General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

EIGHTH PROGRESS REPORT

FOR

RESEARCH INTO FUNDAMENTAL PHENOMENA ASSOCIATED WITH SPACECRAFT ELECTROCHEMICAL DEVICES — CALORIMETRY OF NICKEL-CADMIUM CELLS
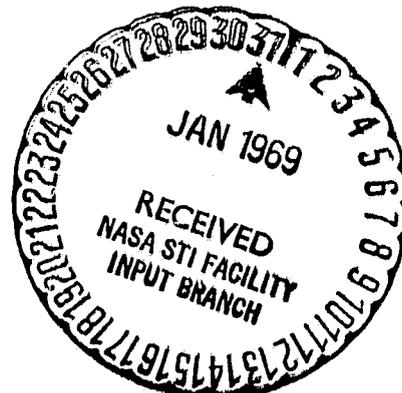
April 1, 1968 — June 30, 1968

Contract No. NAS 5 — 10105

Prepared by

R. T. FOLEY, and G. D. MITCHELL

For

National Aeronautics and Space Administration

Goddard Space Flight Center

Greenbelt, Maryland

The American University

Washington, D. C. 20016

Table of Contents

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 specific experimental work deals with the calorimetry of Ni-Cd cells.

The work completed during this reporting period has dealt with four tasks, the first involving an investigation of the operating conditions of the calorimeter, the other three studies of the thermal characteristics of a 20 ampere-hour nickel-cadmium cell at 25°C and under various conditions.

An investigation of oil flow and thermopile positioning showed that one desirable condition for signal and response time were a flow rate of 45% pump capacity and a thermopile positioning 1/8" from the outlet port.

The average maximum heat output for a 20 ampere-hour, third electrode, nickel-cadmium, cell during 15% depth of discharge and 105% recharge rate was 1.43 watts. The same cell at a 25% depth gave 1.25 watts exothermic heat. Under similar conditions with the exception of the recharge rate of 100% (rundown condition) the heat output was 1.09 watts. This quantity increases with increase of the resistance in the third electrode circuit.

A series of experiments was conducted at 25% depth of discharge and 110% recharge rate with third electrode resistances of 6.8, 47, 100, 200 ohm, and infinite resistance. Above 100 ohms both the heat output and the oxygen pressure rises.

i

List of Figures

List of Tables

Research into Fundamental Phenomena Associated
with Spacecraft Electrochemical Devices-Calorimetry
of Nickel-Cadmium Cells

I. INTRODUCTION

The objectives of this project are

      1) to train electrochemists in the area of battery research and

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

The work completed during the period covered by this report may
be subdivided into four experimental sections. The first section involves
the study of the thermal characteristics of the calorimeter. This con-
siders the effect of flow rate and thermopile positioning on the thermal
response of the system. The second section involves the evaluation of
the thermal output of a 20 ampere-hour nickel-cadmium cell under conditions
of 15% depth of discharge and 105% charge rate at $25^{\circ}C$. In the third
section a study of the thermal output of a 20 ampere-hour cell is made
under the "rundown" conditions of 25% depth of discharge and 100% recharge
rate at $25^{\circ}C$. The fourth section is the evaluation of the effect of the
Adhydrode on the apparent enthalpy (ΔH), the cell pressure, and the thermal
output of the cell at $25^{\circ}C$.

II. CALORIMETER CHARACTERISTICS

Two of the design factors which determine the thermal response of the present calorimetric system are the rate of flow of oil through the calorimeter and the positioning of the upper (hot) thermopile. The mechanics of the flow rate has been discussed previously (1) and will not be reiterated at this time. The effect of flow rate and thermopile position on the measured thermal output have been studied in detail.

The variation in the flow of oil through the calorimeter is measured in terms of the stroke rate of the circulating pump or percent of the full stroke. To determine the stroke rate that yields a maximum signal a complete range of stroke rates must be employed. The procedure used in obtaining this maximum signal is to set the calorimeter heater to give an output of 1 to 2 watts and then with this fixed setting, adjust the stroke rate and record the thermal output. At a known, fixed position for the thermopile there are two factors which are significant in the evaluation. The first is the maximum signal observed by the thermopile and the second is the response time. The response time is recorded in percent (%) of maximum signal observed in 5 minutes.

A wide range of stroke rate vs. heat signal for three thermopile positions was investigated and the results are plotted in figure 1. Table 1 shows such a range for a thermopile position of 0" (where 0" means that the thermopile is zero inches from the upper exit pipe of the calorimeter). Recorded in Table 1 are the data obtained for a 1.3 watt input to the calibration heater. The maximum signal in microvolts is 59 µv with a response in 5 minutes of 56.0%. The objective of these experiments is to establish the optimum combination of thermopile position and stroke rate. Tables 2 and 3 show the results of stroke rate studies at thermopile

