# SEVENTH PROGRESS REPORT

## FOR

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

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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.

The work completed during this period is divided into three tasks, the cycling of a 20 ampere-hour Ni-Cd cell, a charge conditioning and overcharge experiment, and a "trickle" charge experiment. The maximum exothermic output exhibited during the cycling of the 20 ampere-hour Ni-Cd cell (30 minutes discharge at 25% depth and 60 minutes charge at 110% recharge rate) was 1.3 watts. During the charge conditioning and overcharge experiment the cell was charged for a 30-hour period at c/10 or 2 amperes. The heat, pressure, and enthalpy all reached a steady state after about 20 hours. The "trickle" charge experiment was conducted with currents ranging from 2 amperes to 0.14 amp. The ratio of heat energy out to electrical energy in during this set of experiments, ranged from 60% to 132%, increasing with decreasing charging current.

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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 reporting period the main emphasis has been on the performance of experimental work. A 20 ampere-hour Ni-Cd cell was cycled through 90 minute orbits at a 25% depth of discharge and a 110% rate of recharge. The experimentally obtained values for the heat generated during the cycle were compared with results reported in the Fifth Progress Report (1).

In addition to the cycling experiments a number of "trickle charge" experiments were performed on the fully charged cell. Charging rates varying from c/10 to c/140 were used.

For these cycling experiments and trickle charge experiments apparent enthalpies of reaction were calculated for the cell reaction with the objective of using the deviation from theoretical as the basis for interpreting any unusual behavior of the cell.

## II. CYCLING EXPERIMENT ON THE 20 AMPERE-HOUR CELL

Some experimental data were reported in the Fifth Progress Report (1) involving a Gulton Industries type VO-20 HS AD Ni-Cd cell cycled a a 25% depth of discharge and recharged at a rate of 110%. The heat generated during discharge reached the unusually high value of about 4 watts.

Cycling experiments were continued with another similar cell with the same manufacturer's serial No. 233. The experimental data are presented in tables 1-6 in a tabulation similar to that used in previous reports. A representative cycle is plotted in figure 1. The maximum heat generated during discharge is about 1.3 watts, much lower than the previous 4 watt value. The lower 1.3 watt figure is considered more reasonable or more representative of the behavior of a 20 ampere-hour cell on the basis of other experiments at a higher temperature and experiments at different depths of discharge. Also this figure can be reconciled with a maximum heat output of 0.7 watt observed for the 6 ampere-hour cell (2).

The difference in maximum heat generated by the two cells is difficult to explain. After examining many possible explanations it is concluded that both sets of data are correct and the difference lies in the lack of reproducibility from cell to cell, this even considering the fact that the cells were of the same manufacturer's serial number.

The previous cell which generated the 4.0 watts during discharge had other unusual characteristics such as a reluctance to accept overcharge rates and a tendency to build up excessive gas pressure during charging. For example, the cell whose performance is reported in tables 1-6 usually reached a maximum (oxygen) pressure of 12-14 P.S.I.A. as compared to 39.5 P.S.I.A. exhibited by the cell with the higher heat output. Or, during

EXPERIMENTAL SERIES H

Table 1

Orbit #36

1) 30 min. d.c. at 10.00 amp. for 25% D.O.D. 25°C

2) 62 min. c. at 5.50 amp. for 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 | -0.45 | 1.36 | -13.6 | -14.1 | -32.6 | 52 | 13.5 | 105 |
| 5 | -0.88 | 1.30 | -13.0 | -13.9 | -32.1 | 49 | 12.0 | 100 |
| 10 | -0.95 | 1.28 | -12.8 | -13.8 | -31.9 | 43 | 10.5 | 95 |
| 15 | -1.13 | 1.26 | -12.6 | -13.7 | -31.6 | 37 | 9.1 | 81 |
| 20 | -1.22 | 1.25 | -12.5 | -13.7 | -31.6 | 33 | 8.0 | 75 |
| 25 | -1.25 | 1.24 | -12.4 | -13.6 | -31.4 | 29 | 7.3 | 65 |
| 30 | -1.25 | 1.22 | -12.2 | -13.5 | -31.2 | 26 | 6.3 | 58 |
| **Charge** | | | | | | | | |
| 0 | -1.25 | 1.28 | +7.04 | +5.79 | +24.3 | 26 | 6.3 | 80 |
| 5 | -1.04 | 1.32 | +7.26 | +6.22 | +26.1 | 25 | 6.0 | 70 |
| 10 | -0.69 | 1.34 | +7.37 | +6.68 | +27.9 | 23 | 5.7 | 65 |
| 20 | -0.23 | 1.36 | +7.48 | +7.25 | +30.4 | 20 | 4.8 | 55 |
| 25 | -0.11 | 1.38 | +7.59 | +7.48 | +31.4 | 19 | 4.5 | 50 |
| 30 | 0.00 | 1.38 | +7.59 | +7.59 | +31.8 | 18 | 4.4 | 45 |
| 35 | +0.05 | 1.39 | +7.65 | +7.70 | +32.6 | 18 | 4.4 | 45 |
| 40 | +0.07 | 1.40 | +7.70 | +7.77 | +32.6 | 17 | 4.1 | 44 |
| 45 | +0.07 | 1.42 | +7.81 | +7.88 | +33.0 | 20 | 4.8 | 45 |
| 50 | +0.01 | 1.42 | +7.81 | +7.82 | +32.8 | 23 | 5.7 | 56 |
| 55 | -0.11 | 1.44 | +7.92 | +7.81 | +32.7 | 30 | 7.4 | 80 |
| 60 | -0.39 | 1.48 | +8.14 | +7.75 | +32.5 | 42 | 10.4 | 115 |
| 62 | -0.45 | 1.50 | +8.25 | +7.80 | +32.7 | 52 | 13.5 | 155 |

