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SIXTH PROGRESS REPORT

FOR

RESEARCH INTO FUNDAMENTAL PHENOMENA ASSOCIATED WITH SPACECRAFT
ELECTROCHEMICAL DEVICES — CALORIMETRY OF NICKEL-CADMIUM
CELLS

October 1, 1967 — December 31, 1967

Contract No. NAS 5 — 10105

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ABSTRACT

The objectives of this project are to train electrochemists in the area of battery research and to collect electrochemical and thermodynamic data of value to projects being conducted at the Goddard Space Flight Center.

The greater part of the laboratory work completed during the reporting period consisted of improvements and modifications to the experimental apparatus. The modifications can be broken down into two groups: electrical modifications to the supporting electronic components; and mechanical modifications to the calorimeter itself.

In addition to these changes in the experimental setup an extensive literature search was completed. The literature search consisted of 1) an attempt to obtain the best recorded values for the heats of formation of the species involved in the proposed charge reaction so that the best calculation of the enthalpy change could be made; 2) a complete bibliography on the thermochemistry of nickel-cadmium cells.

Also presented is a more detailed discussion of the enthalpy change for the cell reaction from the thermodynamic viewpoint.

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Research Into Fundamental Phenomena Associated With
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I.   INTRODUCTION

The objectives of this project are

1) to train electrochemists in the area of battery research

and

2) to collect electrochemical and thermodynamic data of value to projects being conducted at the Goddard Space Flight Center.

The greater part of the experimental work conducted during this reporting period involved modifications and improvements in the calorimeter and the electrical system. The previous work had suggested the need for several changes. It was felt that the installation of a more versatile cycling device would be desirable. Previously the cell voltage, the cell current, the third electrode signal, and the cell pressure were individually recorded. These recorders were replaced with a multi-point recorder.

In the original design of the internal portion of the calorimeter the cell support and positioning device neither permanently supported the cell nor restrained it sufficiently against bulging caused by internal pressure. For precise measurements the cell must be permanently located with respect to the two thermopiles. Cell bulging must be avoided to prevent plate separation.

The enthalpy change measured during charge and discharge is considered to be significant with respect to interpreting deviations from normal cell operation as discussed below. In order to make an accurate calculation for the standard condition the best values for the heats of formation of the cell reactants and products were collected. These

heat values were used to calculate a "standard" heat of reaction
for the nickel-cadmium cell reaction.

Further consideration has been given to the method of calcula-
tion of the enthalpy change for the reaction going on in the nickel-
cadmium cell. The assumption made to this point has been that all the
work done by the cell on the surroundings is electrical work. The
inclusion of other types of work is necessary when the conditions deviate
from the rigidly defined conditions accepted in our previous analysis.
The more complete analysis will give a better representation of the
situation in the sealed cell.

Finally, in connection with the literature search for the best
value for the enthalpy change accompanying the cell reaction a number
of pertinent references were assembled. These are included in a
Bibliography on Calorimetry of the Nickel-Cadmium Cell.

II. MODIFICATIONS IN THE SYSTEM

A. Electrical Modifications

The major change in the electrical system was the incorporation of a new cycling device. The original cycling device had only two channels and lacked versatility with respect to setting for different modes of charge and discharge. A new device was designed by S. Tiller and fabricated in-house at the Goddard Space Flight Center. The new device provides for programming of cell voltage, cell charge current, and cell discharge current in ten different steps for one cycle. The new, more compact instrument has the advantage of being able to control charge and discharge of a cell at any given time in a cycle.

In the original system the precision voltage measurements were made with a K-3 potentiometer. This has been replaced with a Digital Voltmeter (Hewlett-Packard Model 3440A). This instrument can be switched to give precise readings on cell voltage, third electrode voltage and pressure transducer output. It adds one significant figure to these measurements.

A further improvement was to replace four separate strip chart recorders with a single multi-point recorder. The L & N Speedomax H is a twelve-point instrument and hastens the analysis of the data by removing the need for reading the four separate charts each with a different chart speed axis.