- 2 -
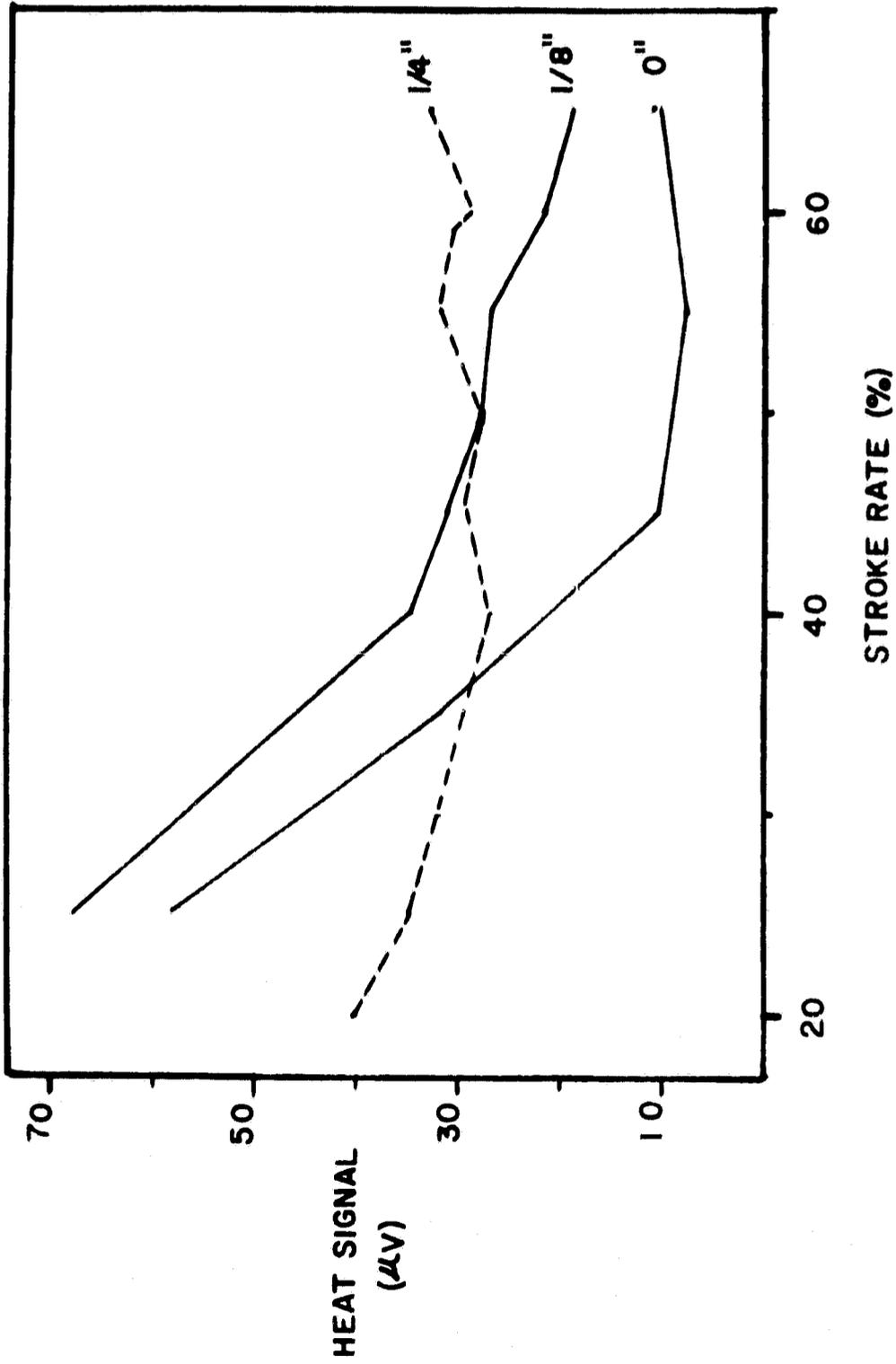
Figure 1.

Heat signal as a function of oil flow rate
(stroke rate) for three thermopile settings

Table 1

Relationship between flow rate and thermal response at 0" setting (1.13 watt input)

Signal (μv)	% Stroke	Response (% in 5 min.)
59	25	56.0
32	35	50.0
11	45	54.5
8	55	37.5
11	65	32.8

Table 2

Relationship between flow rate and thermal response at 1/8" setting (1.13 watt input)

Signal (μv)	% Stroke	Response (% in 5 min.)
67.8	25	62
35	40	69
31	45	79
28	50	79
27.3	55	79
21.6	60	83
19	65	84

Table 3

Relationship between flow rate and thermal
response at 1/4" setting (1.13 watt input)

Signal (mv)	(% stroke)	Response (% in 5 min.)
41	20	75.6
36	25	75.3
31	30	77.4
27	40	81.5
30	45	80.0
28	50	79.0
42	55	81.0
41	57.5	83.0
39	60	89.0
33	65	85.0

positions of 1/8 inch and 1/4 inch respectively. It has been previously established that a 5-minute lag exists between the time that the heater is turned on and the heat is recorded by the heat sensing system. It is considered that a response of less than 75% in 5 minutes is unsatisfactory. As can be seen from Table 3, all of the signals are acceptable from the point of view of response time.

The usual relationship between heat signal and flow rate, encountered during many experiments, is that observed at the 1/8" setting, i.e. as the flow rate increases, the heat signal drops. The flat curve at the 1/4" setting is unusual in this regard suggesting a different flow pattern. It is necessary to make a compromise between maximum signal and a high response time, and much of the work reported below was done with a thermopile setting at 1/8" and a stroke rate of 45%.

Whereas, figure 1 and tables 1-3 illustrate the relationship between the parameters involved, it is necessary to run a new calibration curve whenever the system is disturbed, e.g. in repositioning the cell within the calorimeter.

III. THERMAL BEHAVIOR OF 20 AMPERE-HOUR NICKEL-CADMIUM CELL
AT 15% DEPTH OF DISCHARGE AND 105% RECHARGE RATE

The 20 ampere-hour Ni-Cd cell used for this set of experiments is
the same cell for which data were reported in the Seventh Progress Report (2).
The previous history of the cell prior to this experiment consisted of
regular conditioning, trickle charge experiments, an extended charge condi-
tioning, and 25% depth of discharge experiments. The cell had been subjected
to 146 cycles prior to this experiment.

The two functions which indicate abnormalities are the voltage and
the transducer signal. Experience with this type of cell has shown that
the transducer signal (cell pressure) undergoes a marked increase with
time or increased cycling of the cell. Reference to Table 4 shows that for
a typical cycle at 15% D.O.D. and 105% R.C. at $25^{\circ}C$, the voltage range is
from 1.24 v. to 1.42 v. and the pressure range is from 4.50 p.s.i.a. to
7.75 p.s.i.a. Both the voltage range and the pressure range are well
within the limits of a normal cell.

The heat output of the cell under the conditions of 15% D.O.D. at
$25^{\circ}C$ may be seen in Tables 4 and 5. The data given in these tables were
taken from orbits 37 and 42 respectively. Orbit 42 out of 43 gave the
greatest thermal output in the series. The fluctuation of exothermic heat
during discharge was as follows:

Cycle	20	21	23	24	26	27	29	31
Heat	1.21	1.31	1.42	1.39	1.52	1.47	1.47	1.42

Cycle	33	34	35	36	37	38	42	43
Heat	1.42	1.39	1.39	1.45	1.53	1.45	1.60	1.45

The average heat was 1.43 watts $\pm$ 0.22 watts.

The maximum endothermic point was reached at about 45 minutes into the
charging portion, the steady state portion of the charge occurred during
35-40 minutes into the charge.

Table 4

(1) 30 min. d.c. at 6 amp. for 15% D.O.D.   25°C   Orbit #37
(2) 60 min. c. at 3.15 amp. for 105% R.C.