EXPERIMENTAL SERIES H

Table 2

Orbit #37

1) 30 min. d.c. at 10.00 amp. for 25% D.O.D. 25°C
2) 62 min. c. at 5.50 amp. for 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 | -0.45 | 1.40 | -14.0 | -14.5 | -33.5 | 56 | 14.0 | 105 |
| 5 | -0.83 | 1.30 | -13.0 | -13.8 | -31.9 | 54 | 13.3 | 148 |
| 10 | -1.10 | 1.20 | -12.0 | -13.1 | -30.3 | 48 | 11.9 | 130 |
| 15 | -1.25 | 1.27 | -12.7 | -13.9 | -32.1 | 41 | 10.1 | 127 |
| 20 | -1.30 | 1.25 | -12.5 | -13.8 | -31.9 | 36 | 9.0 | 100 |
| 25 | -1.33 | 1.24 | -12.4 | -13.7 | -31.6 | 32 | 12.9 | 87 |
| 30 | -1.33 | 1.23 | -12.3 | -13.6 | -31.4 | 28 | 7.1 | 75 |
| Charge | | | | | | | | |
| 0 | -1.30 | 1.29 | +7.09 | +5.79 | +24.3 | 28 | 7.0 | 100 |
| 5 | -1.15 | 1.31 | +7.20 | +6.05 | +25.3 | 26 | 6.3 | 82 |
| 10 | -0.77 | 1.33 | +7.32 | +6.55 | +27.4 | 24 | 5.8 | 73 |
| 15 | -0.53 | 1.35 | +7.42 | +6.89 | +28.9 | 22 | 5.4 | 58 |
| 20 | -0.32 | 1.36 | +7.48 | +7.16 | +30.0 | 20 | 4.8 | 50 |
| 25 | -0.12 | 1.37 | +7.54 | +7.42 | +31.1 | 19 | 4.5 | 44 |
| 30 | -0.07 | 1.38 | +7.59 | +7.52 | +31.5 | 18 | 4.4 | 40 |
| 35 | +0.01 | 1.39 | +7.65 | +7.66 | +32.1 | 18 | 4.4 | 37 |
| 40 | +0.05 | 1.40 | +7.70 | +7.75 | +32.5 | 18 | 4.4 | 36 |
| 45 | +0.05 | 1.41 | +7.75 | +7.80 | +32.7 | 19 | 4.5 | 40 |
| 50 | +0.01 | 1.42 | +7.81 | +7.82 | +32.7 | 22 | 5.4 | 50 |
| 55 | -0.08 | 1.44 | +7.92 | +7.84 | +32.8 | 30 | 7.4 | 77 |
| 60 | -0.29 | 1.47 | +8.09 | +7.80 | +32.7 | 42 | 10.4 | 115 |
| 62 | -0.40 | 1.49 | +8.10 | +7.79 | +32.6 | 50 | 12.4 | 146 |

EXPERIMENTAL SERIES H

Table 3

Orbit #38

1) 30 min. d.c. at 10.00 amp. for 25% D.O.D. 25°C

2) 62 min. c. at 5.50 amp. for 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 | 1.34 | -13.4 | -13.8 | -31.9 | 52 | 13.5 | 90 |
| 5 | -0.80 | 1.30 | -13.0 | -13.8 | -31.9 | 49 | 12.0 | 140 |
| 10 | -0.95 | 1.28 | -12.8 | -13.8 | -31.9 | 42 | 10.4 | 125 |
| 15 | -1.25 | 1.26 | -12.6 | -13.9 | -32.1 | 37 | 9.1 | 110 |
| 20 | -1.30 | 1.25 | -12.5 | -13.8 | -31.9 | 32 | 12.9 | 95 |
| 25 | -1.33 | 1.23 | -12.3 | -13.6 | -31.4 | 29 | 7.3 | 85 |
| 30 | -1.33 | 1.22 | -12.2 | -13.5 | -31.9 | 26 | 6.3 | 70 |
| **Charge** | | | | | | | | |
| 0 | -1.33 | 1.28 | +7.04 | +5.71 | +23.9 | 26 | 6.3 | 100 |
| 5 | -1.15 | 1.32 | +7.28 | +6.31 | +25.7 | 24 | 5.8 | 73 |
| 10 | -0.80 | 1.34 | +7.37 | +6.57 | +27.5 | 22 | 5.4 | 60 |
| 15 | -0.50 | 1.36 | +7.48 | +6.98 | +29.5 | 20 | 4.8 | 50 |
| 20 | -0.29 | 1.37 | +7.54 | +7.25 | +30.4 | 19 | 4.5 | 45 |
| 25 | -0.12 | 1.38 | +7.59 | +7.47 | +31.3 | 18 | 4.4 | 40 |
| 30 | -0.03 | 1.39 | +7.65 | +7.62 | +31.9 | 18 | 4.4 | 35 |
| 35 | +0.01 | 1.40 | +7.70 | +7.71 | +32.3 | 18 | 4.4 | 35 |
| 40 | +0.07 | 1.41 | +7.75 | +7.82 | +32.8 | 19 | 4.5 | 37 |
| 45 | +0.07 | 1.42 | +7.81 | +7.88 | +33.0 | 21 | 5.3 | 45 |
| 50 | 0.00 | 1.44 | +7.92 | +7.92 | +33.2 | 25 | 6.0 | 63 |
| 55 | -0.12 | 1.46 | +8.03 | +7.97 | +33.4 | 34 | 8.4 | 93 |
| 60 | -0.32 | 1.43 | +8.14 | +7.82 | +32.8 | 43 | 10.5 | 125 |
| 62 | -0.50 | 1.50 | +8.25 | +7.75 | +32.5 | 58 | 14.4 | 178 |

EXPERIMENTAL SERIES H

Table 4

Orbit #39

1) 30 min. d.c. at 10.00 amp. for 25% D.O.D. 25°C

2) 62 min. c. at 5.50 amp. for 110% R.C.

