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DEVELOPMENT OF A LOW TEMPERATURE BATTERY FOR SPACE PROBE APPLICATIONS

THIRD QUARTERLY REPORT

William F. Meyers, Principal Investigator

December 24, 1964 to March 23, 1965

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-6009

LIVINGSTON ELECTRONIC CORPORATION
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Technical Management
NASA Lewis Research Center
Cleveland, Ohio
Solar and Chemical Power Branch
Mr. Daniel G. Soltis

Livingston Electronic Corporation
Montgomeryville, Pennsylvania

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SUMMARY

The three objectives of this work are to obtain: (I) 72-hour battery performance from liquid ammonia batteries over the temperature range -40°C to -73°C; (II) limited wet stand capabilities to +70°C; and (III) cell performance at -90°C.

During the third quarter, 76 cell tests were conducted over the temperature range of room ambient to -73°C.

Single cells were operated from -73°C to +20°C in excess of the 72-hour requirement as stated for Objective I. Twenty grams of sulfur as an additive to the mercuric sulfate/carbon cathode and the use of partially spent electrolyte have been the stabilizing factors in providing this comparatively long life liquid ammonia battery performance.

Preliminary wet stand tests were conducted at -63°C in order to observe the relative effects of various treatments. Favorable results with the mercuric sulfate/sulfur/carbon cathode were observed by introducing two layers of microporous rubber separation and a very light electrical load. Some indications of wet stand capability were obtained with light load at +20°C, but further work is required in this area. Chemical analyses of the spent electrolyte and gases evolved during the life of two room temperature cells have been conducted; and, though the results are not as yet fully interpreted, the implications are that mercuric sulfate reacts with the electrolyte and that the nitrogen evolved from the cell (cathode local action) is now of significantly greater importance than anode local action.

Equipment suitable for performance of -90°C full-sized cell tests is being constructed.

INTRODUCTION

The primary objective of this program was to obtain 72-hour performance over the temperature range -40°C to -73°C by modification of existing Livingston ammonia battery designs. Effort in this direction during the earlier phases of this work did not provide this. Modifications and testing during the second quarter did provide the major part of this requirement; and during the third quarter, full-sized $Mg/HgSO_4$: S: C cells performed substantially in excess of the required temperature range.

The second objective of this program is to develop limited wet stand capability to an upper temperature of +70°C.

Also in the third quarter, work was initiated on wet stand and the study of the electrochemical and local action mechanisms. Analytical determinations were made of spent electrolyte and the gas evolved from the cells at +20°C. Of considerable interest were the observations that the spent electrolyte did not contain any appreciable quantity of potassium ion, and that the gas evolved was largely nitrogen on an equivalent basis. Further interpretation of the data will be required before the details can be properly presented.

Preliminary wet stand tests have been conducted at -63°C, particularly in the test tube version of the $Mg/HgSO_4$: S: C cell where visual observation was possible. This feature has been particularly helpful in the recent progress of this work.

Magnesium anode stock was vapor-deposited with a thin coating of lead metal. Immersion of these test coupons in electrolyte resulted in a potential of one-half of a volt, reference the $HgSO_4$ cathode, for periods ranging up to five seconds followed by a rapid rise to above two volts. Heavier coatings will apparently be required.

The construction factors of the 76 cell tests run during the third quarter are detailed in Table I-a, starting on page 9, along with the pertinent test data. In Table I-b, starting on page 22, the same tests are re-tabulated by number against the voltage at high and low load after each day for four days of discharge. This method of reporting is especially useful in comparing the performance of various tests. Following the serial presentations of Tables I-a and I-b, these data are abstracted and analyzed as to purpose, type, and major variable.

An Outline of Progress follows for convenience in studying the subsequent tabulations of the experimental work.

OUTLINE OF PROGRESS

1. ANODE: AZ31B sheet 0.025" thick; a favorable compromise between workability and excess magnesium.

2. CATHODE: 1-1/8" nominal diameter best

3. SEPARATORS: Webril M-1365 satisfactory for normal discharge

   Microporous rubber very helpful in wet stand at -63°C (Increased from 41 to 69 hours) (Not tried in wet stand at +20°C)

4. AMOUNT S: With coordination number of 2, 20 grams best.
   With coordination number of 0, 20 grams best.

5. DEGREE OF COORDINATION: 0 grams S at -63°C - coordination unimportant
   0 grams S at -73°C - Diamine superior
   10 grams S at -63°C - coordination unimportant
   20 grams S at -63°C and -73°C - 0 NH_3 distinctly superior
   20 grams S at +20°C - Diamine superior to 0 NH_3

6. CELL TESTS AT +20°C: (72 hours not required by contract)

	Hrs. to 1.3v
Best cell, T-68 = 76 hours to 1.5v 20 g. S, 50% spent, coated anode, activated at -63°C	92
T-90, new electrolyte, coated anode = 52 hours	93
T-62, new electrolyte, not coated = 30 hours	91

   There was a pronounced similarity in the voltages generated by most of the better cells at the end of each day after the first day of discharge. This fact was true under both loads.