Time (hours)	q (watts)	E (volts)	W (watts)	ΔH (watts)	ΔH (kcal/ equiv)	Pressure Trans- ducer(mv)	Pressure (psia)	Adhy- drode (mv)
Discharge								
0	-0.03	1.34	-9.38	-9.35	-30.8	30	7.50	30
5	-0.39	1.31	-9.17	-8.78	-28.9	31	7.75	50
10	-0.86	1.30	-9.10	-8.24	-27.1	29	7.25	50
15	-1.17	1.28	-8.96	-7.79	-25.6	28	7.00	45
20	-1.33	1.27	-8.89	-7.56	-24.9	25	6.25	44
25	-1.43	1.26	-8.82	-7.39	-24.3	24	6.00	40
30	-1.47	1.24	-8.68	-7.21	-23.7	23	5.75	35
Charge								
0	-1.53	1.42	3.90	2.37	17.3	22	5.50	44
5	-1.17	1.32	4.16	2.99	21.9	21	5.25	36
10	-0.75	1.33	4.19	3.44	25.2	20	5.00	32
15	-0.44	1.34	4.22	3.78	27.7	20	5.00	30
20	-0.18	1.35	4.25	4.06	29.7	19	4.75	27
25	0.00	1.36	4.28	4.28	31.3	18	4.50	20
30	+0.10	1.37	4.32	4.42	32.4	18	4.50	17
35	+0.18	1.38	4.35	4.53	33.2	18	4.50	17
40	+0.20	1.38	4.35	4.55	33.3	18	4.50	17
45	+0.23	1.39	4.38	4.61	33.7	19	4.75	18
50	+0.18	1.40	4.41	4.59	33.6	20	5.00	18
55	+0.13	1.41	4.44	4.57	33.5	23	5.75	30
60	0.00	1.42	4.47	4.47	32.7	25	6.25	47

EXPERIMENTAL SERIES I

Table 5

(1) 30 min. d.c. at 6 amp. for 15% D.O.D.   25°C   Orbit #42
(2) 60 min. c. at 3.15 amp. for 105% R.C.

Time (hours	q (watts)	E (volts)	W (watts)	ΔH (watts)	ΔH (kcal/ equiv)	Pressure Trans- ducer(mv)	Pressure (psia)	Adhy- drode (mv)
Discharge								
0	-0.08	1.34	-9.38	-9.30	-30.6	30	7.50	35
5	-0.49	1.31	-9.17	-8.68	-28.6	31	7.75	55
10	-0.99	1.30	-9.10	-8.11	-26.7	30	7.50	50
15	-1.25	1.28	-8.96	-7.71	-25.4	28	7.00	45
20	-1.43	1.27	-8.89	-7.46	-24.5	26	6.50	45
25	-1.58	1.26	-8.82	-7.24	-23.8	24	6.00	43
30	-1.58	1.24	-8.68	-7.10	-23.4	23	5.75	38
Charge								
0	-1.60	1.24	3.90	2.30	16.8	22	5.50	45
5	-1.38	1.32	4.16	2.78	20.4	21	5.25	35
10	-0.93	1.33	4.19	3.26	23.9	20	5.00	30
15	-0.59	1.34	4.22	3.63	26.6	20	5.00	25
20	-0.34	1.35	4.25	3.91	28.6	19	4.75	23
25	-0.18	1.36	4.28	4.10	30.0	18	4.50	20
30	-0.03	1.37	4.32	4.29	31.4	18	4.50	20
35	+0.08	1.38	4.35	4.43	32.4	18	4.50	17
40	+0.10	1.39	4.38	4.49	32.9	18	4.50	17
45	+0.13	1.39	4.38	4.51	30.0	19	4.75	20
50	+0.08	1.41	4.41	4.49	32.9	21	5.25	25
55	+0.05	1.42	4.47	4.52	33.1	24	6.00	33
60	-0.08	1.43	4.50	4.42	32.3	29	7.25	50

The apparent enthalpy during these steady state conditions may be considered as being due to the charging reaction of the Ni-Cd cell (3). The value of the enthalpy (ΔH) during this time, taken from Table 4 which is representative of most of the cycles, is of the order of 33.2 to 33.7 Kcal/equiv. The calculated value for the ΔH of the reaction is 33.6 Kcal/equiv. (3). A graphical representation of the apparent ΔH as a function of time is shown in Figure 2. From this plot it is obvious that during discharge there is a steady decrease in this function for the full 30-minute period. During charge the apparent ΔH rises until it achieves a steady value between 45 and 55 minutes. During this period the value of the apparent ΔH is in very good agreement with that of the calculated or theoretical value.

Observation of the cell pressure during this time period also shows that a steady state condition exists from 25 to 40 minutes. The oxygen pressure in the cell during the cycle at 15% depth of discharge and 105% rate of charge ranged from 4.50 p.s.i.a. to 7.75 p.s.i.a. This constitutes a pressure change of 3.25 p.s.i.a. or 0.221 atm. The gassing tendency of the cell, notably the production of hydrogen, results in a continual increase in its residual pressure. Considering the history of the cell to this point, it is concluded that the cell has not shown any tendency to gas excessively. From Fig. 3 it is seen that the nature of the functions mapping out the curves labeled Adhydrode and Transducer are only roughly similar; no direct proportionality exists between the two measurements.
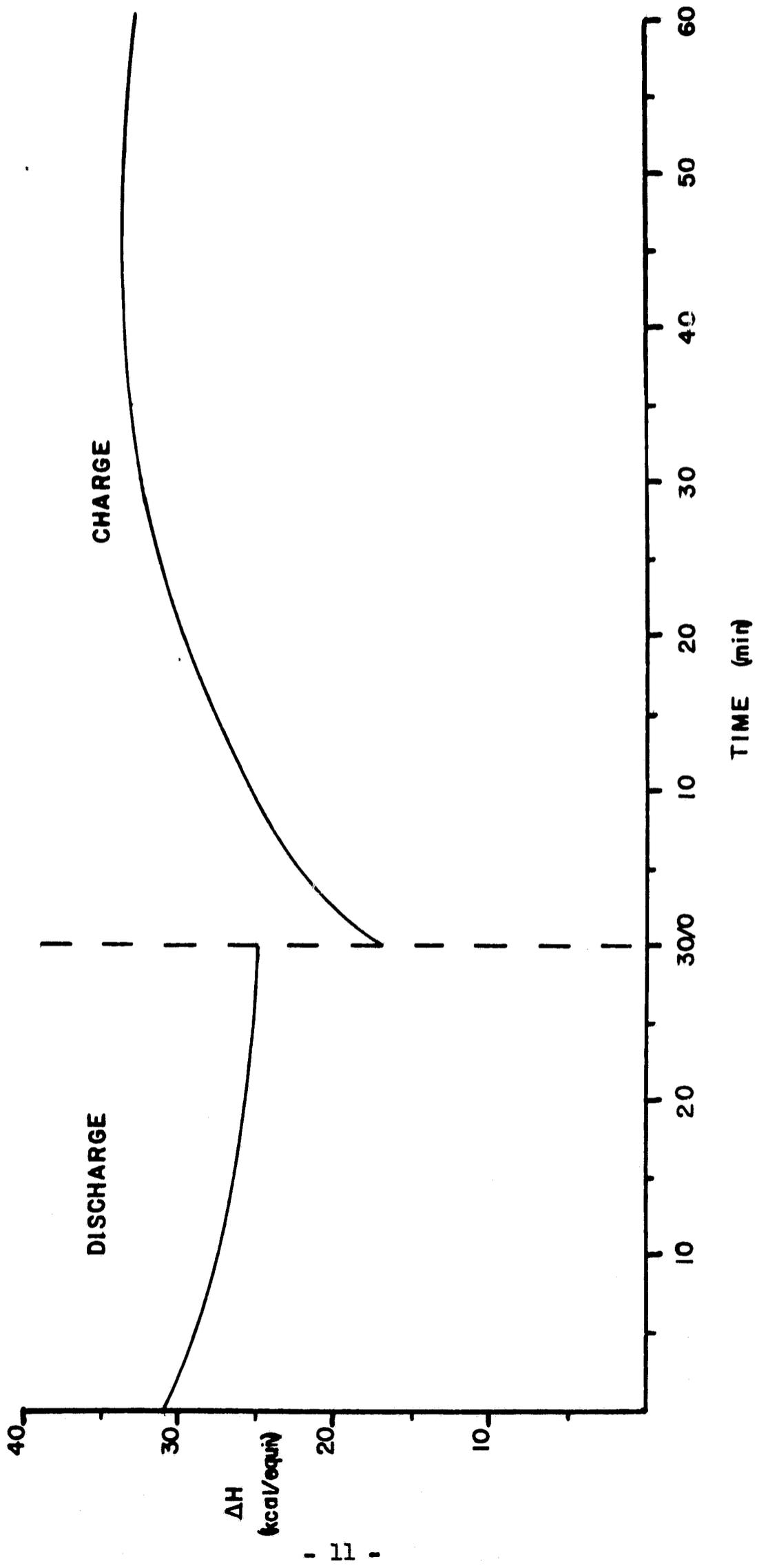
Change of apparent enthalpy of reaction during
90-minute orbit

