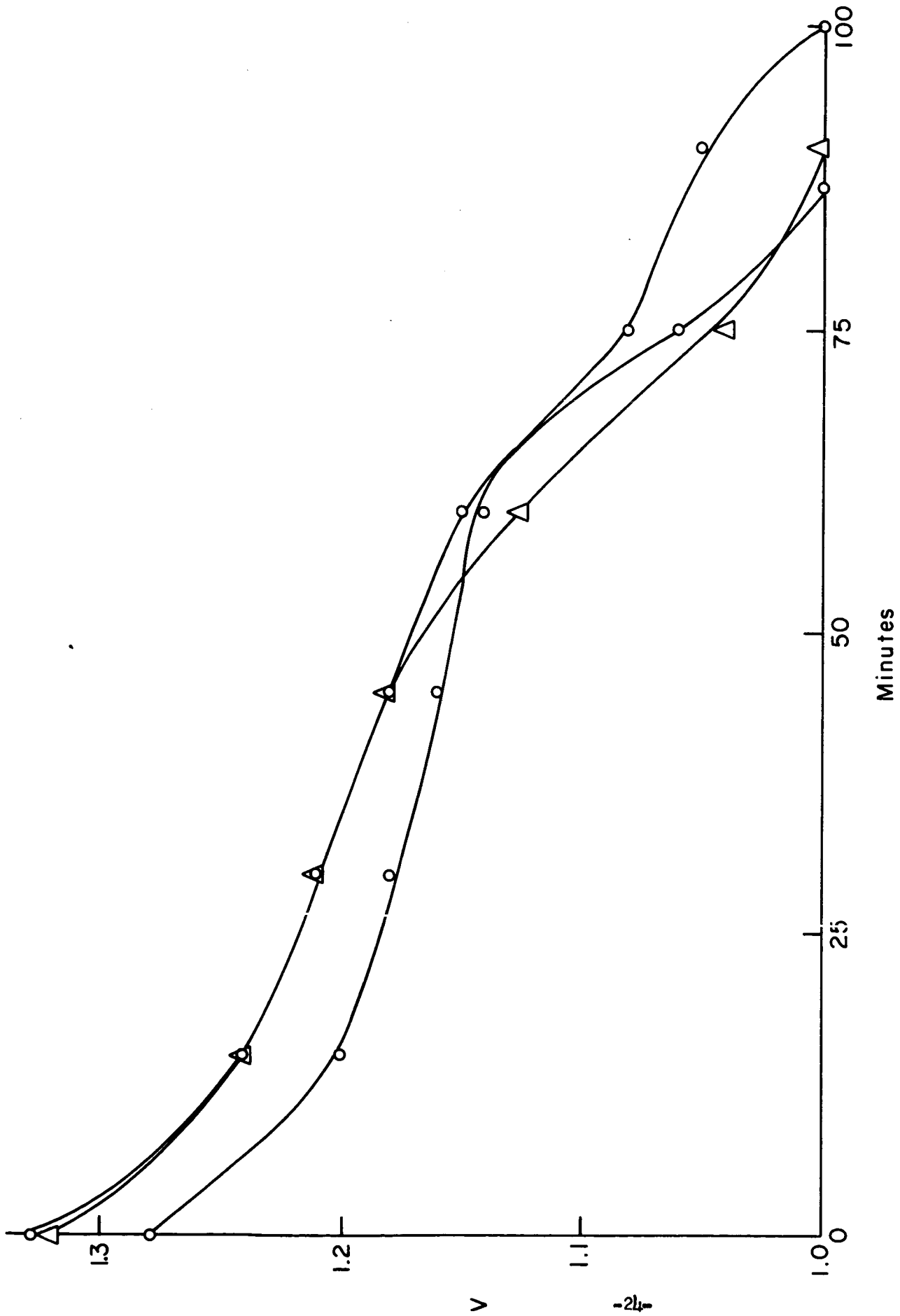FIG. 10. HEAT PROFILE Ni–Cd (LiOH) CELL
