TENTH PROGRESS REPORT
FOR
RESEARCH INTO FUNDAMENTAL PHENOMENA ASSOCIATED WITH SPACECRAFT ELECTROCHEMICAL DEVICES--CALORIMETRY OF NICKEL-CADMIUM CELLS

October 1, 1968 – August 31, 1969

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

In the final reporting period the work was designed to answer questions dealing with heat transfer in the 20 ampere-hour cell and the precision of the data previously reported.

Experiments with a nickel-cadmium cell specially fabricated with an internal calibration heater indicated a higher signal (100-150 mv/watt) but a longer response time (30-50 minutes) than previous experiments with a resistance wire heater mounted under the cell in the calorimeter.

The data on the 6 ampere-hour cell and the 20 ampere-hour cell were evaluated statistically. It was established that the data from the 20 ampere-hour cell has a confidence level of 89% and a 90.5% probability that each measurement will be between ±2 standard error. In an experiment in which the mean heat was -1.035 watts the standard error was 0.068 watts.

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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.

During this final reporting period work was performed to answer two questions. The first dealt with heat transfer in and out of the 20 ampere-hour nickel-cadmium cell. Measurements were made on a specially constructed cell equipped with an internal calibration heater and thermocouple.

The second question dealt with the precision of the heat data obtained in previous experiments on the nickel-cadmium cells. Representative data from a 6 ampere-hour and a 20 ampere-hour cell were subjected to the "Students" t test and an evaluation of the standard error.

II. Heat Transfer in Twenty Ampere-hour Ni-Cd Cell

A. Description of Cell

In order to study the manner in which heat is transferred out of a 20 ampere-hour nickel-cadmium cell experiments were performed with a special cell constructed with an internal resistance heater. This cell was a Gulton Industries cell type VO-20 HS Ni-Cd Cell* fabricated with a strip of resistance alloy and an iron--constantan thermocouple. A sketch of this cell is given in figure 1. The resistance measured from point a to b is 0.56 Ω and the resistance of the internal heater is approximately 0.8 Ω. This cell with the exception of the heater and thermocouple is assumed to be similar to the 20 ampere-hour cell upon which previous experiments were performed.

B. Experimental

Following the reassembly of the calorimeter a set of calibration experiments were performed to determine the volume of oil pumped at given flow rates. A series of measurements were made in which oil was pumped through the calorimeter at different stroke rates of a metering pump and samples of oil were collected over a given time interval. The linear relationship between stroke rate (the setting on the pump) and the volume of oil is shown in table 1 and figure 2. This conversion can be used with the data given below.

The thermal response of the cell with the internal heater was measured at a series of different flow rates and thermopile positions. In each case a current of 1.10 amperes, equivalent to an input of 1.10 watts

* Gulton Drawing No. 552-804750, VO 20 HS Cell Assembly With Heater and Thermocouple.