Figure 2.
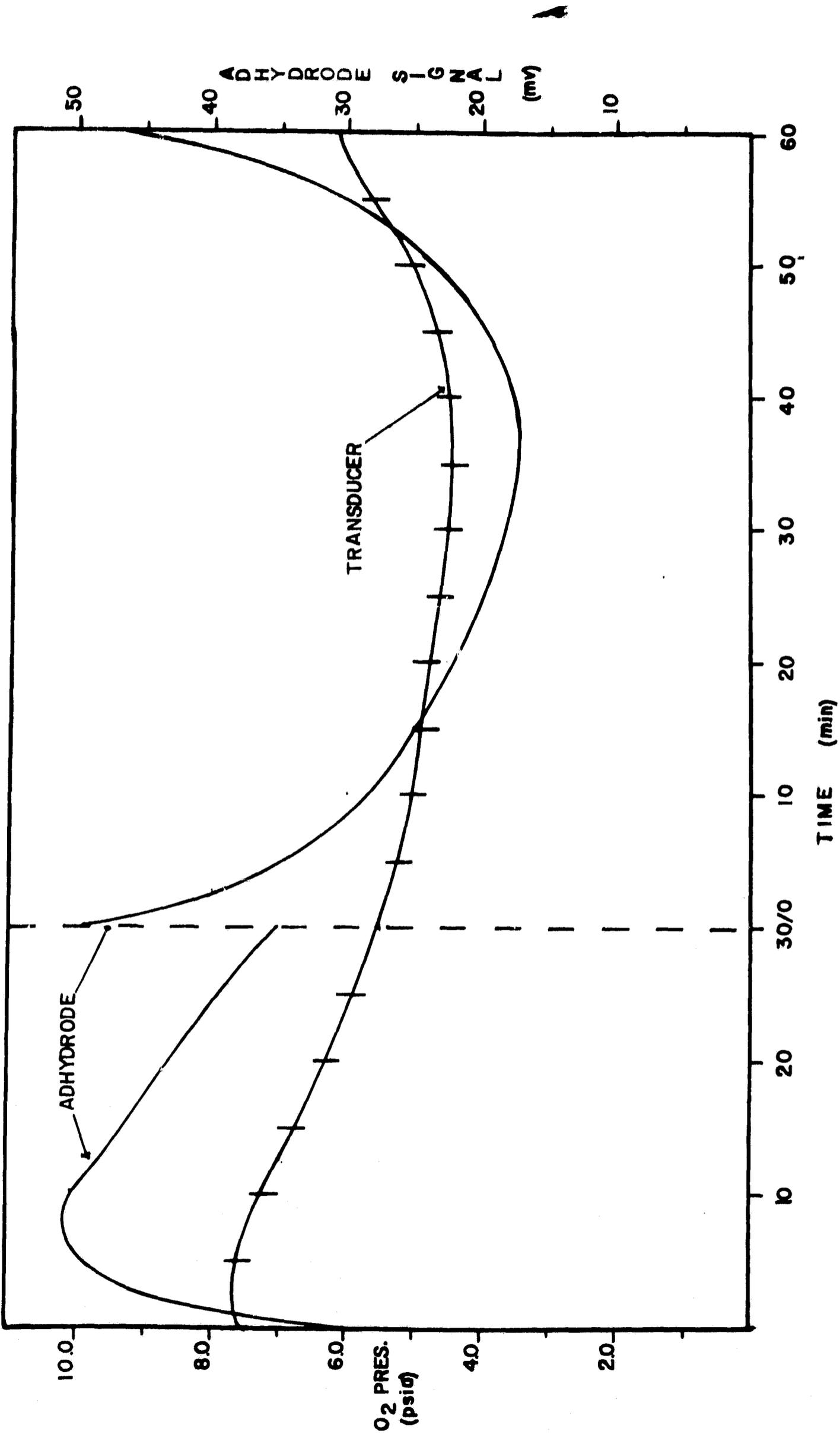
Change of Adhydrode signal and oxygen pressure
(Transducer signal) during 60-minute orbit

Figure 3.