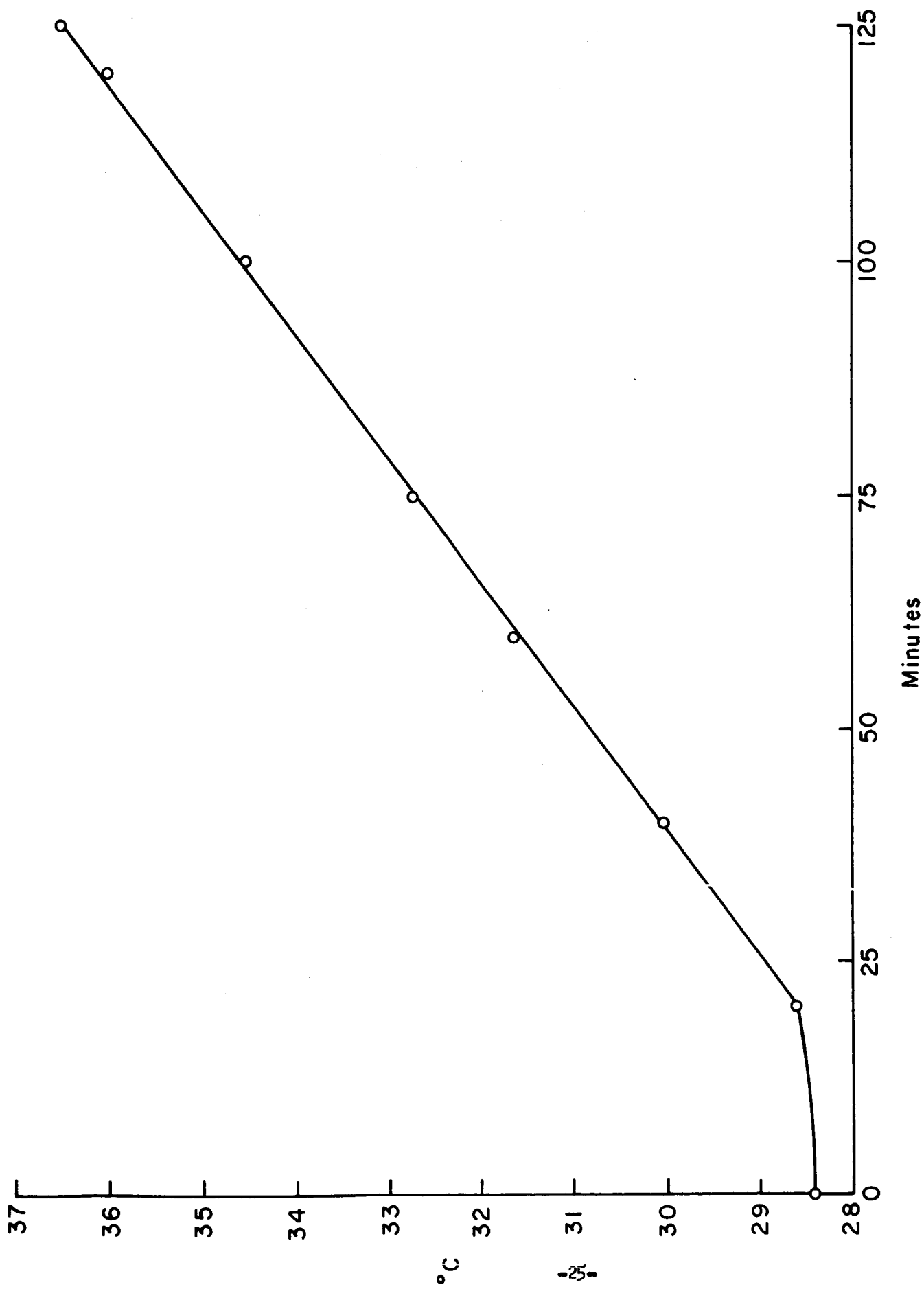
FIG. 11. VOLTAGE PROFILE Ni–Cd (LiOH) CELL