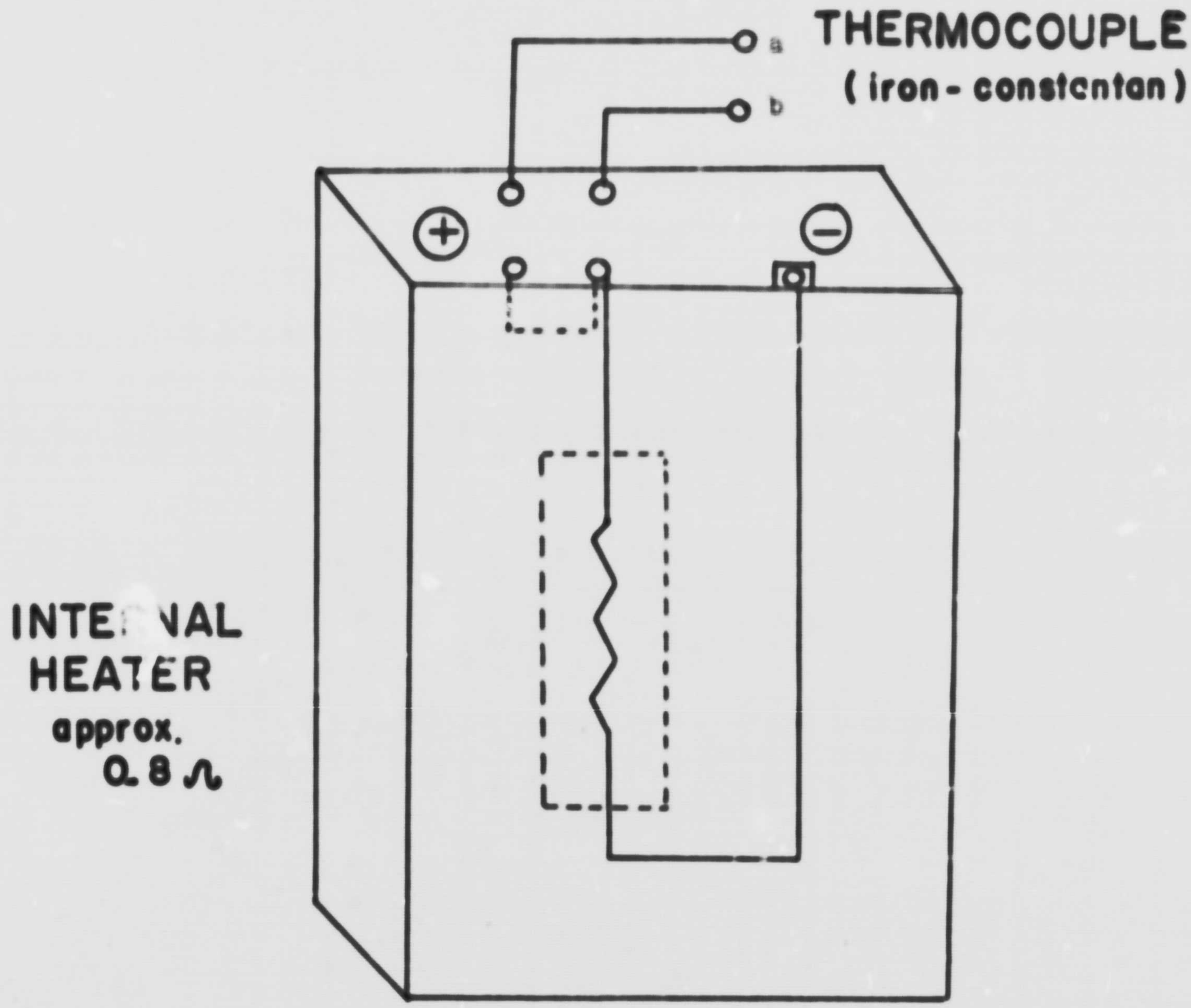

Figure 1. Sketch of special cell with internal calibration heater

TABLE 1. Measurements on Volume of Oil Flow Versus Pump Stroke Rate

STROKE RATE (%)	VOLUME(ml)	TIME (sec)
50	450	10
50	450	10
50	450	10
40	365	10
40	375	10
40	360	10
30	290	10
30	290	10
30	290	10
20	170	10
20	170	10
20	170	10