| Time (hours) | q (watts) | E (volts) | W (watts) | ΔH (watts) | ΔH (kcal/equiv) | Pressure Transducer(mv) | Pressure (psia) | Adhydrode (mv) |
|---|---|---|---|---|---|---|---|---|
| **Discharge** | | | | | | | | |
| 0 | -0.50 | 1.34 | -13.4 | -13.9 | -32.1 | 58 | 14.4 | 150 |
| 5 | -0.83 | 1.30 | -13.0 | -13.8 | -31.9 | 56 | 14.0 | 163 |
| 10 | -1.13 | 1.28 | -12.8 | -13.9 | -32.1 | 48 | 11.9 | 145 |
| 15 | -1.30 | 1.26 | -12.6 | -13.9 | -32.1 | 41 | 10.1 | 127 |
| 20 | -1.33 | 1.25 | -12.5 | -13.8 | -31.9 | 36 | 9.0 | 110 |
| 25 | -1.37 | 1.24 | -12.4 | -13.8 | -31.9 | 32 | 12.9 | 94 |
| 30 | -1.37 | 1.23 | -12.3 | -13.7 | -31.6 | 28 | 7.0 | 80 |
| **Charge** | | | | | | | | |
| 0 | -1.37 | 1.29 | +7.09 | +5.72 | +24.0 | 28 | 7.0 | 100 |
| 5 | -1.13 | 1.32 | +7.26 | +6.13 | +25.7 | 26 | 6.3 | 78 |
| 10 | -0.95 | 1.34 | +7.37 | +6.42 | +26.9 | 24 | 5.8 | 67 |
| 15 | -0.80 | 1.35 | +7.43 | +6.63 | +27.8 | 22 | 5.4 | 60 |
| 20 | -0.33 | 1.35 | +7.43 | +7.10 | +29.7 | 21 | 5.0 | 52 |
| 25 | -0.17 | 1.36 | +7.48 | +7.31 | +30.6 | 19 | 4.5 | 45 |
| 30 | -0.07 | 1.38 | +7.59 | +7.52 | +31.5 | 19 | 4.5 | 40 |
| 35 | +0.01 | 1.39 | +7.65 | +7.53 | +31.6 | 19 | 4.5 | 37 |
| 40 | +0.07 | 1.40 | +7.70 | +7.77 | +32.6 | 19 | 4.5 | 35 |
| 45 | +0.07 | 1.41 | +7.75 | +7.82 | +32.8 | 20 | 4.8 | 37 |
| 50 | +0.01 | 1.42 | +7.81 | +7.82 | +32.8 | 22 | 5.4 | 45 |
| 55 | -0.08 | 1.44 | +7.92 | +7.84 | +32.8 | 28 | 7.0 | 70 |
| 60 | -0.32 | 1.46 | +8.03 | +7.71 | +32.3 | 36 | 9.0 | 105 |
| 62 | -0.42 | 1.49 | +8.19 | +7.77 | +32.6 | 40 | 9.9 | 150 |

EXPERIMENTAL SERIES H

Table 5

Orbit #40

1) 30 min. d.c. at 10.00 amp. for 25% D.O.D. 25°C

2) 62 min. c. at 5.50 amp. for 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 | -32.3 | 52 | 13.5 | 100 |
| 5 | -0.75 | 1.30 | -13.0 | -13.8 | -31.9 | 50 | 12.4 | 155 |
| 10 | -1.04 | 1.28 | -12.8 | -13.8 | -31.9 | 44 | 10.9 | 137 |
| 15 | -1.15 | 1.27 | -12.7 | -13.9 | -32.1 | 39 | 9.6 | 120 |
| 20 | -1.25 | 1.25 | -12.5 | -13.8 | -31.9 | 34 | 7.9 | 105 |
| 25 | -1.27 | 1.23 | -12.3 | -13.6 | -31.4 | 30 | 7.4 | 88 |
| 30 | -1.27 | 1.22 | -12.0 | -13.3 | -30.7 | 26 | 6.3 | 78 |
| **Charge** | | | | | | | | |
| 0 | -1.27 | 1.29 | +7.09 | +5.82 | +24.4 | 26 | 6.3 | 100 |
| 5 | -0.95 | 1.32 | +7.26 | +6.31 | +26.4 | 24 | 5.8 | 77 |
| 10 | -0.79 | 1.34 | +7.37 | +6.68 | +28.0 | 22 | 5.4 | 70 |
| 15 | -0.47 | 1.35 | +7.43 | +7.00 | +29.3 | 21 | 5.0 | 51 |
| 20 | -0.29 | 1.36 | +7.48 | +7.19 | +30.1 | 22 | 5.4 | 43 |
| 25 | -0.12 | 1.37 | +7.54 | +7.42 | +31.1 | 19 | 4.5 | 38 |
| 30 | -0.03 | 1.38 | +7.59 | +7.56 | +31.7 | 18 | 4.4 | 36 |
| 35 | +0.01 | 1.39 | +7.64 | +7.65 | +32.1 | 18 | 4.4 | 36 |
| 40 | +0.07 | 1.41 | +7.75 | +7.82 | +32.7 | 19 | 4.5 | 35 |
| 45 | +0.05 | 1.41 | +7.75 | +7.80 | +32.7 | 21 | 5.0 | 36 |
| 50 | 0.00 | 1.43 | +7.87 | +7.87 | +33.0 | 24 | 5.8 | 40 |
| 55 | -0.12 | 1.45 | +7.98 | +7.86 | +32.9 | 33 | 8.6 | 51 |
| 60 | -0.36 | 1.49 | +8.20 | +7.84 | +32.8 | 46 | 11.4 | 95 |
| 62 | -0.47 | 1.50 | +8.25 | +7.78 | +32.6 | 58 | 14.4 | 155 |

EXPERIMENTAL SERIES H

Table 6

Orbit #42

1) 30 min. d.c. at 10.00 amp. for 25% D.O.D. 25°C

2) 62 min. c. at 5.50 amp. for 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 | -32.3 | 53 | 13.0 | 110 |
| 5 | -0.80 | 1.30 | -13.0 | -13.8 | -31.9 | 50 | 12.4 | 160 |
| 10 | -1.04 | 1.28 | -12.8 | -13.8 | -31.9 | 45 | 11.2 | 140 |
| 15 | -1.22 | 1.26 | -12.6 | -13.8 | -31.9 | 38 | 9.3 | 120 |
| 20 | -1.25 | 1.25 | -12.5 | -13.8 | -31.9 | 34 | 8.2 | 105 |
| 25 | -1.25 | 1.23 | -12.3 | -13.6 | -31.4 | 30 | 7.4 | 90 |
| 30 | -1.25 | 1.22 | -12.2 | -13.5 | -31.2 | 28 | 7.0 | 76 |
| Charge | | | | | | | | |
| 0 | -1.25 | 1.22 | +6.71 | +5.46 | +22.9 | 24 | 5.8 | 103 |
| 5 | -1.04 | 1.32 | +7.26 | +6.22 | +27.7 | 22 | 5.4 | 73 |
| 10 | -0.75 | 1.34 | +7.37 | +6.62 | +27.7 | 21 | 5.0 | 63 |
| 15 | -0.32 | 1.35 | +7.43 | +7.11 | +29.8 | 19 | 4.5 | 51 |
| 20 | -0.27 | 1.36 | +7.48 | +7.21 | +30.2 | 18 | 4.4 | 44 |
| 25 | -0.11 | 1.37 | +7.54 | +7.43 | +31.1 | 18 | 4.4 | 38 |
| 30 | -0.03 | 1.38 | +7.59 | +7.57 | +31.7 | 18 | 4.4 | 35 |
| 35 | +0.05 | 1.39 | +7.65 | +7.61 | +31.9 | 18 | 4.5 | 34 |
| 40 | +0.07 | 1.41 | +7.76 | +7.83 | +32.8 | 19 | 4.5 | 35 |
| 45 | +0.07 | 1.42 | +7.81 | +7.88 | +33.0 | 20 | 4.8 | 40 |
| 50 | +0.05 | 1.43 | +7.87 | +7.92 | +33.2 | 22 | 5.4 | 62 |
| 55 | -0.08 | 1.45 | +7.98 | +7.90 | +33.1 | 32 | 8.9 | 89 |
| 60 | -0.29 | 1.47 | +8.09 | +7.80 | +32.7 | 43 | 10.6 | 125 |
| 62 | -0.33 | 1.49 | +8.20 | +7.87 | +33.0 | 50 | 12.2 | 150 |