IV. "RUNDOWN" EXPERIMENT

A "rundown" experiment is defined here as one in which the capacity returned to the cell is less than the amount withdrawn. For the 25% depth of discharge "rundown" experiment the conditions were 10.00 ampere discharge for 30 minutes' period and 5.00 amperes charge for 60 minutes recognizing that the charging process is less than 100% efficient. In addition to this charge-discharge condition the Adhydrode resistor was varied during several of the orbits. The Adhydrode resistor is put across the cadmium electrode and the third electrode to supply a circuit to reduce oxygen. The values of the resistors used were 6.8 Ω, 47 Ω, and 100 Ω. Under normal operating conditions the manufacturer's recommendation is a "low resistance" resistor. As a carry-over from the experiments performed on the 6 ampere-hour cell a 6.8 Ω resistor is considered as the normal operating resistor.

The data shown in Tables 6, 7 and 8 were produced during the "rundown" experiments. Each table represents the performance of the cell after a steady state condition was achieved. For the three resistors, 6.8 Ω, 47 Ω, and 100 Ω, 32, 11, and 13 cycles, respectively were run. Table 6 may be considered the reference data for this set of experiments as the 6.8 Ω resistor was used during this experiment. The maximum heat output under these normal experimental conditions is 1.09 watts. The heat output as a function of the Adhydrode resistor may be considered. In Tables 7 (47 Ω resistor) and 8 (100 Ω resistor) it is seen that the maximum heat output is 1.11 watts and 1.17 watts respectively. This constitutes increases of 0.02 and 0.08 watts respectively. The relationship between the exothermic output and the Adhydrode resistor will be discussed in more detail in the next section. At this point several observations will be made concerning apparent trends during this set of experiments.

Table 6

(1) 30 min. d.c. at 10.00 amp. for 25% D.O.D.   25°C   6.8Ω
(2) 60 min. c. at 5.00 amp. for 100% R.C.

Time (hours)	q (watts)	E (volts)	W (watts)	ΔH (watts)	ΔH (kcal/ equiv)	Pressure Trans- ducer(mv)	Pressure (psia)	Adhy- drode (mv)
Discharge								
0	+0.28	1.32	-13.2	-12.9	-29.8	19	4.75	0
5	+0.02	1.28	-12.8	-12.6	-29.1	19	4.75	0
10	-0.39	1.26	-12.6	-13.0	-30.0	19	4.75	0
15	-0.65	1.24	-12.4	-13.1	-30.3	19	4.75	0
20	-0.83	1.21	-12.1	-12.9	-29.8	18	4.50	0
25	-0.93	1.21	-12.1	-13.0	-30.0	18	4.50	0
30	-1.04	1.19	-11.9	-12.9	-29.8	18	4.50	0
Charge								
0	-1.09	1.24	6.20	5.11	23.6	18	4.50	20
5	-0.91	1.29	6.45	5.54	25.5	18	4.50	22
10	-0.59	1.31	6.55	5.96	27.5	18	4.50	22
15	-0.36	1.32	6.60	6.24	28.8	18	4.50	23
20	-0.13	1.33	6.65	6.52	30.1	18	4.50	23
25	-0.03	1.34	6.70	6.67	30.7	18	4.50	20
30	+0.11	1.35	6.75	6.86	31.6	18	4.50	20
35	+0.15	1.36	6.80	6.95	32.0	18	4.50	20
40	+0.18	1.37	6.85	7.03	32.4	18	4.50	20
45	+0.26	1.37	6.85	7.11	32.8	18	4.50	20
50	+0.26	1.38	6.90	7.16	33.0	18	4.50	20
55	+0.28	1.39	6.95	7.23	33.3	19	4.75	20
60	+0.28	1.39	6.95	7.23	33.3	19	4.75	21

EXPERIMENTAL SERIES I

Table 7

(1) 30 min. d.c. at 10.00 amp. for 25% D.O.D. 25°C   47Ω
(2) 60 min. c. at 5.0 amp. for 100% R.C.

Time (hours)	q (watts)	E (volts)	W (watts)	ΔH (watts)	ΔH (kcal/equiv)	Pressure Trans-ducer(mv)	Pressure (psia)	Adhy-drode (mv)
Discharge								
0	+0.20	1.32	-13.2	-13.0	-30.0	15	3.75	10
5	-0.03	1.29	-12.9	-12.8	-29.6	15	3.75	7
10	-0.39	1.26	-12.6	-12.2	-28.2	15	3.75	3
15	-0.65	1.24	-12.5	-11.9	-27.5	14	3.50	0
20	-0.86	1.23	-12.3	-11.4	-26.3	14	3.50	0
25	-0.98	1.21	-12.1	-11.1	-25.6	14	3.50	0
30	-1.06	1.19	-11.9	-10.8	-24.9	14	3.50	0
Charge								
0	-1.11	1.19	5.95	4.84	22.3	14	3.50	0
5	-0.96	1.29	6.45	5.49	25.3	15	3.75	35
10	-0.65	1.31	6.55	5.90	27.2	15	3.75	42
15	-0.42	1.32	6.60	6.18	28.5	15	3.75	47
20	-0.18	1.33	6.65	6.47	29.8	15	3.75	47
25	-0.39	1.34	6.70	6.31	29.1	15	3.75	45
30	+0.07	1.35	6.75	6.82	31.4	15	3.75	45
35	+0.13	1.36	6.80	6.93	31.9	15	3.75	47
40	+0.18	1.37	6.85	7.03	32.4	15	3.75	43
45	+0.23	1.37	6.85	7.08	32.6	15	3.75	43
50	+0.23	1.38	6.90	7.13	32.9	15	3.75	43
55	+0.26	1.39	6.95	7.21	33.2	15	3.75	44
60	+0.26	1.39	6.95	7.21	33.2	15	3.75	45

Table 8

(1) 30 min. d.c. at 10.00 amp. for 25% D.O.D. 25°C 100Ω
(2) 60 min. c. at 5.00 amp. for 100% R.C.