To prevent excessive build-up of pressure in the cell a safety device was installed. Since nickel-cadmium cells generate oxygen on charging, it is very desirable to have this provision. The new pressure

cutoff can be pre-set to stop the charge or discharge cycle when the pressure in the cell exceeds 25, 35, or 50 psia. The pressure cutoff senses the voltage developed by the pressure transducer on the cell. When this voltage exceeds the pre-set value, the cycling unit places the cell on open circuit.

B. Mechanical Modifications

The objectives of the mechanical modifications to the calorimeter were to provide a better positioning arrangement for the cell and also the means of restraining the cell's walls during pressure build-up within the cell. A cylindrical internal sleeve for the calorimeter was constructed out of stainless steel as shown in figure 1. Two stainless steel strips (support brackets) with a series of sixteen threaded holes, vertically spaced, were welded, 180° apart, on the inside of the sleeve, as shown in figure 2. Teflon capped, stainless steel feet were threaded into the vertically arranged holes. These feet, adjusted externally with a screwdriver, provide rigid supports for the nickel-cadmium cell. By positioning the feet on opposite sides of the cell, the cell is rigidly held and restrained from gas induced bulging. The two lowest feet on the bracket are used to hold a cell support which also serves as a support for the calibration heater. The calibration heater was constructed from fourteen inches of #18 manganin resistance wire wound in a spiral around a thin, flat section of fiber board. The fiber board was positioned in the calorimeter sleeve as shown in figure 1 and the cell rested in an indentation