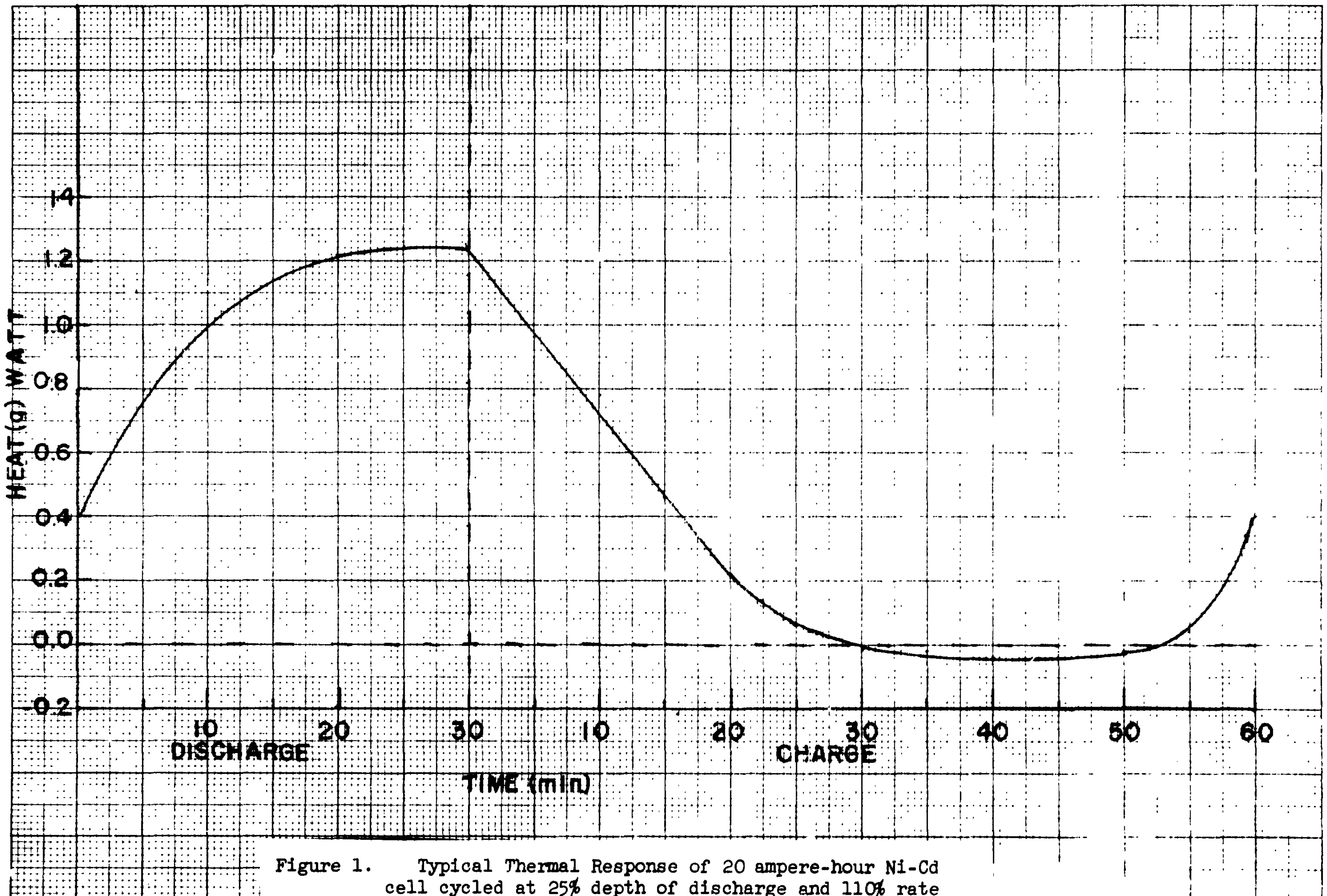


Figure 1. Typical Thermal Response of 20 ampere-hour Ni-Cd cell cycled at 25% depth of discharge and 110% rate of charge (from Table 3). At 25°C

cycling, the cell undergoes a pressure change of 9-10 P.S.I.A. under normal conditions compared with 30-35 P.S.I.A. change for an unusual cell. Thus, high heat generation is associated with excessive gas generation and build-up of pressure within the sealed cell. It seems reasonable to assume that both should be attributed to the same exothermic reaction. It is obvious that the gassing tendency varies from cell to cell and this must be associated with electrode construction, area, etc.

Concerning the other functions, also tabulated in Tables 1-6, the cell voltage goes to a maximum of about 1.50 volts at the end of charge and falls to about 1.22 volts of the end of discharge. It is noted that both the heat output and the cell voltage return to the same point, orbit after orbit, which is a good indication of reproducibility.

Both cell pressure (either as transducer signal or oxygen pressure) and Adhydrode signal also return to about the same value cycle after cycle, but there seems to be less reproducibility in their agreement. The evolution of a small amount of oxygen can change cell pressure and the Adhydrode signal greatly, but not enough to effect much of a change in heat output or cell voltage. In figure 2 the cell pressure as indicated by the pressure transducer and the Adhydrode signal are plotted as a function of time. It is apparent that although the signals follow the same course qualitatively there is no direct proportional correspondence.