FIG. 12. HEAT PROFILE Ni – Cd (DIDYMIUM) CELL
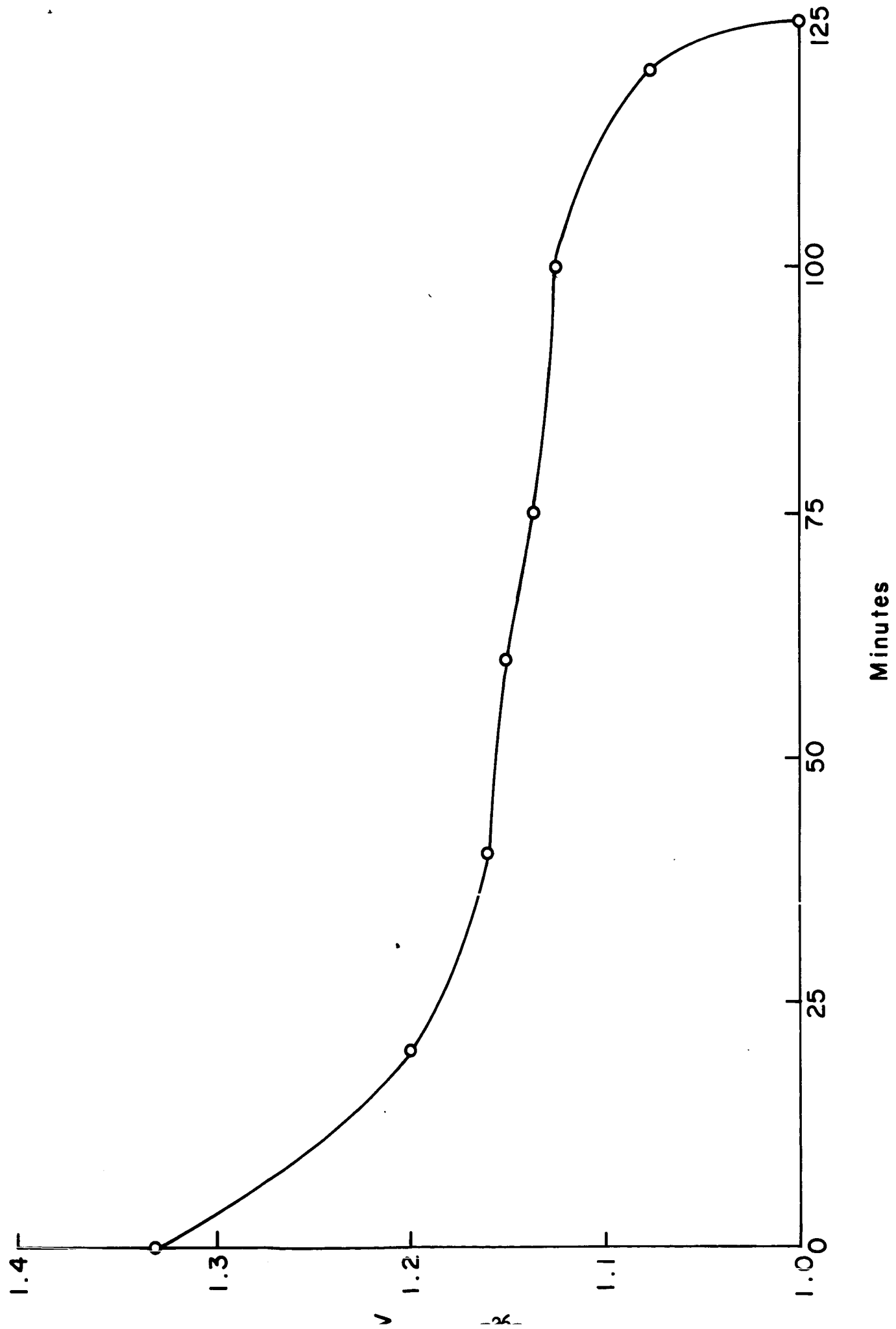