7. PROPORTIONS OF $HgSO_4$: S: C: 20 grams S with a $HgSO_4$: C ratio of approximately 7 : 3 best. Increased S and C and decreased $HgSO_4$; increased coulombs/gram. S only reduced hours, but increased coulombs/gram to 900.

8. $HgSO_4$ vs OTHER OXIDANTS: $HgSO_4$ is best, particularly with S at -63°C and -73°C.

OUTLINE OF PROGRESS Continued

9. ADDITION OF SULFATES TO CATHODES: None advantageous

10. ELECTROLYTE STUDIES: Half spent electrolyte useful at +20°C.
Half spent electrolyte decreased the performance slightly at -63°C and more so at -73°C.
17 weight per cent $Mg(SCN)_2$ reasonably good at +20°C and at -63°C.
10 weight per cent KSCN unsatisfactory.
50 weight per cent KSCN gave long life, but lower voltages under heavy load.
25 weight per cent best for most low temp. cells.

11. REPRODUCIBILITY: Average variation between pairs to 1.5 v was 9 per cent.

12. ACTIVATED STAND: Most of the preliminary wet stand tests were conducted at -63°C in order to observe the relative effects of various treatments. The best results were obtained with Cell No. T-107:
Cathode: 106 g. $HgSO_4 \cdot 0\, NH_3$, 20 g. S, 60 g. carbon
Separators: M-1365 Webril paper + double layer of MPR
Load during stand: 2700Ω
After a 65-hour wet stand, cell ran 69 hours to 1.5 volt under the required cyclic loading.
Cell No. T-109 was subjected to a 65-hour wet stand at +20°C. When discharged under cyclic loading at -63°C, it ran only 3 hours to 1.3v and 75 hours to 0.80 v.

The investigation of other electrolytes and oxidants is indicated.

NOTES AND CODE TO TABLE I-a

[1] TT = Pyrex Test Tube

[2] Loads shown as A/B represent cyclic loads of AΩ for 6 minutes and BΩ for 54 minutes

[3] M-1365 Webril in multiple layers, 0.004"/layer

[4] After 23 hours, added KSCN

[5] Coordination No. 0 = $HgSO_4$
No. 2 = $HgSO_4 \cdot 2NH_3$ (ammoniated)
No. 4 = $HgSO_4 \cdot 4NH_3$ (slaked)

[6] "Oxidants" includes major oxidant, sulfur and additive if an oxidant

[c] anode coated on outside with rubber cement

[d] pure magnesium anode

[e] cell life = 3 hours to 1.3 volts; 75 hours to 0.80 volts, based on heavy load

*based on lighter load

**cumulative hours, based on heavy load

Electrolyte Code:

A - 25 weight percent KSCN in liquid ammonia

B - 50 percent spent electrolyte from similar discharged cell, plus 50 percent of (A)

C - liquid ammonia

D - 80 percent spent electrolyte plus 20 percent liquid ammonia

E - 10 weight percent KSCN in liquid ammonia

NOTES AND CODE TO TABLE I-a Continued

Electrolyte Code Continued:

F - 12.5 weight percent $Mg(SCN)_2$ in liquid ammonia; saturated $MgSO_4$

G - 50 percent of (A) plus 50 percent of (F)

H - 50 percent of a 17 weight percent solution of $Mg(SCN)_2$ in liquid ammonia plus 50 percent of (A)

I - 25 weight percent KSCN in liquid ammonia was electrolyzed 3 minutes using two Mg electrodes at 0.75 volts.

J - 50 weight percent KSCN in liquid ammonia

Computation of Observed Coulombs per grams of oxidants:

$$\frac{\frac{E}{R} \times T}{gms.} = \text{coulombs per gram, where}$$

E = average of peak closed circuit voltage and end voltage of 1.50

R = mean resistance in ohms between light and heavy loads

T = discharge time in seconds to 1.50 volts under heavy load

gms. = combined weight of oxidants

TABLE I-a

ELECTROCHEMICAL CELL TESTS-

Test Number	T-35	T-36	T-37	T-38	T-39
Major Variables	+Sulfur Temp.	+Sulfur	+Sulfur	+Sulfur Temp.	+Sulfur Temp.
Electrolyte	A	A	A	A	A
Reference (page No.)	29	28	27	33	29
Vehicle[1]	TT	TT	TT	A-624	A-624
Net Cell Volume (in.^{3})	30	30	30	37	37
Wet Stand, Hrs/Temp. °C					
Temperature °C, Discharge	-63	-63	-63	+20	-73
Hrs. to End Voltage (1.5/1.3v)**	72/78	67/73	97/98	11/19	68/77
Anode (AZ31B Mg) Sheet - Thickness, ins.	0.016	0.016	0.016	0.016	0.016
Anode Area (cm^2)	377	368	368	368	368
Cathode, Major Oxidant	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$
gm. Major Oxidant	133	137	126	133	133
gm. Sulfur	10	5	20	10	10
gm. Carbon	57	58	54	57	57
Additive					
Additive, gms.					
$HgSO_4 \cdot NH_3$ Coordination No.[5]	2	2	2	4	2
Cathode Collector Area (cm^2)(Ag wire)	14.7	14.7	14.7	14.7	14.7
Separator Thickness[3], inches	0.028	0.028	0.028	0.028	0.028
Initial Closed Circuit Voltage*	2.15	2.10	2.15	2.05	2.20
Peak Closed Circuit Voltage*	2.25	2.25	2.30	2.30	2.35
End Voltage (under maximum load)	1.50	1.50	1.50	1.50	1.50
End Voltage (under light load)	1.70	1.70	1.70	2.04	1.75
Peak Anode C.D. (mA/cm^2)*	0.44	0.45	0.46	0.46	0.47
Peak Cathode Collector C.D. (mA/cm^2)*	11.3	11.3	11.5	11.5	11.7
Observed Coulombs/gram Oxidants[6]	376	352	502	58	365
Observed F/mol Cathode Oxidants[6]	0.78	0.91	0.76	0.12	0.76
Watt Hours/Inch^3 of Net Cell	0.94	0.87	1.29	0.12	0.76

Bobbin Configuration - Load, Ω^2 = 2.7/13.5

T-40	T-41	T-42	T-43	T-44	T-45	T-46	T-47
Cathode Diam. 1.5"	Cathode Diam. 1.13"	+Sulfur Temp.	1. NH_3 Activation Temp.	+Sulfur	Temp. Mg tube anode	Active Stand Cathode Only	$HgSO_4 \cdot ONH_3$ No S
A	A	A	C	A	A	A	A
27	26	29	33	29	33	46	29
TT	TT	A-624	A-624	TT	A-624	TT	TT
59	59	35	37	40	35	40	40
						64/-63°	
-63	-63	-73	+20	-63	+20	-63	-63
48/72	84/107	63/85	0	72/97	5.5/9.5	12/17	56/57
0.016	0.016	0.016	0.016	0.016	0.062	0.016	0.16
248	368	368	368	368	270	337	368
$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$
126	126	126	126	112	126	126	126
20	20	20	20	40	20	20	0
54	54	54	54	48	54	54	60
2	2	2	4	2	4	2	0
6.5	14.7	14.7	14.7	14.7	14.7	14.7	11.0
0.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028
1.65	2.15	2.30	1.52	2.18	2.10	1.95	1.95
2.37	2.25	2.30		2.27	2.10	2.05	2.00
1.50	1.50	1.50		1.50	1.50	1.50	1.50
2.00	1.78	1.90		1.90	1.84	1.67	1.92
0.70	0.45	0.46		0.45	0.57	0.45	0.40
26.8	11.2	11.5		11.3	10.5	10.3	13.4
253	430	326		355	27	58	309
0.38	0.65	0.49		0.35	0.04	0.09	0.95
0.34	0.55	0.72		0.71	0.06	0.11	0.48

TABLE I-a

ELECTROCHEMICAL CELL TESTS-

Test Number	T-48	T-49	T-50	T-51	T-52
Major Variables	In-creased C & S	1. NH_3 Activa-tion Note 4	Activ. at -63°	Slaked	Mg rod Center anode
Electrolyte	A	C	A	A	A
Reference (page No.)	34		31	30	33
Vehicle[1]	TT	TT	A-624	TT	A-624
Net Cell Volume ($in.^3$)	40	40	35	40	35
Wet Stand, Hrs/Temp. °C					
Temperature °C, Discharge	-63	-63	+20	-63	+20
Hrs. to End Voltage (1.5/1.3v)**	78/93	41	49/76	38	33/45
Anode (AZ31B Mg) Sheet - Thickness, ins.	0.016	0.016	0.016	0.016	
Anode Area (cm^2)	368	368	368	368	140
Cathode, Major Oxidant	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$
gm. Major Oxidant	72	126	126	126	126
gm. Sulfur	36	20	20	20	20
gm. Carbon	72	54	54	54	54
Additive					
Additive, gms.					
$HgSO_4 \cdot NH_3$ Coordination No.[5]	2	2	2	4	2
Cathode Collector Area (cm^2)(Ag wire)	15.5	14.9	15.5	13.6	15.5
Separator Thickness[3], inches	0.028	0.028	0.028	0.028	0.028
Initial Closed Circuit Voltage*	2.15	2.15	2.35	1.70	2.15
Peak Closed Circuit Voltage*	2.25	2.20	2.37	2.15	2.22
End Voltage (under maximum load)	1.50	1.50	1.50	1.50	1.50
End Voltage (under light load)	1.82	1.82	1.70	1.92	1.97
Peak Anode C.D. (mA/cm^2)*	0.45	0.44	0.47	0.43	1.17
Peak Cathode Collector C.D. (mA/cm^2)*	10.7	10.9	11.2	11.6	10.5
Observed Coulombs/gram Oxidants[6]	534	207	259	189	167
Observed F/mol Cathode Oxidants[6]	0.44	0.31	0.39	0.28	0.25
Watt Hours/$Inch^3$ of Net Cell	0.76	0.39	0.58	0.35	0.36