$\Delta H$ (in either watts or kcal per equiv.) represents the sum of W, the electrical work, and, q, the heat evolved by the cell. $\Delta H$ is representative of the reaction taking place; if there is but one reaction taking place the enthalpy of the reaction is $\Delta H$. The measurement of $\Delta H$ in this manner is only correct when all the energy put into the cell goes into either the charging reaction or heat evolution. If some of the energy is being used up by one

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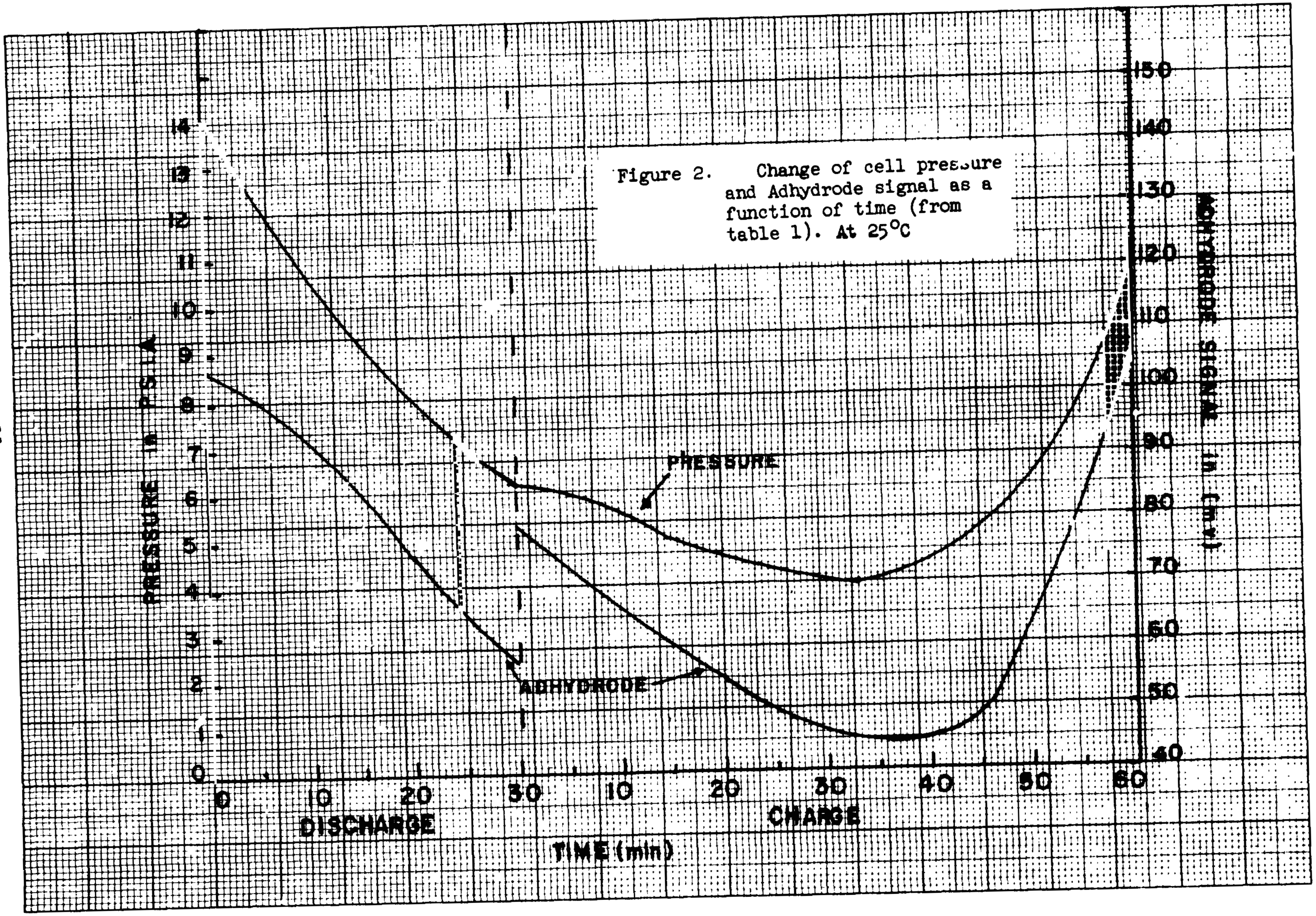


Figure 2. Change of cell pressure and Adhydrode signal as a function of time (from table 1). At 25°C



20 Squares to the Inch

or more additional reactions, $\Delta H$ will not be the true $\Delta H$ for the cell reaction. This was discussed in the Sixth Progress report (3) and the significant relationships will be examined in more detail in future reports.

## III. CONDITIONING AND OVERCHARGE

A new 20 ampere-hour cell (Gulton Industries No. VO-20 HS AD Serial No. 233) was obtained for this series of experiments. The cell was conditioned twice in the following manner: charged for 16 hours at 2 amp; discharged to 1.00 volt at 10 amp; then shorted across a 4 watt, 1-ohm resistor until a potential of zero was reached. During the course of the work one of these conditioning cycles was intentionally lengthened to 30 hours so that it would be possible to observe the cell during an overcharge period of fourteen hours. The data for this experiment are reported in Table 7.

The apparent enthalpy change calculated on the basis of the assumptions given above is plotted as a function of time in figure 3. The enthalpy remains relatively constant during the charging period, then drops, until about twenty hours after which time it levels off and remains constant for the remainder of the charging period. This trend is very possibly due to the fact that during the period up to nine hours the charging reaction predominates and that the enthalpy of this reaction is very close to 32 kcal/equiv. the theoretical value for the cha ging reaction. After nine hours other reactions assume significance. The heat evolved increases continually for the first nineteen hours, as it would in a transient situation such as a cell charging. But finally the heat levels off and becomes constant at twenty hours, signifying the system's arrival at a steady state condition, which continues until the end of the overcharge.

The pressure and Adhydrode data plotted in figure 4 also seem to confirm this view. Both are indicative of a steady state condition being achieved after 19 hours. The cell pressure reaches a steady value while the Adhydrode signal drops probably as a result of the electrode surface becoming saturated.