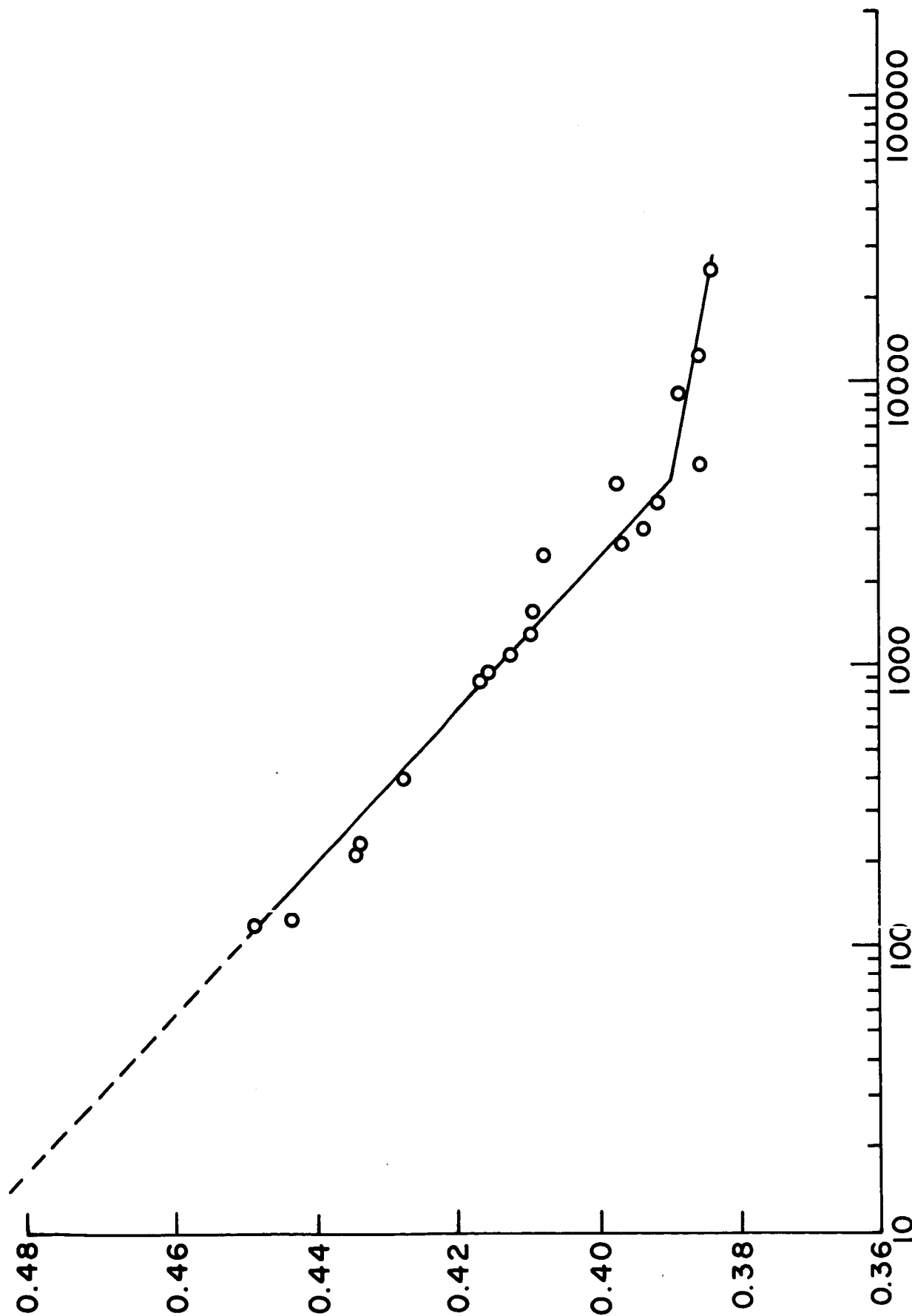
FIG. 13. VOLTAGE PROFILE Ni-Cd (DIDYMIUM) CELL