CONTINUED

Bobbin Configuration - Load, Ω^2 = 2.7/13.5

T-53	T-54	T-55	T-56	T-57	T-58	T-59	T-60
Center & Outer Anodes	+Sulfur	Sulfur Only S:C = 1:3	Sulfur Only S:C = 1:3	m-DNB	m-DNB Active Stand	Sulfur Only S:C = 1:2	$HgSO_4 \cdot ONH_3$
A	A	A	A	A	A	A	A
33	29	34	34	36	36	34	27
A-624	TT	TT	TT	TT	TT	TT	TT
35	40	40	40	40	40	40	40
					70/-63		
+20	-63	-63	-63	-63	-63	-63	-63
35/62	71/92	41/45	33/45	22/57	0/18	25/45	106/119
	0.016	0.016	0.016	0.016	0.016	0.016	0.016
508	368	368	368	368	368	368	368
$HgSO_4$	$HgSO_4$	S	S	m-DNB	m-DNB	S	$HgSO_4$
126	122	30	30	30	30	42	106
20	25			0	0		20
54	53	90	90	90	90	84	60
2	2						0
15.6	15.6	15.6	14.3	14.3	14.3	15.6	13.0
.032/.028	0.028	0.028	0.028	0.028	0.028	0.028	0.028
2.20	2.20	1.85	2.05	2.07	1.63	1.93	2.20
2.20	2.25	2.05	2.06	2.07	1.83	2.13	2.25
1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
2.00	1.85	1.80	1.90	1.85	1.73	1.85	1.72
0.32	0.45	0.41	0.41	0.41	0.73	0.43	0.45
10.4	10.6	9.7	10.6	10.6	9.4	10.0	12.7
176	361	968	775	524		431	628
0.27	0.48	0.32	0.26	0.91		0.14	0.84
0.38	0.69	0.36	0.29	0.19		0.23	1.03

TABLE I-a

ELECTROCHEMICAL CELL TESTS-

Test Number	T-61	T-62	T-63
Major Variables	Coord. No. Temp.	Coord. No. Temp.	wet stand Open Circuit
Electrolyte	A	A	A
Reference (page No.)	31	31	46
Vehicle[1]	A-624	A-624	TT
Net Cell Volume (in.^{3})	35	35	40
Wet Stand, Hrs/Temp. °C			66/-63°
Temperature °C, Discharge	-73	+20	-63
Hrs. to End Voltage (1.5/1.3v)**	85/102	30/91	10/16
Anode (AZ31B Mg) Sheet - Thickness, ins.	.040	.040	0.016
Anode Area (cm^2)	368	368	368
Cathode, Major Oxidant	$HgSO_4$	$HgSO_4$	$HgSO_4$
gm. Major Oxidant	106	106	120
gm. Sulfur	20	20	20
gm. Carbon	60	60	60
Additive			
Additive, gms.			
$HgSO_4 \cdot NH_3$ Coordination No.[5]	0	0	2
Cathode Collector Area (cm^2)(Ag wire)	12.3	12.3	15.6
Separator Thickness[3], inches	0.028	0.028	0.028
Initial Closed Circuit Voltage*	2.22	2.25	2.15
Peak Closed Circuit Voltage*	2.28	2.35	2.15
End Voltage (under maximum load)	1.50	1.50	1.50
End Voltage (under light load)	1.88	1.82	1.85
Peak Anode C. D. (mA/cm^2)*	0.46	0.47	0.43
Peak Cathode Collector C. D. (mA/cm^2)*	13.6	14.0	10.1
Observed Coulombs/gram Oxidants[6]	506	187	52
Observed F/mol Cathode Oxidants[6]	0.67	0.25	0.08
Watt Hours/Inch^3 of Net Cell	0.96	0.37	0.09