calorimeter wall
sleve
support bracket

foot

lower
support

20 AH
Ni-Cd

LOWER SUPPORT

collar

teflon tip

tightining slot
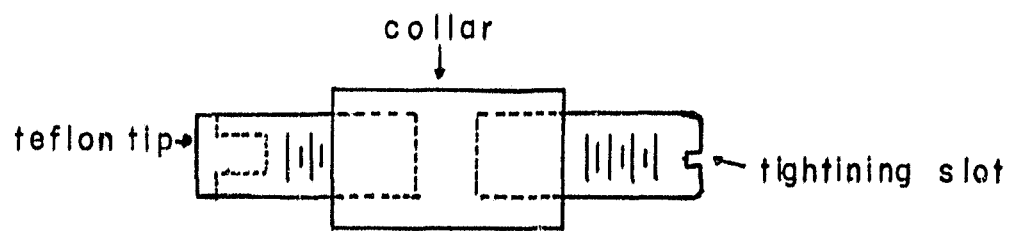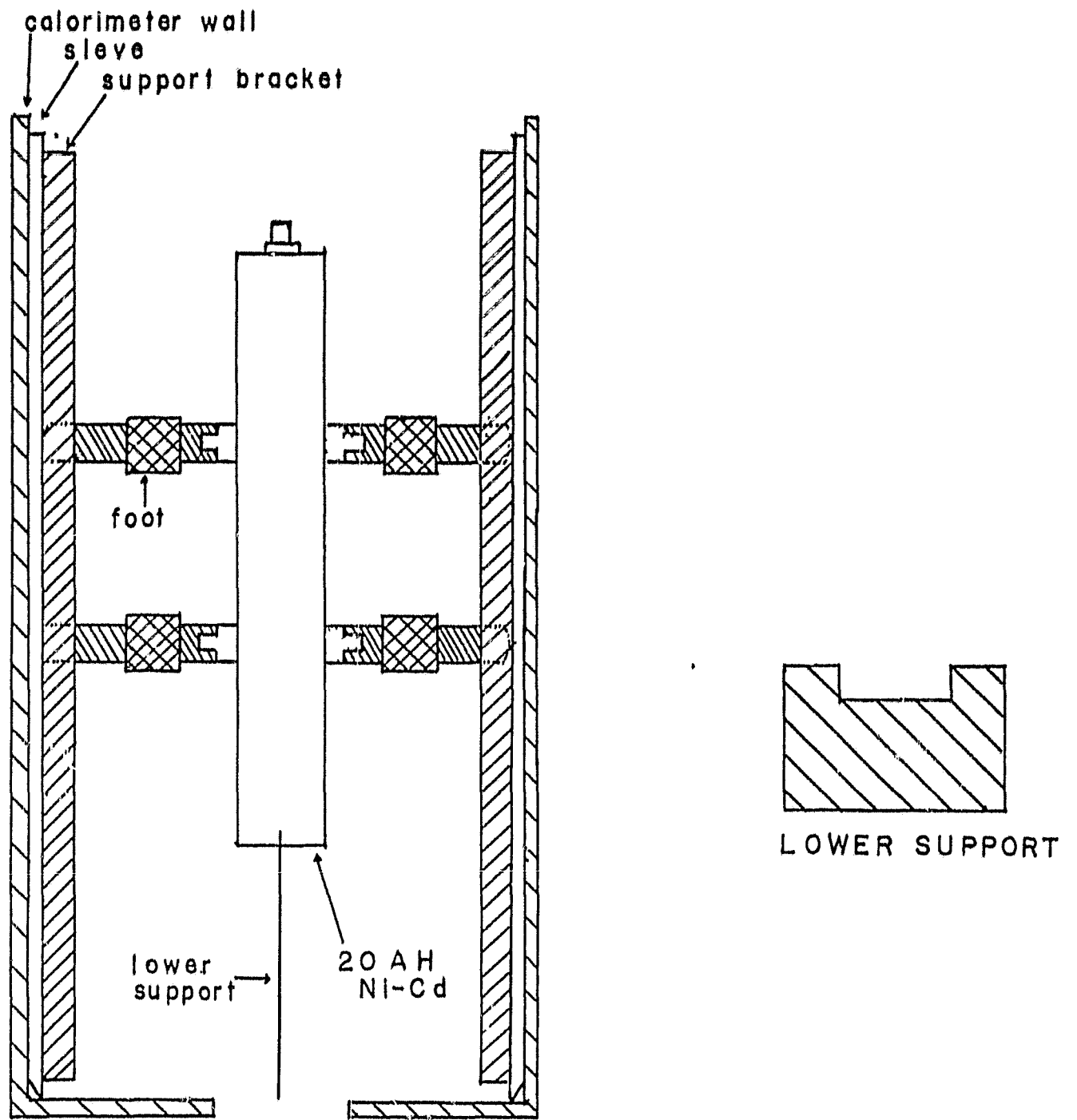
DETAIL OF FOOT