Minutes

-26-

FIG. 14. Effect of Temperature on the Potential
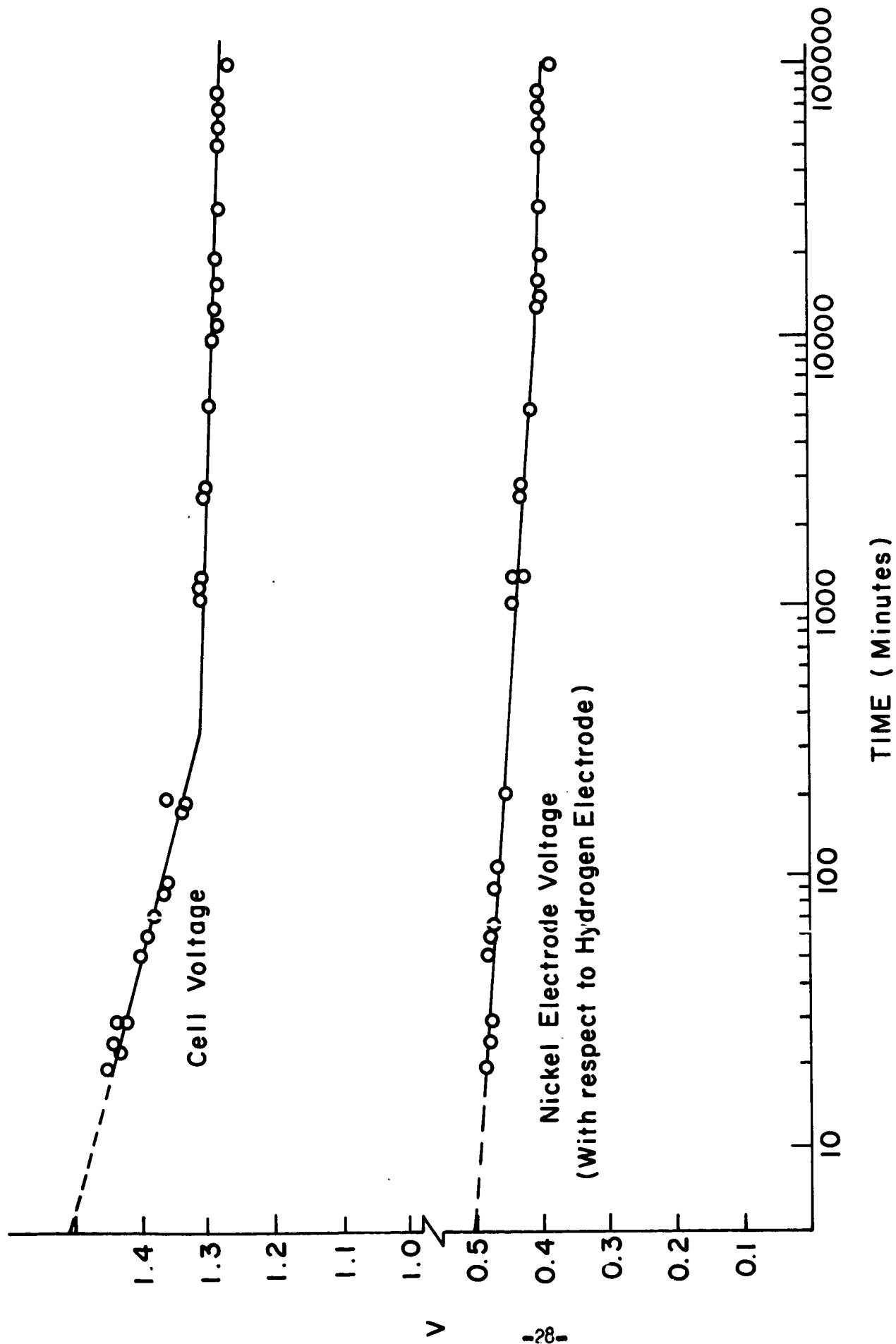of Nickel Electrodes

TIME (Minutes)