Continued

Bobbin Configuration - Load, Ω^2 = 2.7/13.5

T-64	T-65	T-66	T-67	T-68	T-69	T-70	T-71
thick anode	triple cathode single anode	pure Mg anode	spent electro-lyte	spent electro-lyte	cathode electrolyte treated	$Hg(SCN)_2$	HgS alone
A	A	A	B	B	C	A	A
26	27	27	39	32	42	36	36
TT	TT	TT	TT	A-624	TT	TT	TT
40	40	40	40	35	40	40	40
-63	-63	-63	-63	+20	-63	-63	-63
71/88	63/74	87/94	101/109	76/92	30/45	63/74	21/28
.040	0.040	0.014[d]	.040	0.040	0.040	0.040	0.040
368	245	348	368	368[c]	368	368	368
$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$Hg(SCN)_2$	HgS
120	106	106	106	106	77	106	130
20	20	20	20	20	15	20	0
60	60	60	60	60	45	60	56
					KSCN		
					83		
2	0	0	0	0	0	0	0
15.6	27.2	11.7	11.7	11.7	14.2	14.2	14.2
0.028	0.016	0.028	0.028	0.028	0.028	0.028	0.028
2.17	2.25	2.30	2.30	2.25	1.70	2.15	2.20
2.25	2.25	2.30	2.34	2.25	2.25	2.25	2.20
1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
1.78	1.65	1.72	1.75	1.65	1.80	1.65	1.65
0.45	0.68	0.49	0.47	0.45	0.45	0.45	0.44
10.6	6.1	14.5	14.7	14.2	11.7	11.7	11.4
379	374	520	611	450	244	374	119
0.56	0.50	0.69	0.81	0.60	0.32	0.51	0.29
0.69	0.61	0.87	1.03	0.85	0.29	0.61	0.20

TABLE I-a

ELECTROCHEMICAL CELL TESTS —

Test Number	T-72	T-73	T-74	T-75
Major Variables	spent electro-lyte	$Hg(SCN)_2$ Temp.	spent electro-lyte	cathode electrolyte treated
Electrolyte	B	A	D	E
Reference (page No.)	39	36	39	42
Vehicle[1]	A-624	A-624	TT	TT
Net Cell Volume ($in.^3$)	35	35	40	40
Wet Stand, Hrs/Temp. °C				
Temperature °C, Discharge	-73	-73	-63	-63
Hrs. to End Voltage (1.5/1.3v)**	67/75	60/74	78/87	0/23
Anode (AZ31B Mg) Sheet - Thickness, ins.	0.040	0.040	0.040	0.040
Anode Area (cm^2)	368	368	368[c]	368
Cathode, Major Oxidant	$HgSO_4$	$Hg(SCN)_2$	$HgSO_4$	$HgSO_4$
gm. Major Oxidant	106	106	106	77
gm. Sulfur	20	20	20	15
gm. Carbon	60	60	60	45
Additive				KSCN
Additive, gms.				83
$HgSO_4 \cdot NH_3$ Coordination No.[5]	0	0	0	0
Cathode Collector Area (cm^2)(Ag wire)	11.7	14.2	11.0	14.2
Separator Thickness[3], inches	0.028	0.028	0.028	0.028
Initial Closed Circuit Voltage*	2.20	2.24	2.00	1.95
Peak Closed Circuit Voltage*	2.20	2.24	2.25	1.95
End Voltage (under maximum load)	1.50	1.50	1.50	1.50
End Voltage (under light load)	1.75	1.80	1.72	---
Peak Anode C. D. (mA/cm^2)*	0.44	0.45	0.45	0.39
Peak Cathode Collector C. D. (mA/cm^2)*	13.8	11.6	15.0	10.1
Observed Coulombs/gram Oxidants[6]	390	354	462	---
Observed F/mol Cathode Oxidants[6]	0.52	0.48	0.62	---
Watt Hours/Inch[3] of Net Cell	0.72	0.66	0.76	---

Continued

Bobbin Configuration - Load, $\Omega^2 = 2.7/13.5$

T-76	T-77	T-78	T-79	T-80	T-81	T-82	T-83	T-84
Amt. S	HgS + S	$Hg(SCN)_2$ spent electrolyte	wet stand open circuit	increased C & S	electrolyte and $MgSO_4$	triple cells	amt. S electrolyte	amt. S electrolyte
A	A	B	A	A	F	A	G	G
29	36	41	46	34	37	27	32	leaked
TT	TT	TT	TT	TT	TT	TT	A-624	A-624
40	40	40	40	40	40	40	35	35
			66/-63°					
-63	-63	-63	-63	-63	-63	-63	+20	+20
72/80	35/40	60/70	15/20	83/98	49/57	55/59	49/76	12/13
0.040	0.040	0.040	0.040	0.040	0.040	0.016	0.040	0.040
258[c]	368[c]	368[c]	258[c]	310[c]	258[c]	348[c]	258[c]	258[c]
$HgSO_4$	HgS	$Hg(SCN)_2$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$
116	106	106	106	75	106	106	116	106
10	20	20	20	39	20	20	10	20
60	60	60	60	72	60	60	60	60
					$MgSO_4$			
					10			
0	0	0	0	0	0	0	0	0
12.3	15.6	15.6	11.6	13.6	13.0	23.3	12.3	11.3
0.028	0.028	0.028	0.028	0.028	0.028	0.016	0.028	0.028
2.10	2.12	2.16	2.05	2.25	1.92	2.13	---	---
2.23	2.20	2.34	2.15	2.25	2.20	2.25	2.33	2.35
1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
1.73	1.78	1.75	1.70	1.85	1.87	1.68	1.65	2.05
0.64	0.44	0.47	0.61	0.53	0.63	0.48	0.66	0.67
13.3	10.4	11.0	13.6	12.2	12.4	7.1	13.9	15.3
424	204	363	87	544	286	326	297	73
0.79	0.25	0.49	0.12	0.44	0.38	0.43	0.55	0.10
0.70	0.33	0.61	0.14	0.81	0.46	0.54	0.57	0.14