Figure 1. Sideview of Cell Support Brackets
and Calorimeter Sleeve

CELL SUPPORT BRACKET

TOP VIEW

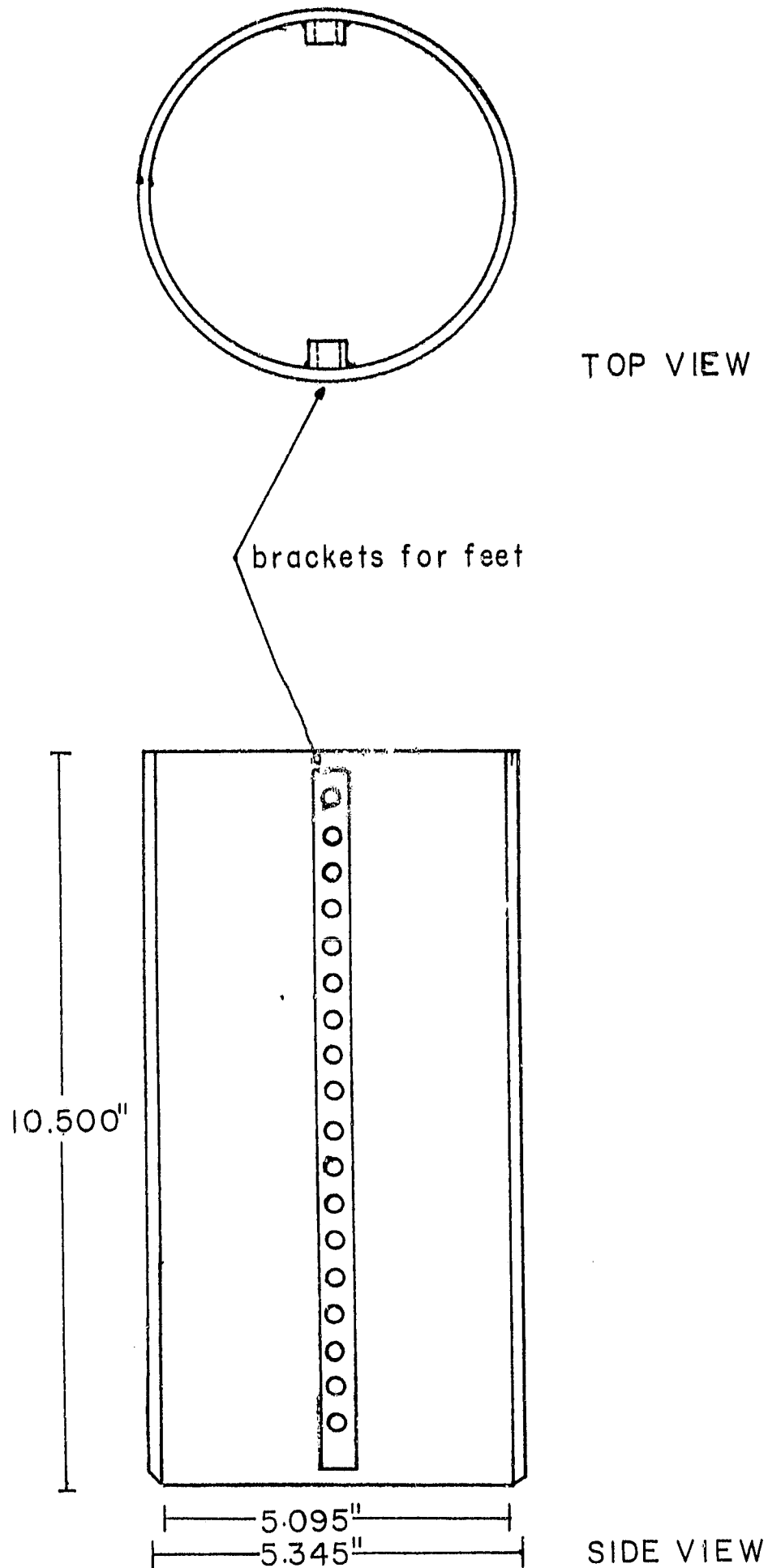brackets for feet

10.500"

5·095"

5.345"

SIDE VIEW

Figure 2.   Topview of Calorimeter Sleeve and
Sideview of Cell Support Brackets

in the board.

This new calorimeter sleeve and cell positioning arrangement not only gives improved support for the cell but should result in more reproducible data as the exact position of the cell within the calorimeter can now be precisely determined.

III SELECTED VALUES FOR THE HEATS OF FORMATION

The chemical reaction occurring in a nickel-cadmium cell during charging may be written

$$2 \ Ni(OH)_2 + Cd(OH)_2 = 2 \ Ni(OH)_3 + Cd \qquad (1)$$
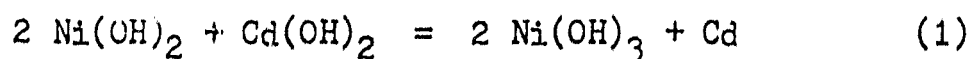
It is important in the interpretation of our data to have the best value for the heat of this reaction. The calculation of this heat can in turn only be made from the best values for the heats of formation of the reactants and products. For this reason the literature was examined to ascertain the best values for these thermodynamic quantities.