FIG. 15. VOLTAGES OF NICKEL CADMIUM CELLS
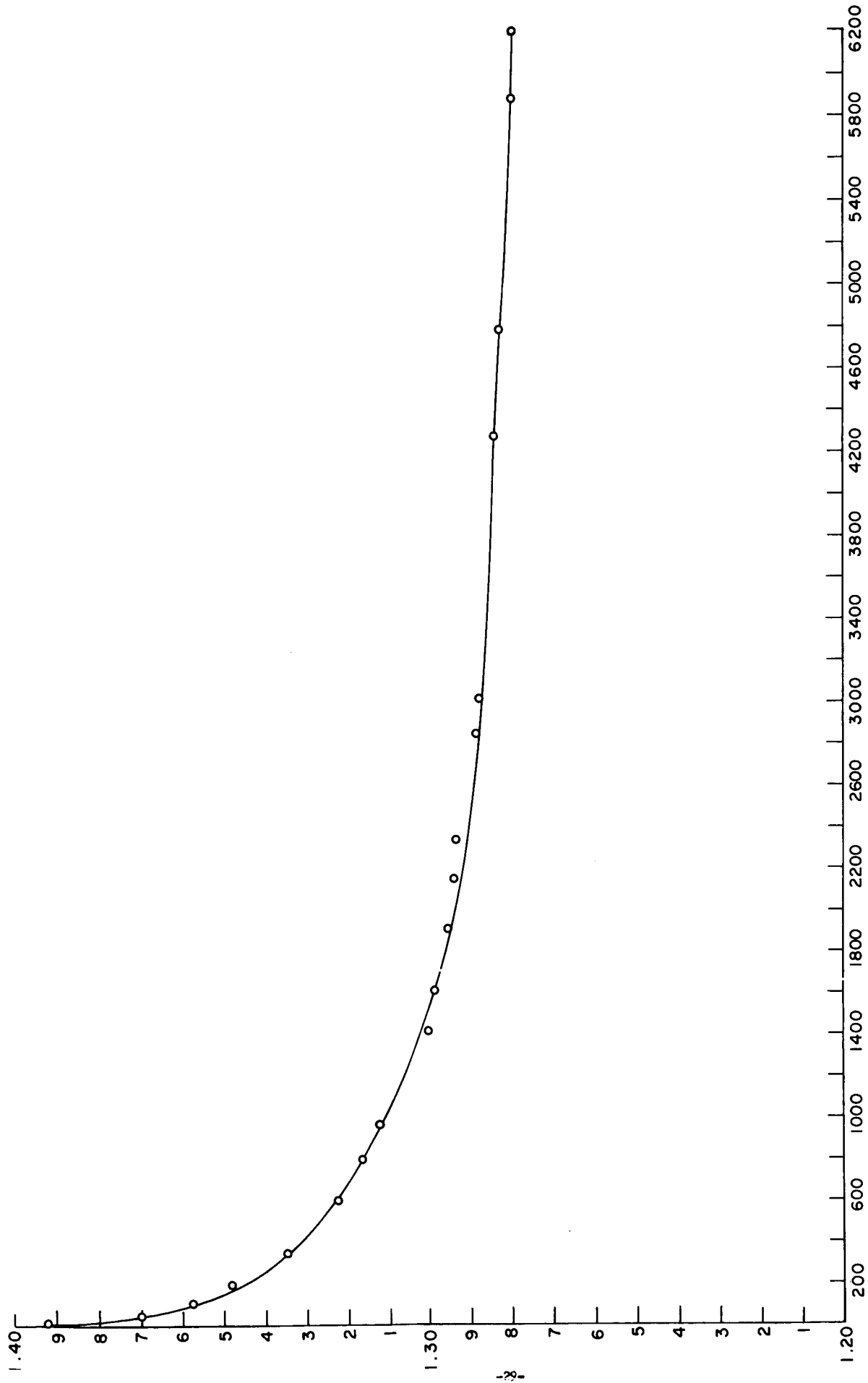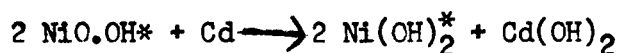AND OF NICKEL ELECTRODES STORED
AT 110°F (43.3°C)

FIGURE 16. VOLTAGE DECAY Ni-Cd (LiOH) CELL (43.3 °C)

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VII. DISCUSSION

The generally accepted reaction taking place when the nickel-cadmium cell is discharged is

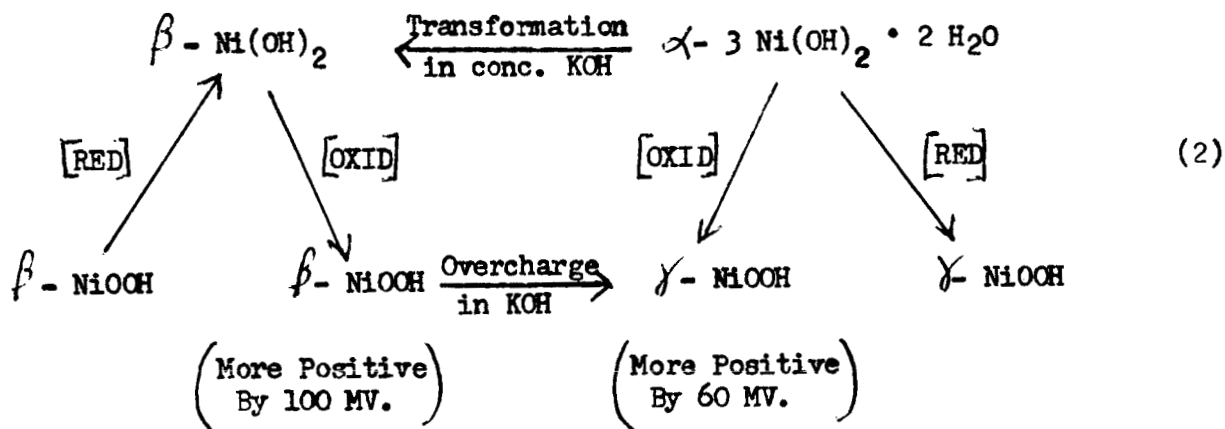$$2 \ NiO.OH* + Cd \longrightarrow 2 \ Ni(OH)_2^* + Cd(OH)_2$$