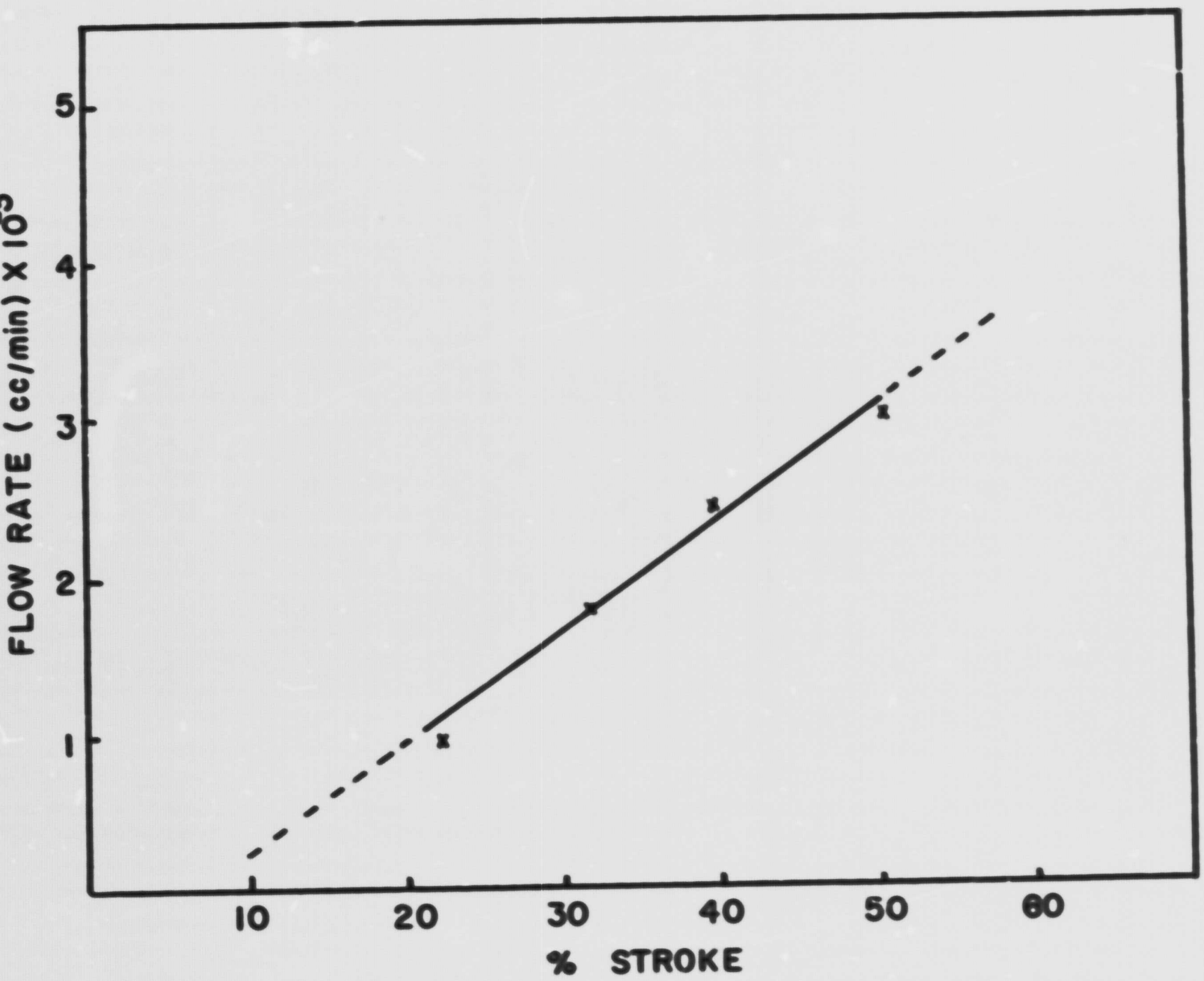

Figure 2. Flow rate of oil through calorimeter versus percent pump stroke

was applied to the heater and the millivolt response was measured over a period of time until a steady state was achieved. In tables 2, 3, and 4 measurements are given for three thermopile positions, 0", 1/4", and 1/2" respectively. These latter figures indicate the positioning of the thermopile with respect to the exit port of the calorimeter, e.g. 1/4" indicates that the end of the thermopile was located 1/4 inch from the exit port.

Inspection of table 2-4 indicates that the signal was higher than that observed in calibration experiments wherein a heater wire was located beneath the cell in the calorimeter. Tables 5 and 6 are taken from the Eighth Progress Report (1) for comparison. In this previous series of experiments a typical response was 40 mv/watt. The calorimeter response to the internal heater was 100-150 mv/watt. On the other hand the response time in the latter case is considerably longer. A typical response in 5 minutes was 20-25% of the signal achieved at the plateau (after 30-50 minutes). There is no obvious explanation to the non-linear behavior associated with the positioning of the thermopile, i.e. the response at 1/4" is not half way between that of 0" and 1/2". At this time it can only be assigned to the pattern of oil flow within the calorimeter.

C. Conclusions

The purpose in testing a cell with an internal heater was to provide a method of calibration that more closely resembled that of the actual operating cell. It is obvious that the internal heater operates more efficiently in the sense of sensing all of the heat put in. However, the internal heater must heat the entire cell before a plateau is reached in the signal and in this sense does not reproduce the mechanism as it occurs in the operating cell. In the cell as it is supplying electrical

TABLE 2. Flow rate and thermal response at a setting of 0" (30 min)

Signal (mv)	% Stroke	Response (% 5 min)
80	65	12.5
97.5	60	15.8
187.5	50	13.2
175.0	40	14.3
200.0	30	15.0

TABLE 3. Flow rate and thermal response at a setting of 1/4" (40-50 min)

Signal (mv)	% Stroke	Response (% in 5 min)
35	65	10
92.5	60	13.5
80	50	12.5
137.5	40	17
157.5	30	20.5

TABLE 4. Flow rate and thermal response at a setting of 1/2" (near 30 min)

Signal (mv)	% Stroke	Response (% in 5 min)
102.5	60	20.5
145	50	25.8
145	40	25.8
162.5	30	22.3

TABLE 5. Relationship between flow rate and thermal response at 1/8" setting (1.13 watt input)

Signal (mv)	% 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 6. 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

energy the heat is generated at the electrodes and heat is only involved after the electrically generated heat has supplied the heat sufficient to meet the heat capacity requirements of the cell materials. The main point here is that we are interested in the heat as it appears at the cell wall. The response time indicated in tables 2-4 can not be tied to the battery cycling without taking into account the heat capacity of the material within the cell.