Time (hours)	q (watts)	E (volts)	W (watts)	ΔH (watts)	ΔH (kcal/ equiv)	Pressure Trans- ducer(mv)	Pressure (psia)	Adhy- drode (mv)
Discharge								
0	+0.31	1.32	-13.2	-13.5	-31.2	125	31.3	12
5	0.00	1.29	-12.9	-12.9	-29.8	105	26.3	12
10	-0.39	1.26	-12.6	-12.2	-28.2	100	25.0	12
15	-0.68	1.24	-12.4	-11.7	-27.0	95	23.8	12
20	-0.86	1.22	-12.2	-11.3	-26.1	90	22.5	12
25	-0.89	1.20	-12.0	-11.0	-25.4	83	20.8	12
30	-1.09	1.16	-11.6	-10.5	-24.3	65	16.3	12
Charge								
0	-1.17	1.16	5.80	4.63	21.3	57	14.3	12
5	-1.01	1.28	6.40	5.39	24.8	150	37.5	11
10	-0.70	1.30	6.50	5.80	26.7	160	40.0	11
15	-0.49	1.32	6.60	6.61	28.2	165	41.3	11
20	-0.21	1.33	6.65	6.44	29.7	172	43.0	11
25	-0.05	1.34	6.70	6.65	30.7	175	43.8	11
30	+0.05	1.35	6.67	6.72	31.0	175	43.8	11
35	+0.13	1.36	6.80	6.93	31.9	175	43.4	11
40	+0.18	1.37	6.85	7.03	32.4	174	43.5	11
45	+0.23	1.37	6.85	7.08	32.6	173	43.3	11
50	+0.23	1.38	6.90	7.13	32.9	173	43.3	11
55	+0.26	1.38	6.90	7.16	33.0	174	43.5	11
60	+0.28	1.39	6.95	7.23	33.5	177	43.3	11

Whereas, in going from the 6.8 Ω resistor to the 47 Ω resistor
there is a drop in pressure from 4.75 p.s.i.a. to 3.75 p.s.i.a., the
employment of a 100 Ω resistor results in the pressure rising to 43.8 p.s.i.a.
The implication is that the circuit with this resistor is not effective in
combining oxygen. As a result of the absence of an overcharge, the endo-
thermic nature of the cell processes dominate until the system is well
into the discharge portion of the cycle. At the same time the apparent
enthalpy ΔH (Kcal/equiv.) over the latter part of the charging period
suggests that the nature of the electrode processes are the same as those
encountered during the experiment described in section II above. This is
indicated by a value of about 33.0 Kcal/equiv. which is consistent with that
experiment. The further observation to be made concerning this set of
experiments is that of the behavior of the Adhydrode. The Adhydrode elec-
trode during the normal set of experiments (Table 6) gave a signal of zero
during discharge and remained constant at about 20 mv for charge. These
values were not observed during the experiments in which the higher re-
sistances were used.

The behavior of the Adhydrode as a function of its resistor can
better be established in a separate study under conditions such that the
cell has a return in charge of greater than 100% of its capacity.

V. ADHYDRODE EXPERIMENTS

The Adhydrode experiments were designed to establish the influence
of various resistors across the Adhydrode (third electrode) and the cadmium
(negative) electrode. The cycling conditions for this experiment involved a
10.00 ampere discharge for 30 min. and a 5.5 ampere charge for 60 min. at
$25^{\circ}C$, which constitutes a 25% depth of discharge with a 110% recharge rate.
A 0.8 Ω resistor was used in the same manner as reported in a previously
reported 25% D.O.D. experiment (2). The data collected under this experi-
mental condition is considered as the reference data for the other experiments.
The additional resistors, under which the Adhydrode performance was evaluated,
were 47 Ω, 100 Ω, 200 Ω and ∞ Ω. The number of cycles run with each re-
sistor were 49, 6, 10, 10, and 15 respectively.

The data reported in Table 9 approximates the previous 25% D.O.D. data
(2). The maximum exothermic output was in the vicinity of 1.25 watts
and the maximum endothermic output was 0.07 watt. The apparent enthalpy
(ΔH) at 35 minutes into charge/minimum pressure point) was 32.3 Kcal/
equiv. The behavior of the cell pressure as observed by the transducer
is also in keeping with previously reported data. Overall, the data
reported in Table 9 is in very good agreement with that reported in
Tables 1-6 of the Seventh Progress Report (2) and it would appear justified
to use this performance as a reference point for the evaluation of the
Adhydrode under other conditions.

The influence of the Adhydrode resistor on the maximum exothermic
output may be estimated from the data given in Tables 10 - 13. It was
observed that the Adhydrode resistance must exceed a value of 100 Ω
before a significant deviation in heat output from the accepted value of
1.25 watts is achieved. For a 47 Ω resistor the measured heat output is

Table 9

Adhydrode Experiment 6.8Ω

(1) 30 min. d.c. at 10.00 amps. 25% D.O.D.
(2) 60 min. b. at 5.50 amps. 110% R.C.

Time (hours)	q (watts)	E (volts)	W (watts)	ΔH (watts)	ΔH (kcal/ equiv)	Pressure Trans- ducer(mv)	Pressure (psia)	Adhy- drode (mv)
Discharge								
0	-0.40	1.36	-13.6	-14.0	-32.2	53	13.3	110
5	-0.80	1.30	-13.0	-13.8	-31.7	50	12.5	160
10	-1.04	1.28	-12.8	-13.8	-31.7	45	11.3	140
15	-1.22	1.26	-12.6	-13.8	-31.7	38	9.50	120
20	-1.25	1.25	-12.5	-13.8	-31.7	34	8.50	105
25	-1.25	1.23	-12.3	-13.6	-31.3	30	7.50	90
30	-1.25	1.22	-12.2	-13.5	-31.1	26	7.00	76
Charge								
0	-1.25	1.22	6.71	5.46	22.9	24	6.00	103
5	-1.04	1.23	6.77	5.73	24.0	22	5.50	73
10	-0.75	1.34	7.37	6.62	27.7	21	5.25	63
15	-0.32	1.35	7.43	7.11	29.8	19	4.75	51
20	-0.27	1.36	7.48	7.21	30.2	18	4.50	44
25	-0.11	1.37	7.54	7.43	31.1	18	4.50	38
30	-0.03	1.38	7.59	7.53	31.7	18	4.70	35
35	+0.05	1.39	7.65	7.70	32.3	18.5	4.63	34
40	+0.07	1.41	7.76	7.83	32.8	19	4.75	35
45	+0.07	1.42	7.81	7.88	33.0	20	5.00	40
50	+0.05	1.43	7.87	7.92	33.2	22	5.50	63
55	-0.08	1.45	7.97	7.89	33.1	32	8.00	89
60	-0.29	1.47	8.08	7.79	32.6	43	10.8	125

Table 10

Adhydrode Experiment 47Ω

(1) 30 min. d.c. at 10.00 amp. 25% D.O.D.
(2) 60 min. c. at 5.5 amp. 110% R.C.