where the asterisks indicate hydration or solvation of NiOOH and Ni(OH)$_2$, respectively. Utilizing the heat of reaction measured, and the literature[21] values for the standard molar heats of formation of the reactants and products, one can calculate the heat of formation of NiOOH*. The literature values for ΔH_f in the order given above, are x, 0.0, -128.6 and -133.6 Kcal mole^{-1}. Using these values and the ΔH value found for the reaction (-66.30 Kcal/mole), the ΔH_f for NiOOH is 162.1 Kcal/mole. This value for the heat of formation of NiOOH is in agreement with the only value listed for a valence three hydroxide of nickel, Ni(OH)$_3$. A similar calculation for the Ni-Cd (LiOH) cell gave a value of 157.55 Kcal/mole for NiOOH*, where the ΔH of the reaction was 75.4 Kcal/mole. Again, the only literature value close to this value is the one for Ni(OH)$_3$.

In a series of papers and communications[9-13], Bode et al have found that the charge-discharge process on the nickel hydroxide electrode cannot be represented by a single equation (1) as proposed by Glemser and Einerhand[14],

$$Ni(OH)_2 + OH^- \longrightarrow \beta \ NiOOH + H_2O + e^- \tag{1}$$
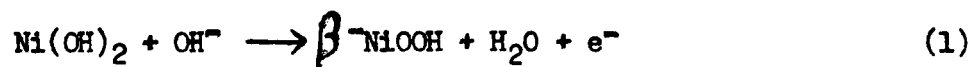
but that at least two reactions (2) can be formulated, with different starting materials and different end products. The oxidized phases of the β and γ nickel hydroxides occur in two "states", which differ in their energy contents, but their analyses and x-ray patterns do not

differ significantly.
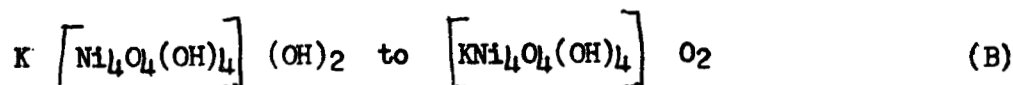
$$\beta - Ni(OH)_2 \xrightarrow[\text{in conc. KOH}]{\text{Transformation}} \alpha - 3 Ni(OH)_2 \cdot 2 H_2O \qquad (2)$$

$$[RED] \quad [OXID] \qquad [OXID] \quad [RED]$$

$$\beta - NiOOH \qquad \beta - NiOOH \xrightarrow[\text{in KOH}]{\text{Overcharge}} \gamma - NiOOH \qquad \gamma - NiOOH$$

$$\left(\begin{array}{c}\text{More Positive}\\ \text{By 100 MV.}\end{array}\right) \qquad \left(\begin{array}{c}\text{More Positive}\\ \text{By 60 MV.}\end{array}\right)$$

The γ-nickel hydroxide can be oxidized to the higher nickel hydroxides. Two compounds are thereby obtained. One of the compounds (A) which was prepared by Glemser and Einerhand had an oxidation value corresponding to $NiO_{1.5}$ and contained water of hydration.

$$\left[Ni_4O_4(OH)_4\right] \cdot 3 H_2O \qquad (A)$$

The other compound (B) was obtained by oxidation electrochemically in KOH as the electrolyte. It contained potassium and its oxidation level was higher than $NiO_{1.5}$. It can be characterized as potassium nickel (III., IV.) oxide hydroxide, or simply as potassium nickelate (III., IV.). This compound exhibits some phase latitude. It can be represented by the idealized limiting formulas

$$K\left[Ni_4O_4(OH)_4\right](OH)_2 \quad \text{to} \quad \left[KNi_4O_4(OH)_4\right]O_2 \qquad (B)$$

or

$$NiO_{1.63} \qquad \text{to} \qquad NiO_{1.87}$$

It is not known whether compound (A) exists in the battery, but the higher oxide (B), which contains potassium, has been demonstrated to

be present on extended overcharge by Feitknecht[1]; and Salkind and Bruins[4].