The first source of tabulated data consulted was the National Bureau of Standards Circular 500 (1). Table I gives the selected values reported in Circular 500 which, at the time of publication, represented the best experimentally determined values. Due to changes in experimental techniques, purity of materials, and atomic weight scale the data reported in Circular 500 **are being** revised. The data revised to date are reported in N. B. S. Technical note 270-3 (2). In the new publication the quantities have been selected from the original literature, corrected for standard conditions, evaluated, and then certified as the best available

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Table 1

Compound	State	$\Delta H^o_{f\ 298}$ Kcal/mole	ΔG^o_f Kcal/mole	S^o_{298} Kcal/deg.mole
Ni(OH)$_2$	c	-128.6 *(5,6)	-108.3 (7,8)	19
Ni(OH)$_3$	c	-162.7 (5)		
Cd(OH)$_2$	c	-133.26 (4,5)	-112.46 (3)	22.8

Table 2

CdO	c	0.0	0.0	13.1
CdO	c	-61.7	-54.6	23
Cd(OH)$_2$	c	-134.0	-113.2	
Cd(OH)$_2$	aq	-128.08	-93.73	-22.6

Table 3

Ni(OH)$_2$	c	-126.6	-106.9	21
Ni(OH)$_2$	aq	-122.8	-86.1	-35.9
Ni(OH)$_3$	c	-160		

* Reference number.

Selected Values of Chemical Thermodynamic Properties

experimentally determined values for $\Delta H^o_{f\ 298}$, $\Delta G^o_{f\ 298}$, and ΔS^o_{298}. The data reported in Table II were taken from N. B. S. Technical Note 270-3. Table III gives data for $Ni(OH)_2$ and $Ni(OH)_3$ received in private communication (9).

Using equation (1) above and the heats of formation for the compounds in the crystalline state given in Tables II and III the heat for the charging reaction was calculated as 67.2 Kcal/mole or 33.6 Kcal/equiv.

IV. ENTHALPY CHANGE DURING CHARGE AND DISCHARGE

The enthalpy change during the reaction, by definition is,

$$\Delta H = \Delta E + \Delta PV$$

In our tabulations of the data we have calculated ΔH at that part of the cycle where there is no change of pressure and for the cell of constant volume

$$\Delta PV = 0$$

and

$$\Delta H = \Delta E$$

ΔE by definition is

$$\Delta E = q - w$$

where q is the heat absorbed by the system, and w is the work done by the system on the surroundings. Only electrical work, $w_{electrical}$, has been considered here. Therefore

$$\Delta H = q - w_{electrical}$$

It is always recognized that the complete relationship for a constant volume process is

$$\Delta H = q - w + V\Delta P$$

in which w is all the work done by the system.

During certain parts of the cycle, such as overcharge, the simple relationship does not hold. At such points, the total work is

$$w = w_{electrical} + w_{electrolysis} + w_{I^2R} + w_{pressure-volume}$$

Here, $w_{electrical}$ is the work done in charging the cell (equation (1) on page 7.); $w_{electrolysis}$ is the work done in producing oxygen by electrolysis; w_{I^2R} is the work done in Joulian heating; and $w_{pressure-volume}$ is the work done in developing the oxygen pressure within the cell.

Thus, the total enthalpy for the system becomes

$$\Delta H = q - (w_{electrical} + w_{electrolysis} + w_{I^2R} + w_{pressure-volume}) + V\Delta P$$

Because part of the electrical work goes into the electrolysis of the alkaline solution, ΔH of the system is no longer equal to ΔH for the nickel-cadmium reaction as given in equation 1 on page 7. The complicating item is the energy expended in the production of oxygen on charging as well as any other side reactions not defined.

It is intended to evaluate this part of the reaction so that a better understanding of the significance of the calculated ΔH's may be achieved.

V. BIBLIOGRAPHY ON THERMOCHEMISTRY OF NICKEL-CADMIUM CELLS

The following bibliography is a compilation of selected references that deal with nickel-cadmium cells and specifically with thermal effects associated with the operation of these cells. These references were searched to establish the best value for the enthalpy of reaction.

1. G. Arcand.
    Contract JPL 951887. 2nd Quarterly report.
    The Reactions Pertaining to Zn-Ag and Cd-Ag Batteries. Electrochemical preparation of tagged precipitates of Zn(II) and Cd(II).