EXPERIMENTAL SERIES H

Table 7

30-Hour Charge Conditioning

C/10 = 2 Amps    20 Ah Ni-Cd cell    25°C

| Time. (hours) | q (watts) | E (volts) | W (watts) | ΔH (watts) | ΔH (kcal/equiv) | Pressure Trans-ducer(mv) | Pressure (psia) | Adhy-drode (mv) |
|---|---|---|---|---|---|---|---|---|
| 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 8.0 | 2.5 | 0.00 |
| 1 | +0.05 | 1.38 | +2.76 | +2.81 | +32.3 | 10 | 2.5 | 13 |
| 2 | +0.03 | 1.38 | +2.76 | +2.79 | +32.1 | 12 | 3.0 | 14 |
| 3 | +0.02 | 1.38 | +2.76 | +2.78 | +32.0 | 12 | 3.0 | 14 |
| 4 | +0.02 | 1.39 | +2.78 | +2.80 | +32.2 | 12 | 3.0 | 15 |
| 5 | +0.01 | 1.39 | +2.78 | +2.79 | +32.1 | 14 | 3.4 | 15 |
| 6 | 0.00 | 1.40 | +2.80 | +2.80 | +32.2 | 14 | 3.4 | 19 |
| 7 | 0.00 | 1.40 | +2.80 | +2.80 | +32.2 | 16 | 4.0 | 23 |
| 8 | -0.04 | 1.41 | +2.82 | +2.78 | +32.0 | 17 | 4.3 | 25 |
| 9 | -0.04 | 1.41 | +2.82 | +2.78 | +32.0 | 18 | 4.5 | 30 |
| 10 | -0.07 | 1.41 | +2.82 | +2.75 | +31.6 | 18 | 4.5 | 30 |
| 11 | -0.10 | 1.42 | +2.84 | +2.74 | +31.5 | 18 | 4.5 | 40 |
| 12 | -0.12 | 1.42 | +2.84 | +2.72 | +31.3 | 20 | 5.0 | 50 |
| 13 | -0.17 | 1.42 | +2.84 | +2.67 | +30.7 | 20 | 5.0 | 65 |
| 14 | -0.25 | 1.42 | +2.84 | +2.59 | +29.8 | 22 | 5.5 | 85 |
| 15 | -0.42 | 1.43 | +2.86 | +2.44 | +28.1 | 30 | 5.5 | 130 |
| 16 | -0.68 | 1.45 | +2.90 | +2.22 | +25.5 | 53 | 7.5 | 235 |
| 17 | -1.41 | 1.46 | +2.92 | +1.51 | +17.4 | 66 | 13.5 | 310 |
| 18 | -1.70 | 1.46 | +2.92 | +1.22 | +14.0 | 70 | 16.3 | 308 |
| 19 | -1.77 | 1.46 | +2.92 | +1.15 | +13.2 | 72 | 17.3 | 300 |
| 20 | -1.88 | 1.46 | +2.92 | +1.04 | +12.0 | 74 | 17.8 | 297 |
| 21 | -1.88 | 1.46 | +2.92 | +1.05 | +12.0 | 74 | 18.3 | 295 |
| 22 | -1.80 | 1.46 | +2.92 | +1.12 | +12.9 | 74 | 18.3 | 293 |
| 23 | -1.80 | 1.46 | +2.92 | +1.12 | +12.9 | 75 | 18.5 | 290 |
| 24 | -1.80 | 1.46 | +2.92 | +1.12 | +12.9 | 75 | 18.5 | 290 |
| 25 | -1.80 | 1.46 | +2.92 | +1.12 | +12.9 | 75 | 18.5 | 290 |
| 26 | -1.80 | 1.46 | +2.92 | +1.12 | +12.9 | 75 | 18.5 | 270 |
| 27 | -1.80 | 1.46 | +2.92 | +1.12 | +12.9 | 73 | 18.0 | 278 |
| 28 | -1.72 | 1.46 | +2.92 | +1.20 | +13.8 | 75 | 18.5 | 278 |
| 29 | -1.77 | 1.46 | +2.92 | +1.15 | +13.2 | 75 | 18.5 | 277 |
| 30 | -1.80 | 1.46 | +2.92 | +1.12 | +12.9 | 75 | 18.5 | 285 |

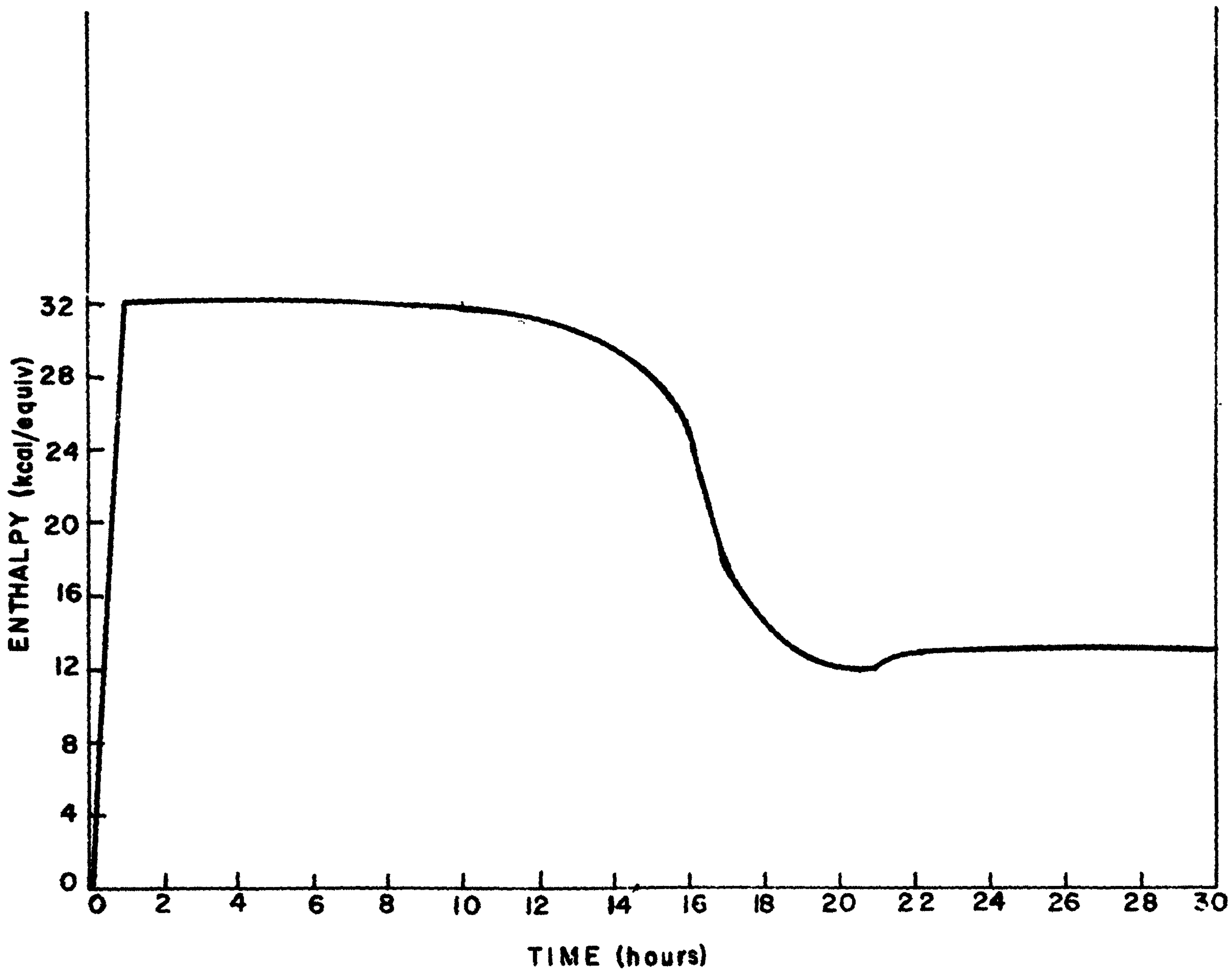


Figure 3. Change in apparent $\Delta H$ during prolonged overcharge (from Table 7) At 25°C