Time (hours)	q (watts)	E (volts)	W (watts)	ΔH (watts)	ΔH (kcal/ equiv)	Pressure Trans- ducer(mv)	Pressure (psia)	Adhy- drode (mv)
Discharge								
0	-0.39	1.36	-13.6	-14.0	-32.2	48	12.0	320
5	-0.77	1.30	-13.0	-13.8	-31.7	45	11.3	330
10	-1.01	1.28	-12.8	-13.8	-31.7	39	9.75	320
15	-1.14	1.26	-12.6	-13.7	-31.7	34	8.50	310
20	-1.21	1.25	-12.5	-13.7	-31.7	30	7.50	290
25	-1.24	1.24	-12.4	-13.6	-31.3	26	6.50	270
30	-1.24	1.23	-12.3	-13.5	-31.1	24	6.00	253
Charge								
0	-1.24	1.29	7.09	5.85	24.5	24	6.00	275
5	-1.06	1.32	7.26	6.20	26.0	22	5.50	260
10	-0.67	1.34	7.37	6.70	28.1	20	5.00	237
15	-0.49	1.35	7.43	6.94	29.1	18	4.50	210
20	-0.28	1.36	7.48	7.20	30.2	17	4.25	190
25	-0.13	1.38	7.59	7.46	31.3	17	4.25	173
30	-0.05	1.39	7.64	7.59	31.8	16	4.00	162
35	+0.02	1.40	7.70	7.72	32.3	16	4.00	130
40	+0.02	1.41	7.76	7.78	32.6	17	4.25	132
45	+0.02	1.42	7.81	7.83	32.8	19	4.75	173
50	-0.05	1.43	7.86	7.81	32.7	24	6.00	220
55	-0.20	1.44	7.92	7.72	32.3	32	8.00	309
60	-0.46	1.48	8.14	7.68	32.2	46	11.5	390

Table 11

Adhydrode Experiment 100Ω

(1) 30 min. d.c. at 10.00 amp. 25% D.O.D.
(2) 60 min. c. at 5.5 amp. 110% R.C.

Time (hours)	q (watts)	E (volts)	W (watts)	ΔH (watts)	ΔH (kcal/ equiv)	Pressure Trans- ducer(mv)	Pressure (psia)	Adhy- drode (mv)
Discharge								
0	-0.36	1.36	-13.6	-14.0	-32.?	52	13.0	385
5	-0.27	1.30	-13.0	-13.7	-31.5	48	12.0	425
10	-1.01	1.28	-12.8	-13.8	-31.7	42	10.5	420
15	-1.16	1.27	-12.7	-13.9	-32.0	37	9.25	400
20	-1.21	1.25	-12.5	-13.7	-31.5	33	8.25	377
25	-1.2?	1.24	-12.4	-13.7	-31.5	29	7.25	357
30	-1.27	1.23	-12.3	-13.6	-31.3	26	6.50	330
Charge								
0	-1.27	1.28	7.04	5.77	24.2	26	6.50	357
5	-1.06	1.32	7.26	6.20	26.0	24	6.00	335
10	-0.72	1.34	7.37	6.65	27.9	22	5.50	315
15	-0.44	1.36	7.48	7.04	29.5	21	5.25	295
20	-0.26	1.37	7.52	7.27	30.5	20	5.00	275
25	-0.10	1.38	7.59	7.49	31.4	19	4.75	357
30	0.00	1.39	7.64	7.64	32.0	19	4.75	240
35	0.00	1.40	7.70	7.70	32.3	18	4.50	227
40	+0.07	1.41	7.76	7.83	32.8	19	4.75	227
45	+0.07	1.42	7.81	7.88	33.0	21	5.25	243
50	0.00	1.43	7.86	7.86	32.9	26	6.50	295
55	-0.10	1.46	8.03	7.93	33.2	36	9.00	365
60	-0.44	1.50	8.25	7.91	33.1	54	13.50	454

EXPERIMENTAL SERIES I

Table 12

Adhydrode Experiment 200Ω

(1) 30 min. d.c. at 10.00 amp. 25% D.O.D.
(2) 60 min. c. at 5.5 amp. 110% R.C.

Time (hours)	q (watts)	E (volts)	W (watts)	ΔH (watts)	ΔH (kcal/ equiv)	Pressure Trans- ducer(mv)	Pressure (psia)	Adhy- drode (mv)
Discharge								
0	-0.44	1.33	-13.3	-13.7	-31.5	64	16.0	500 +
5	-0.85	1.30	-13.0	-13.9	-32.0	58	14.5	500 +
10	-1.11	1.38	-12.8	-13.9	-32.0	50	12.5	500 +
15	-1.29	1.26	-12.6	-13.9	-32.0	44	11.0	500 +
20	-1.32	1.25	-12.5	-13.8	-31.7	40	10.0	500 +
25	-1.34	1.23	-12.3	-13.6	-31.3	35	8.75	500 +
30	-1.37	1.22	-12.2	-13.6	-31.3	32	8.00	500 +
Charge								
0	-1.37	1.22	6.71	5.34	22.4	32	8.00	500 +
5	-1.16	1.32	7.26	6.10	25.6	29	7.25	480
10	-0.75	1.34	7.37	6.62	27.7	27	6.75	450
15	-0.46	1.35	7.43	6.97	29.2	24	6.00	423
20	-0.26	1.36	7.48	7.22	30.3	23	5.75	395
25	-0.10	1.37	7.53	7.43	31.1	22	5.50	370
30	0.00	1.38	7.59	7.59	31.8	21	5.25	350
35	+0.04	1.39	7.64	7.68	32.2	21	5.25	337
40	+0.10	1.40	7.70	7.80	32.7	22	5.50	327
45	+0.10	1.42	7.81	7.91	31.1	24	6.00	335
50	+0.02	1.43	7.86	7.88	33.0	28	7.00	390
55	-0.13	1.46	8.03	7.90	33.1	37	9.25	470
60	-0.44	1.49	8.19	7.75	32.5	58	14.5	500 +

EXPERIMENTAL SERIES I

Table 13

Adhydrode Experiment ∞Ω

(1) 30 min. d.c. at 10.00 amp. 25% u.O.O.
(2) 60 min. c. at 5.5 amp. 110% R.C.