TABLE I-a Continued

ELECTROCHEMICAL CELL TESTS
Bobbin Configuration - Load, Ω^2 = 2.7/13.5

Test Number	T-85	T-86	T-87	T-88
Major Variables	Acetyl. Black	in-creased C & S	Acetyl. Black electro-lyte	amt. S electro-lyte
Electrolyte	A	A	H	H
Reference (page No.)	34	34	38	32
Vehicle[1]	TT	TT	TT	A-624
Net Cell Volume (in.^{3})	40	40	40	35
Wet Stand, Hrs/Temp. °C				
Temperature °C, Discharge	-63	-63	-63	+20
Hrs. to End Voltage (1.5/1.3v)**	79/95	83/96	85/93	67/78
Anode (AZ31B Mg) Sheet - Thickness, ins.	0.040	0.040	0.040	0.040
Anode Area (cm^2)	258^c	310^c	258^c	258^c
Cathode, Major Oxidant	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$
gm. Major Oxidant	106	50	106	116
gm. Sulfur	20	50	20	10
gm. Carbon	54	80	54	60
Additive	acet. blk.		acet. blk.	
Additive, gms.	6		6	
$HgSO_4 \cdot NH_3$ Coordination No.[5]	0	0	0	0
Cathode Collector Area (cm^2)(Ag wire)	12.3	14.9	13.0	12.3
Separator Thickness[3], inches	0.028	0.028	0.028	0.028
Initial Closed Circuit Voltage*	2.18	2.05	1.92	2.27
Peak Closed Circuit Voltage*	2.25	2.25	2.24	2.27
End Voltage (under maximum load)	1.50	1.50	1.50	1.50
End Voltage (under light load)	1.85	1.92	1.72	1.66
Peak Anode C. D. (mA/cm^2)*	0.64	0.53	0.64	0.65
Peak Cathode Collector C. D. (mA/cm^2)*	13.5	11.1	12.7	13.6
Observed Coulombs/gram Oxidants[6]	468	620	501	400
Observed F/mol Cathode Oxidants[6]	0.62	0.37	0.67	0.74
Watt Hours/Inch^3 of Net Cell	0.77	0.81	0.82	0.75

TABLE I-a

ELECTROCHEMICAL CELL TESTS -

Test Number	T-89	T-90	T-91	T-92
Major Variables	wet stand 3000Ω	temp. coated anode	temp. electro-lyte	wet stand 3000Ω
Electrolyte	A	A	H	A
Reference (page No.)	46	32	32	46
Vehicle[1]	TT	A-624	A-624	TT
Net Cell Volume ($in.^3$)	40	35	35	40
Wet Stand, Hrs/Temp. °C	45/-63			65/-63
Temperature °C, Discharge	-63	+20	+20	-63
Hrs. to End Voltage (1.5/1.3v)**	30/39	52/93	60/86	41/58
Anode (AZ31B Mg) Sheet -Thickness, ins.	0.040	0.040	0.040	0.040
Anode Area (cm^2)	258[c]	310[c]	310[c]	310[c]
Cathode, Major Oxidant	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$
gm. Major Oxidant	106	106	106	106
gm. Sulfur	20	20	20	20
gm. Carbon	60	60	60	60
Additive				
Additive, gms.				
$HgSO_4 \cdot NH_3$ Coordination No.[5]	0	0	0	0
Cathode Collector Area (cm^2)(Ag wire)	11.0	11.7	13.0	11.7
Separator Thickness[3], inches	0.028	0.028	0.028	0.028
Initial Closed Circuit Voltage*	2.13	2.23	2.41	2.26
Peak Closed Circuit Voltage*	2.17	2.23	2.41	2.28
End Voltage (under maximum load)	1.50	1.50	1.50	1.50
End Voltage (under light load)	1.82	1.73	1.65	1.80
Peak Anode C.D. (mA/cm^2)*	0.62	0.53	0.57	0.54
Peak Cathode Collector C.D. (mA/cm^2)*	14.5	14.0	13.6	14.3
Observed Coulombs/gram Oxidants[6]	174	307	370	244
Observed F/mol Cathode Oxidants[6]	0.23	0.41	0.49	0.32
Watt Hours/$Inch^3$ of Net Cell	0.28	0.57	0.73	0.40