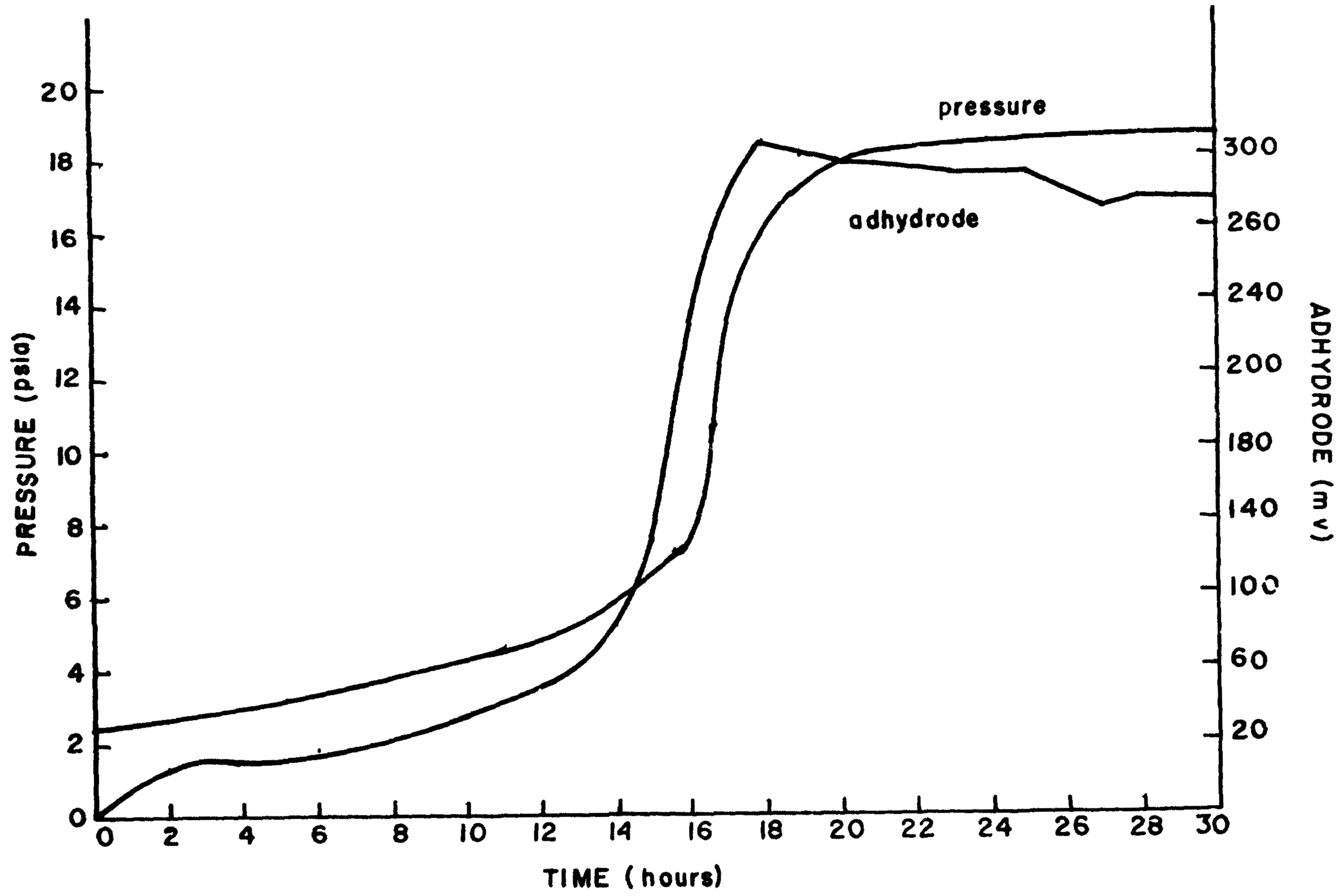


Figure 4. Cell pressure and Adhydrode signal during prolonged overcharge (from Table 7). At 25°C

## IV. TRICKLE CHARGE EXPERIMENTS

The heat evolved from the same Gulton 20 A-H Ni-Cd cell, during overcharge at various charge rates, was measured. These charging currents, or trickle charges, varied from 2.0 amperes to 0.14 amperes. The results of this experiment are tabulated in table 8.

It is apparent that the ratio of heat energy out to electrical energy in rises as the rate of overcharing current is decreased, until at 0.25 ampere the efficiency reaches 100%. At the lowest charge rate, 0.14 amperes, the efficiency was found to be about 132%.

There is no readily available answer as to why or how efficiencies greater than 100% were encountered, but it is postulated that the electrodes are undergoing self-discharge at the lower rates.

Some similar data from another Laboratory have been recently reported and are given in table 9 (4). These efficiencies were obtained for a 35 ampere-hour cell with an adiabatic calorimeter.

From the two tables it is seen that at a charge rate of one ampere the efficiency of the two cells is about equal, but at 0.5 ampere charging current the Gulton cell's efficiency increases while the Lockheed cell's efficiency decreases.

The work reported in table 9 was done at a temperature of about 5°C higher than the work reported in table 8 but this is not thought to be significant.

Figure 5 shows the relationship between efficiency and charge rate (expressed as the fraction: cell capacity C(or 20) divided by a whole number) (i.e., c/40 = 20/40 or .5 amperes).