Time (hours)	q (watts)	E (volts)	W (watts)	ΔH (watts)	ΔH (kcal/equiv)	Pressure Trans-ducer(mv)	Pressure (psia)	Adhy-drode (mv)
Discharge								
0	-0.41	1.35	-13.5	-13.9	-32.0	65	16.3	445
5	-0.85	1.30	-13.0	-13.9	-32.4	62	15.5	426
10	-1.16	1.28	-12.8	-14.0	-32.2	55	13.8	425
15	-1.29	1.26	-12.6	-13.9	-32.0	47	11.8	424
20	-1.37	1.25	-12.5	-13.9	-32.0	43	10.8	420
25	-1.42	1.23	-12.3	-13.7	-31.5	39	9.75	420
30	-1.42	1.22	-12.2	-13.6	-31.3	35	8.75	417
Charge								
0	-1.42	1.28	7.04	5.62	23.5	34	8.50	430
5	-1.16	1.32	7.26	6.10	25.6	32	8.00	450
10	-1.12	1.34	7.37	6.25	26.2	29	7.25	451
15	-0.80	1.35	7.43	6.63	27.8	28	7.00	450
20	-0.49	1.36	7.48	6.99	29.3	26	6.50	450
25	-0.28	1.37	7.53	7.25	30.3	25	6.25	450
30	-0.13	1.38	7.59	7.46	31.3	24	6.00	450
35	0.00	1.39	7.64	7.64	32.0	24	6.00	450
40	+0.04	1.40	7.70	7.74	32.4	25	6.25	450
45	+0.10	1.41	7.76	7.86	32.9	26	6.50	453
50	+0.10	1.43	7.83	7.96	33.6	30	7.50	455
55	-0.08	1.46	8.03	7.95	33.3	40	10.0	463
60	-0.36	1.49	8.19	7.83	32.8	58	14.5	475

1.24 watts and for 100 Ω it is 1.27 watts, both values within the errors of experimental measurements. The significant increase of 0.12 watt in heat output comes with a 200 Ω resistor. With the increase of the resistance to infinity (∞) the exothermic quantity is 1.42 watts, an increase of 0.17 watt. This increased heat output must be related to the increase in O_2 pressure which appears as a result of the change in Adhydrode resistance. Under the experimental conditions outlined in Tables 9 through 13 the maximum pressure goes from 13.3 to 16.3 p.s.i.a., a change of 3 p.s.i.a. or 0.20 atm. Utilizing the 47 Ω resistor (Table 10), the observed pressure during the various parts of the cycle are lower than those of the Table 9 reference. The apparent enthalpy of the cell during these experiments shows that for both charge and discharge the overall cell reaction must be essentially the same as that for a regular 25% D.O.D. experiment.

A study of the Adhydrode signal as the Adhydrode resistance is changed yields several interesting results. During one complete cycle at a resistor reading of 6.8 Ω the Adhydrode signal exhibits a low value of 34 mv during charge to a maximum value of 160 mv during discharge. This behavior is similar to that exhibited during previous 25% D.O.D. experiments. With an increase in Adhydrode resistance to 47 Ω or 100 Ω there is considerable increase in signal. A resistor increase to 200 Ω shows an increase in Adhydrode signal to one in excess of 500 mv during discharge. The limiting range of the recorder used in these measurements is from 0 to 500 mv. The minimum value during charge also shows a further increase over the minimums reported for 47 Ω and 100 Ω resistor experiments. The last observation to be made is one of the behavior of the Adhydrode under open circuit conditions. Table 13 shows that the Adhydrode signal remains relatively stable with the difference between the maximum and the

minimum during a given cycle being less than 60 mv. This behavior would

be expected because at this point the third electrode is no longer

participating in the cell reaction.

VI. CONCLUSIONS

The heat generated during the 15% D.O.D. experiment was greater by 0.18 watts than that generated during the 25% depth experiment at the same temperature. This experiment was run after the 25% depth experiment and certain aging characteristics of the cell may be involved to a minor extent. Examining the data from the 15% and 25% D.O.D. experiment discloses certain trends. The endothermic nature of the cell reaction appears at about 35 minutes of the charging period. At the same time the cell pressure appears to be approaching a constant value. At this point the potential of the cell is approaching 1.40 v.

It would appear that in the interpretation of the data, consideration should be given to at least two reactions, the first, the stoichiometric nickel-cadmium reaction, usually written for the cell reaction, and the second, an oxygen cycling reaction, grossly included under "electrolysis" reactions in the Sixth Progress Report (3). Depending upon the experimental conditions one of the above reactions will dictate the thermal behavior of the cell. Considering the heat (q) in Tables 4 and 9, it is seen that the exothermic reaction starts during the overcharge period and continues throughout the discharge whereas the effect of the endothermic reaction is not seen until approximately 5 minutes after charging has started. Since the two reactions are competing, the 5-minutes period above may be considered the heat lag in the system. The lag is mainly due to the limited heat capacity of the oil which flows through the calorimeter. The above characteristics of the heat (q) for the 20 ampere-hour Ni-Cd cell is consistent throughout this set of experiments. The only variation is in the rundown experiment where there is no overcharging. Therefore, the difference of 0.18 watt output between 15% and 25% D.O.D. may be explained on the basis of the predominance of one of the competing reactions.

Further studies into the nature of the reactions is being considered as future work to throw more light on this phenomenon.

A combination of Adhydrode studies during the "rundown" and during the "Adhydrode experiments" leads to the conclusion that further evaluation would be useful at the 47 Ω resistor to better interpret the results. The Adhydrode appears to have an effect upon the nature of the exothermic reaction (See Tables 9 and 10). From the data given in Tables 9 (6.8Ω) and 10 (47Ω) the only apparent effect of the change in Adhydrode resistance is the lower heat output in the latter table. But, the real significance of these quantities must be established.

The Adhydrode study also shows that the efficiency of the Adhydrode as an oxygen consuming electrode is decreased as the Adhydrode's resistance is increased. As a result of the decrease in efficiency of oxygen combination both an increase in cell pressure and the heat output occurs.

VII. FUTURE WORK

In the continuing investigation of the thermal characteristics of the 20 ampere-hour nickel-cadmium cell an experiment at $25^{\circ}C$ wherein the discharge is at the 40% depth will be undertaken.

To provide data of significance to Goddard Space Center projects it is also planned to investigate the performance of the 20 ampere-hour nickel-cadmium cell under special conditions, These include

a) trickle charging at $32^{\circ}C$

b) 15% and 25% depth of discharge experiments at $32^{\circ}C$.

A computer program will be written to assist in the calculation and the assimilation of the data.

A summary of the 20 ampere-hour and 6 ampere-hour data collected to this point will be made.

VIII. REFERENCES

1. G. D. Mitchell and F. T. Foley, Fourth Progress Report on Contract No. NAS 5-10105 April 1, 1967 - June 30, 1967.

2. F. T. Foley, G. D. Mitchell, and G. W. Roberts, Seventh Progress Report on Contract No. NAS 5-10105, January 1, 1968 - March 31, 1968.

3. F. T. Foley, G. D. Mitchell, and G. W. Roberts, Sixth Progress Report on Contract No. NAS 5-10105, October 1, 1967 - December 31, 1967.