Continued

Bobbin Configuration - Load, Ω^2 = 2.7/13.5

	T-93	T-94	T-95	T-96	T-97	T-98	T-99
	25% wt. % KSCN electrolyzed 3 mins.	wet stand 645Ω	wet stand 3000Ω High S & C	$PbSO_4$ and Sulfur	Microporous rubber separator 0.045" Thk.	3000Ω MPR separator	High S & C
	I	A	A	A	A	A	A
	40	46	46	36	27	46	34
	TT	TT	TT	TT	TT	TT	TT
	40	40	40	40	40	40	40
		65/-63	65/-63			65/-63	
	-63	-63	-63	-63	-63	-63	-63
	75/89	41/50	45/54	34/53	107/119	58/76	60/72
	0.040	0.040	0.040	0.025	0.025	0.025	0.025
	258^c	310^c	310^c	310^c	258^c	258^c	310^c
	$HgSO_4$	$HgSO_4$	$HgSO_4$	$PbSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$
	106	106	50	108	106	106	40
	20	20	50	20	20	20	60
	60	60	80	60	60	60	80
	0	0	0		0	0	0
	11.7	11.7	14.3	13.6	11.7	13.0	15.5
	0.028	0.028	0.028	0.028	0.036	0,028	0.028
	2.20	2.25	2.13	2.06	2.25	2.27	2.25
	2.21	2.25	2.20	2.06	2.28	2.27	2.27
	1.50	1.50	1.50	1.50	1.50	1.50	1.50
	1.83	1.75	2.00	1.91	1.70	1.75	2.00
	0.63	0.53	0.52	0.49	0.65	0.65	0.54
	13.9	14.1	11.3	11.1	14.3	12.8	10.8
	440	243	331	188	637	346	451
	0.58	0.32	0.20	0.25	0.85	0.46	0.23
	0.72	0.40	0.42	0.30	1.05	0.57	0.59

TABLE I-a

ELECTROCHEMICAL CELL TESTS -

Test Number	T-100	T-101	T-102	T-103
Major Variables	$(NH_4)_2SO_4$	50 wt. % KSCN	10 wt. % KSCN	MPR Sep. masked narrow 3000Ω
Electrolyte	A	J	E	A
Reference (page No.)	37	40	40	44
Vehicle[1]	TT	TT	TT	TT
Net Cell Volume (in.^{3})	40	40	40	40
Wet Stand, Hrs/Temp. °C				65/-63
Temperature °C, Discharge	-63	-63	-63	-63
Hrs. to End Voltage (1.5/1.3v)**	87/115	103/108	52/60	61/88
Anode (AZ31B Mg) Sheet - Thickness, ins.	0.025	0.025	0.025	0.025
Anode Area (cm^2)	258^c	258^c	258^c	258^c
Cathode, Major Oxidant	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$
gm. Major Oxidant	106	106	106	106
gm. Sulfur	20	20	20	20
gm. Carbon	60	60	60	60
Additive	$(NH_4)_2SO_4$			
Additive, gms.	10			
$HgSO_4 \cdot NH_3$ Coordination No.[5]	0	0	0	0
Cathode Collector Area (cm^2)(Ag wire)	12.3	11.6	11.6	11.6
Separator Thickness[3], inches	0.028	0.028	0.028	0.028
Initial Closed Circuit Voltage*	2.20	2.28	2.26	2.25
Peak Closed Circuit Voltage*	2.25	2.28	2.26	2.25
End Voltage (under maximum load)	1.50	1.50	1.50	1.50
End Voltage (under light load)	1.75	2.00	1.94	1.87
Peak Anode C.D. (mA/cm^2)*	0.64	0.65	0.64	0.64
Peak Cathode Collector C.D. (mA/cm^2)*	13.5	14.5	14.3	14.3
Observed Coulombs/gram Oxidants[6]	516	615	308	362
Observed F/mol Cathode Oxidants[6]	0.69	0.82	0.41	0.48
Watt Hours/Inch^3 of Net Cell	0.85	1.01	0.51	0.59