2. H. T. Barnes.
    Phil Trans (London) Series A, 199, 152 (1902).
    Dr. H. T. Barnes on The Capacity for Heat of Water.
    Gives general theory of continuous flow Calorimeter and method of construction.

3. P. Bauer.
    Electrochem. Technol. 3, 43 (1965).
    Pressure Characteristics of Sealed Ni-Cd Cells.
    Build-up of excessive pressure in sealed cells was investigated using balanced hydraulic pressure technique and low rate overcharge methods. High pressure related to appearance of voltages greater than 1.50 V and open circuit stand time.

4. T. R. Beck and F. S. Kemp.
    NASA Contract NAS 1-3800.
    Heat Generation in Lunar Orbiter Battery.
    Used 12 AH NiCd, measured rate and amount of heat generation.

5. A. Brenner and S. L. Catey.
    J. Electrochem. Soc. 111, 1225 (1964).
    Electrochemical Calorimetry, IV. Measurement of the Reverse Heat Effect Attendant Passage of Electric Current Across a Liquid Junction.
    HCl-KCl, Measured total heat by measuring area under heat profile curve; used large U tube as calorimeter.

6. P. F. Bruins, S. M. Caulder, A. J. Salkind.
    Contract NGR-33-006-015.
    Calorimetric Study of the Thermodynamic Properties of Ni-Cd Cells.
    Used adaibatic calorimeter. ΔH of reaction changes with electrolyte, not independent of the system.
    ΔH reaction 33.15 Kcal/equiv
    ΔH reaction of Ni-Cd(LiOH) cell 37.7 Kcal/equiv
    ΔH formation NiOOH·LiOH 157.55.

7. E. Colston.
   GSFC Report #X-716-67-610.
   Internal Temperatures and Gassing Characteristics of a Ni-Cd Cell.
   Construction of a Ni-Cd with internal thermocouples. Discusses
   characteristics of reverse charge to negative terminal voltage.

8. J. C. Duddy and A. J. Salkind.
   J. Electrochem. Soc. 108, 717 (1961).
   High Energy to Weight Ratio Ni-Cd Cells.
   Constructed a 40 Watt-hr/Kgm cell. Active and conductive
   materials are dispersed in a microporous plastic structure.

9. M. I. Gillibrand and B. L. Wilde.
   Electrochim. Acta. 9, 401 (1964).
   Thermodynamic Properties of Electrochemical Storage Cells.
   Used an adiabatic calorimeter, found it difficult to obtain
   equilibrium conditions.
   Heat content change 32.9 $Kcal/F^{o}$
   Free energy change 30.1 $Kcal/F^{o}$

10. F. G. Keyes et al.
    J. Am. Chem. Soc. 44, 708 (1922).
    A Continuous Flow Calorimeter, and the Determination of the Heat
    of Neutralization of a Solution of HCl by one of NaOH.
    Gives design principles of calorimeter, the method has less than
    0.1% error by the least squares method.

11. F. P. Kober.
    J. Electrochem. Soc. 112, 1064 (1965).
    Analysis of the Charge-Discharge Characteristics of NiO Electrode
    by Infrared Spectroscopy.
    Discharge state is $Ni(OH)_2$ while charge is accompanied by forma-
    tion of a hydrogen bonded structure. During discharge hydrogen
    bonds are continuously broken reforming $Ni(OH)_2$.

12. F. P. Kober.
    J. Electrochem. Soc. 114, 3, 215 (1967).
    Infrared Spectroscopic Investigation of Charged $Ni(OH)_2$ Electrodes.
    Gives data on peaks of Ni electrode with charge state and time.
    Intensity of band due to hydrogen bonding, charging reaction gives
    rise to formation of active oxygen sites.

13. E. Lifshin, J. Weininger.
    Electrochem. Technol. 5, 5 (1967).
    Electron Microbeam Probe Analysis of Ni-Cd Battery Plates.
    Gives concentration of Cd vs charge and discharge states.