Table 8

| Charge Rate | Current (amps) | Electrical Energy in (watts) | Heat Out (watts) | Efficiency* (%) | Temperature (°C) |
|---|---|---|---|---|---|
| C/10 | 2.00 | 2.92 | 1.75 | 59.9 | 25 |
| C/20 | 1.00 | 1.43 | 1.05 | 73.4 | 25 |
| C/40 | 0.50 | 0.71 | 0.62 | 87.3 | 25 |
| C/60 | 0.33 | 0.47 | 0.42 | 89.4 | 25 |
| C/80 | 0.25 | 0.35 | 0.35 | 100 | 25 |
| C/100 | 0.20 | 0.28 | 0.31 | 111 | 25 |
| C/140 | 0.14 | 0.19 | 0.25 | 132 | 25 |

* where efficiency is defined as:

$$\frac{\text{heat out}}{\text{electrical energy in}}$$

Table 9

| Charge Rate | Current (amps) | Electrical Energy in (watts) | Heat Out (watts) | Efficiency (%) | Temperature (°C) |
|---|---|---|---|---|---|
| C/32 | 1.0 | 1.42 | 0.98 | 69.0 | 29.8 |
| C/64 | 0.5 | 0.699 | 0.358 | 51.2 | 29.8 |

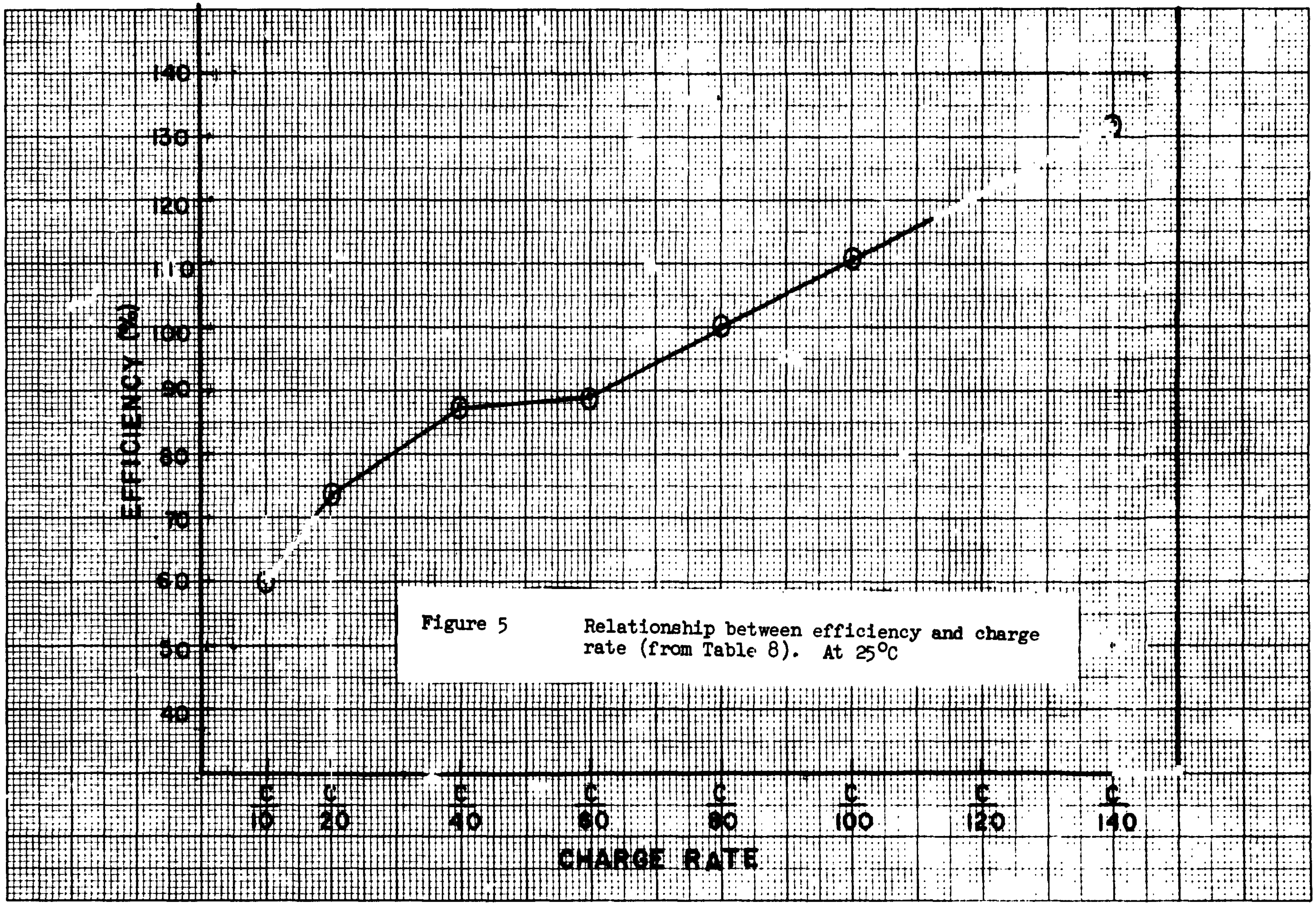


Figure 5 Relationship between efficiency and charge rate (from Table 8). At 25°C

## V. CONCLUSIONS

From the work done during this reporting period it would appear that the maximum thermal output of the 20 ampere-hour cell under the indicated conditions (25% D.O.D., 110% R. C. and 25°C) is about 1.3 watts. This fits in with other experimental observations. On extended overcharge at a C/10 rate a steady state heat of about 1.8 watts is achieved. This is considered to be a net value involving the cell discharge reaction and oxygen cycling in the sealed cell. At lower trickle charge rates the heat drops with current. At a rate of C/80 the electrical energy in matches the thermal energy out.

## VI. FUTURE WORK

It is planned to continue cycling experiments at 25°C with the 20 ampere-hour Ni-Cd cell at depths of discharge of 15% and 40%.

It is also intended to examine the functioning of the Adhydrode electrode particularly from its involvement in the generation of heat and control of oxygen production.

## VII. REFERENCES


(1) G. D. Mitchell and R. T. Foley, Fifth Progress Report For Research Into Fundamental Phenomena Associated With Spacecraft Electrochemical Devices - Calorimetry of Nickel-Cadmium Cells. Contract No. NAS 5-10105, July 1, 1967 - September 30, 1967.

(2) W. H. Webster and R. T. Foley, Second Progress Report, Contract NAS 5-10105, October 1, 1966 - December 31, 1966.

(3) R. T. Foley, G. D. Mitchell, and G. N. Roberts, Sixth Progress Report, Contract NAS 5-10105, October 1, 1967 - December 31, 1967.

(4) Lockheed Fact Report No. 56, "Program 461 RTS-I Thermodynamic Properties of Type VII Battery Cells," August 1965.