III. Statistical Evaluation of Data

A. Assumptions

Any evaluation or interpretation of the calorimetric data on the project must be restricted by the precision and accuracy of the experiments. The only previous attempt to establish the internal consistency of the data was that given in the First Progress Report (2) wherein a number of tables of data were reported and the inspection of which indicated a good reproducibility of the experimental measurements. Because of this indication of reproducibility the data for the six ampere-hour cell is taken as standard or reference data. In order to make a comparison between the 6 ampere-hour cell and the 20 ampere-hour cell it was assumed that there were no factors involved in the manufacture of either type of cell that affects the reproducibility of operation of cells in a comparative sense.

B. Statistical Treatment

The data shown in tables 7 and 8 were taken from previously reported experiments on the 6 ampere-hour and 20 ampere-hour cells respectively (2,3). They were both conducted at 25% depth of discharge and 110% rate of charge and represent typical runs. In these tables "x" is the heat absorbed in watts; the subscript indicates a particular cycle.

The evaluation of the data for the two cells was begun by using the "Student's" t test. The application of the t test to the data shown in table 7 and 8 allows a statement to be made concerning the differences between the 6 ampere-hour cell and the 20 ampere-hour cell. By the calculation of the values for t it can be concluded that the probability

TABLE 7. Selected data from 25% depth of discharge experiments on the 6 ampere-hour nickel-cadmium cell.

(Taken from reference 2)

DISCHARGE

Time	x_1	x_2	x_3	x_4	x_5	x_6
10	-0.66	-0.66	-0.66	-0.66	-0.66	-0.66
20	-0.63	-0.[illegible]	-0.64	-0.63	-0.62	-0.63
30	-0.58	-0.59	-0.60	-0.58	-0.58	-0.59

CHARGE

Time	x_1	x_2	x_3	x_4	x_5	x_6
10	-0.15	-0.14	-0.14	-0.14	-0.13	-0.10
20	+0.04	+0.06	+0.06	+0.04	+0.05	+0.06
30	+0.10	+0.10	+0.10	+0.08	+0.10	+0.11
40	+0.09	+0.11	+0.09	+0.10	+0.11	+0.10
50	+0.05	+0.06	+0.06	+0.04	+0.06	+0.02

TABLE 8. Selected data from 25% depth of discharge experiments on the 20 ampere-hour nickel-cadmium cell.

(Taken from reference 3)

DISCHARGE

Time	x_1	x_2	x_3	x_4	x_5	x_6
10	-1.04	-0.95	-1.10	-0.95	-1.15	-1.04
20	-1.25	-1.22	-1.30	-1.30	-1.35	-1.25
30	-1.25	-1.25	-1.35	-1.35	-1.37	-1.27

CHARGE

Time	x_1	x_2	x_3	x_4	x_5	x_6
10	-0.75	-0.69	-0.77	-0.80	-0.95	-0.79
20	-0.27	-0.25	-0.32	-0.29	-0.35	-0.29
30	-0.05	0.00	-0.07	-0.05	-0.07	-0.05
40	+0.07	+0.07	+0.05	+0.07	+0.07	+0.07
50	+0.05	+0.01	+0.01	0.00	+0.01	0.00

of being wrong in saying that a definite difference exists between the 6 ampere-hour cell and the 20 ampere-hour cell each of the times tested is $\ll 0.01$. Table 9 shows the probability taken for four points of three sets of data, i.e. three cycles labeled A, B, and C successively. The relation used in calculating the value for t is the one used for the comparison of unpaired variables,

$$t = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\frac{\Sigma(x_{1i} - \bar{x}_1)^2 + \Sigma(x_{2i} - \bar{x}_2)^2}{N_1 + N_2 - 2}\left(\frac{1}{N_1} + \frac{1}{N_2}\right)}}$$

wherein

x_{1i} = individual measurement from 20 ampere-hour data

x_{2i} = individual measurement from 6 ampere-hour data

$\bar{x}_1$ = mean of the 20 ampere-hour measurements

$\bar{x}_2$ = mean of the 6 ampere-hour measurements

N_1 = number of measurements of x_1 variables

N_2 = number of measurements of x_2 variables

The comparison of t (calculated) with t (tabulated) shows it be greater in every case. This indicates that a probability of $\ll 0.01$ that differences between the two cells was by chance only.

The second test performed on the data was a measure of the standard error (S.E.) of the averages. For the number of measurements taken, the data exhibited a 89% confidence level for 2 S.E. The probability that each measurement will fall between $\pm$ 2 S.E. is 90.5%. (5). Table 10 gives the standard error calculations for the six sets of data taken from table 7 for the 6 ampere-hour cell and table 11 for the 20 ampere-hour cell (table 8 data).