14. W. H. Metzger, M. Weinreb and J. M. Sherfey.
    Goddard Report #1-650-62-15.
    Heat Effects of Ni-Cd "F" Cells.
    Gives temperature vs time for charge, discharge and open circuit,
    calculated ΔH values range from 31.8 to 33.2.

15. W. H. Metzger, Jr., and J. M. Sherfey.
Electrochem. Technol. 2, 285 (1964).
Electrochemical Calorimetery III. Thermal Effects of Ni-Cd Batteries.
ΔH of reaction 60.25 Kcal/mole.

16. Ritterman et al.
Contract NAS 3-7620.
Investigation of Battery Active Ni Oxides.
Investigated battery plates under different conditions by X-ray diffraction, chemical analysis and spectroscopy, discuss presence of γ-NiOOH in overcharge.

17. K. Sizemore.
GSFC Report #x-716-66-200.
Use of the Adsorption Hydrogen Electrode and the Oxygen Fuel Cell Electrode in Ni-Cd Cells.
Two types of auxillary electrodes investigated. Hydrogen electrode good for charge control due to linear response, and stability in KOH. Fuel cell electrode a factor of 20 better for recombination but too sensitive to O_2 for charge control.

18. K. Sizemore and T. Hennigan.
Report X-716-66-200.
Auxillary Electrode Instrumentation for Ni-Cd Cells.
Third electrode used as charge control in battery pack cycling.

19. J. M. Sherfey and A. Brenner.
J. Electrochem. Soc. 105, 665 (1958).
Electrochemical Calorimetery.
Used a Dewar flask as an adiabatic calorimeter.

20. J. M. Sherfey.
J. Electrochem. Soc. 110, 213 (1963).
Calorimetric Determination of Half Cell Entropy Changes.
Used a 2 compartment Dewar flask, difference between the two gave reversible heat.

21. A. J. Salkind and J. C. Duddy.
J. Electrochem. Soc. 101, 360 (1962).
Thermal Runaway Conditions in Ni-Cd Cells. Performance Characteristics of a Sealed Light Weight Cell.
Gave discharge and overcharge characteristics, gassing can be avoided by proper charge control.

22. A. J. Salkind and P. F. Bruins.
J. Electrochem. Soc. 109, 356 (1962).
Ni-Cd Cells I. Thermodynamics and X-ray Studies.
Measured voltage decay between -18° and 52°. Designed special cell to fit X-ray diffractometer. ΔH_{rx} -64 Kcal/gm-mole.

23. D. T. Turner.
    Electrochem. Technol. $\underline{2}$, 313 (1964).
    The Effect of State of Charge of the Cd Electrode on Oxygen
    Recombination in Sealed Ni-Cd Cells.
    The rate of O_2 recombination on overcharge is directly proportional
    to the amount of Cd^0 on the negative plate, i.e., the state of
    charge of the Cd electrode.

24. L. Wilson.
    Report TG-942.
    Characteristics of Hermetically Sealed Ni-Cd Batteries.
    Summarizes basic thermodynamics, electrochemistry and internal
    energy losses of sattelite Ni-Cd cells.

25. L. Wilson and S. Voltz.
    J. Chem. Eng. Data $\underline{8}$, 444 (1963).
    A Calorimetric Study of Ni-Cd Cells.
    Molar enthropy of the cell reaction 64 Kcal/gm-mole. Used Dewar
    flask with a silicon fluid. Heat losses of cell during discharge
    approximately 15% total energy obtained from the cell.

VI. PLANNED FUTURE WORK

It is planned to continue the investigation of the thermal characteristics of the 20 ampere-hour cell utilizing depths of discharge of 15%, 25%, and 40%. It is also planned to investigate the thermal behavior of the fully charged cell when maintained at various levels of trickle charge.

VII. REFERENCES

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    Technical Note 270-3, "Selected Values of Chemical Thermo-
    dynamic Properties." 1968.

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    their Potential in Aqueous Solution." Prentice Hall, Inc.,
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