The potassium ion may be replaced by Ba^{+2}, Na^+, and Li^+, but the incorporation of Li^+ probably occurs in a different manner due to its ionic size. This leads us to believe that the higher heat of reaction found in lithium hydroxide electrolyte is due to a change in the amount of alkali metal ions in the nickel hydroxide lattice, and to a different degree of hydration.

VIII. CONCLUSIONS, WORK IN PROGRESS, AND RECOMMENDATION FOR FURTHER WORK

1)   The calorimeter constructed is suitable for the thermal evalua-
tion of electrochemical cells. However, since automatic cooling was not
included, it is not capable of quantitative data during those special
portions of charge cycles where the cells are endothermic, without fur-
ther modifications. This does not affect its ability to characterize
overall heats of reactions. The calorimeter was capable of detecting
a $0.04^{\circ}C$ temperature rise within the cell. With the specific mass of
the cells utilized, this corresponded to a heat lag of approximately
3.2 calories on initiation of a reaction.

2)   In checking out the calorimeter, a heat of reaction for the
nickel-cadmium cell in 31%(8N) KOH of 33.15 Kcal. equiv.$^{-1}$ was de-
termined. Utilizing this value, the heat of formation of NiOOH was
calculated to be 162.1 Kcal mole^{-1}. This value is in close agreement
with other recent values of 32.9 Kcal/equiv.[7], and 33.0 Kcal/equiv.[8],
which were found calorimetrically, and a value of 32.0 Kcal/equiv.[4]
which was obtained from EMF measurements.

3)   The heat of reaction of the Ni-Cd cell containing 12.7% (6.3N)
LiOH electrolyte was found to be 37.7 Kcal/equiv. If it is assumed that
this corresponds to a change of heat of formation of the Ni- electrode
alone, and that this change is mainly concerned with the charge state,
then the heat of formation of the NiOOH·LiOH compound would be 157.55
Kcal/mole. The exact nature of how the lithium is incorporated in the
nickel hydroxide lattice is not known, but if all the potassium were
replaced by lithium, then the charged products should be different due
to the different size of these ions.

4)   Cells with nickel electrodes fabricated so as to have some co-precipitated didymium hydroxide gave the same results with respect to electrochemical capacity and heat of reaction, as the conventional Ni-electrode (KOH) cells used in our tests.

5)   The accuracy of a determination of the ΔH of an electrochemical reaction, by means of calorimetry, is dependent on the absence of secondary reactions, both chemical and electrochemical. These types of secondary reactions occur in the Ni-Cd cell. This sensitivity of the measurement to side reactions points to the value of calorimetry in elucidating the nature, rate, and extent of such reactions.

6)   WORK IN PROGRESS
      A)   Ni-Cd cells are now being cycled in cesium and Rubidium hydroxides.

      B)   Ni-electrodes cycled in LiOH are being further investigated by x-ray, TGA and DTA techniques.

7)   RECOMMENDATION FOR FURTHER WORK
      A)   Since it is apparent that the electrolyte affects the heat of reaction of the Ni-Cd cell, to elucidate the mechanism cells should be cycled in electrolyte which cannot hydrate the nickel hydroxide electrode.

      B)   With the existing calorimeter it would be possible to obtain entropy measurements on cells with various electrolytes.

      C)   The techniques discussed in this report could be utilized to determine the heat balance data on sealed cells in overcharge or reversal.

      D)   The equipment described here could be very fruitfully utilized to determine the effects of electrolyte type and conc. in Ag-Zn and Ag-Cd systems, or in other systems.

E) The technique described here, with modifications in the calorim-eter, could be used to determine certain thermodynamic properties of single electrode reactions.

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