TABLE 9. Evaluation of "t" for four points

25% DOD 20Ah Discharge

	x_{1_A}	x_{1_B}	x_{1_C}	$\bar{x}_1$	$t_{calc.}$	$t_{tab.(0.01)(ref\ 4)}$	P
t_5	-0.17	-0.25	-0.12	-0.18	14.7	3.143	< 0.01
t_{10}	-0.51	-0.61	-0.48	-0.53	5.94	3.143	< 0.01
t_{20}	-0.82	-0.90	-0.82	-0.85	6.01	3.143	< 0.01
t_{30}	-0.90	-1.00	-0.90	-0.93	9.24	3.143	< 0.01

25% DOD 6Ah Discharge

	x_{2_A}	x_{2_B}	x_{2_C}	$\bar{x}_2$
t_5	-0.74	-0.75	-0.75	-0.75
t_{10}	-0.76	-0.76	-0.76	-0.76
t_{20}	-0.68	-0.66	-0.69	-0.68
t_{30}	-0.60	-0.60	-0.62	-0.61

In these tables the variance was calculated as

$$\sigma_i^2 = \sum_{i=1}^{i=6} (x_{ii} - \bar{x}_i)^2$$

and the standard error

$$S.E. = \frac{\sigma_i}{\sqrt{N}}$$

The precision of each measurement of this type is represented by the standard error given in the 4th column of the tables. The data for the 6 ampere-hour cell has been assumed to be the standard or reference data and thus the standard errors given in table 10 is considered to be the experimental error for a measurement of this type.

C. Conclusions

In comparing the 20 ampere-hour data there are two significant factors, the first, a larger cell was tested and secondly, a larger calorimeter was used. The calculations from table 9 indicate that there is an inherent difference between the 6 and 20 ampere-hour cells. There is no indication that the precision involved in using the larger calorimeter will be less than that with the smaller. The significant conclusion drawn from this study is that the data from the previous reports on the calorimetry of the 20 ampere-hour nickel-cadmium cell has a confidence level of 89% and a 90.5% probability that each measurement will be between $\pm$ 2 standard error.

Table 10. Standard Errors of the Averages for the 6 ampere-hour data

Time (Min)	Mean ($\bar{x}_1$)	(σ_1^2) Variance	(σ_1)	Standard Error (S.E.)	$\bar{x}_1 \pm 2$ S.E.
Discharge					
10	-0.660	0.00	0.00	0.00	-0.660 ± 0
20	-0.632	2.8×10^{-4}	0.0167	0.0068	-0.623 ± 0.0136
30	-0.587	9.7×10^{-4}	0.0031	0.0013	-0.587 ± 0.0026
Charge					
10	-0.133	15×10^{-4}	0.0387	0.0158	-0.133 ± 0.0316
20	+0.051	4.8×10^{-4}	0.0221	0.0091	$+0.051 \pm 0.0182$
30	+0.081	22×10^{-4}	0.0496	0.0192	$+0.081 \pm 0.0384$
40	+0.085	17×10^{-4}	0.0412	0.0168	$+0.085 \pm 0.0336$
50	+0.046	13×10^{-4}	0.0360	0.0147	$+0.046 \pm 0.0294$

Table 11. Standard Errors of the Averages for the 20 ampere-hour data

Time (min)	Mean ($\bar{x}$)	Variance (σ^2)	(σ)	Standard Error (S.E.)	$\bar{x} \pm 2$ S.E.
Discharge					
10	-1.035	0.0277	0.1664	0.068	-1.055 ± 0.136
20	1.275	0.0085	0.0922	0.0377	-1.275 ± 0.075
30	-1.300	0.0126	0.1122	0.0459	-1.300 ± 0.092
Charge					
10	-0.792	0.0278	0.1670	0.0682	-0.542 ± 0.1364
20	-0.288	0.0064	0.0800	0.0320	-0.288 ± 0.0640
30	-0.028	0.0043	0.0655	0.0268	-0.028 ± 0.0536
40	+0.066	0.0003	0.0175	0.0070	+0.066 ± 0.0140
50	+0.011	0.0017	0.0412	0.0168	+0.011 ± 0.0336

References

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2. W. H. Webster and R. T. Foley, First Progress Report, on Contract NAS 5-10105, January 1, 1966 - September 30, 1966.

3. R. T. Foley, G. D. Mitchell and G. N. Roberts, Seventh Progress Report on Contract NAS 5-10105, January 1, 1968 - March 31, 1968.

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