Continued

Bobbin Configuration - Load, Ω^2 = 2.7/13.5

T-104	T-105	T-106	T-107	T-108	T-109	T-110
1" dia. cathode	2700Ω ½ spent electrolyte	MPR Sep. masked wide 2700Ω	MPR double layer 2700Ω	K_2SO_4	wet stand at +20°C MPR .045" Thk 3000Ω	m-DNB added
A	B	A	A	A	A	A
27	45	44	45	37	45	36
TT	TT	TT	TT	TT	A-624	TT
40	40	40	40	40	35	40
	65/-63	65/-63	65/-63		65/+20	
-63	-63	-63	-63	-63	-63	-63
96/105	16/44	64/74	69/78	84/99	0/75[e]	106/121
0.025	0.025	0.025	0.025	0.025	0.025	0.025
258[c]	258[c]	258[c]	354[c]	258[c]	258[c]	258[c]
$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$	$HgSO_4$
106	106	106	106	106	106	106
20	20	20	20	20	20	20
60	60	60	60	60	60	60
				K_2SO_4		m-DNB
				10		10
0	0	0	0	0	0	0
13.0	11.7	11.7	11.7	12.3	11.6	13.0
0.028	0.028	0.036	0.028	0.028	0.036	0.028
2.22	2.15	2.21	2.33	2.20	1.81	2.06
2.30	2.18	2.22	2.33	2.24	1.81	2.25
1.50	1.50	1.50	1.50	1.50	0.80	1.50
1.75	2.00	1.95	1.70	1.70	0.98	1.70
0.66	0.62	0.63	0.48	0.64	0.52	0.64
13.0	13.7	13.9	14.6	13.4	11.5	12.7
575	93	375	417	496	307	581
0.77	0.12	0.50	0.56	0.66	0.41	0.79
0.96	0.15	0.61	0.70	0.81	0.40	1.03

TABLE I-b

CELL VOLTAGES ON SUCCESSIVE DAYS AND END VOLTAGES TO 1.5 AND 1.3

Test No. T-	High Load Voltage After:				Low Load Voltage After:				Hours to*:	
	1 day	2 days	3 days	4 days	1 day	2 days	3 days	4 days	1.5v	1.3v
50	1.85	1.50	1.35		2.00	1.70	1.60		49	76
51	Recorder failed to print								38	--
52	1.65	1.25			2.02	1.80			33	45
53	1.70	1.40	1.20		1.90	1.60	1.45		35	62
54	2.05	1.85	1.49	1.24	2.25	2.10	1.85	1.60	71	92
55	1.70	1.25			2.00	1.60			41	45
56	1.62	1.23			2.02	1.75			33	45
57	1.47	1.41	0.90		1.82	1.73	1.14		22	57
58									0	--
59	1.50	1.45	1.00		1.85	1.72	1.18		25	45
60	2.15	2.10	1.95	1.55	2.26	2.25	2.15	1.80	106	119
61	1.98	1.82	1.76	1.42	2.20	2.16	2.00	1.70	85	102
62	1.74	1.46	1.44	1.15	1.96	1.73	1.65	1.42	30	91
63	0.85				1.12				10	16
64	2.05	1.86	1.48	1.10	2.25	2.12	1.77	1.40	71	87
65	2.10	1.85	1.32	0.85	2.25	2.05	1.60	1.00	63	74
66	2.20	2.00	1.62	1.25	2.30	2.20	1.85	1.50	87	94

*under heavy load

TABLE I-b Continued

CELL VOLTAGES ON SUCCESSIVE DAYS AND END VOLTAGES TO 1.5 AND 1.3

Test	High Load Voltage After:				Low Load Voltage After:				Hours to*:	
No. T-	1 day	2 days	3 days	4 days	1 day	2 days	3 days	4 days	1.5v	1.3v
67	2.21	1.97	1.95	1.60	2.32	2.22	2.10	1.78	101	109
68	1.98	1.53	1.51	1.20	2.06	1.77	1.66	1.40	76	92
69	1.55	1.24			1.95	1.60			30	45
70	2.05	1.60	1.36	0.80	2.22	1.85	1.60	1.00	63	74
71	1.46	1.20			1.60	1.48			21	28
72	1.70	1.68	1.37		2.15	2.00	1.70		67	75
73	2.05	1.82	1.35		2.25	2.00	1.62		60	74
74	2.12	1.94	1.65	1.05	2.25	2.10	1.95	1.32	78	87
75	1.28	0.84			1.60	1.25			0	23
76	2.10	1.92	1.50	0.95	2.20	2.20	1.73	1.16	72	80
77	1.85	1.12			2.06	1.57			36	41
78	2.05	1.80	1.25		2.22	2.04	1.61		60	70
79	1.15				1.42				15	20
80	2.12	1.95	1.65	1.35	2.25	2.15	1.98	1.67	83	98
81	1.87	1.51	1.00		2.10	1.90	1.30		49	57
82	2.08	1.73			2.20	1.92			55	59
83	2.05	1.50	1.35		2.20	1.65	1.60		49	76
84									Leaked	

*under heavy load

TABLE I-b Continued

CELL VOLTAGES ON SUCCESSIVE DAYS AND END VOLTAGES TO 1.5 AND 1.3

Test No. T-	High Load Voltage After: 1 day	2 days	3 days	4 days	Low Load Voltage After: 1 day	2 days	3 days	4 days	Hours to*: 1.5v	1.3v
85	2.18	1.93	1.70	1.26	2.25	2.15	1.99	1.62	79	95
86	2.04	1.86	1.60	1.32	2.20	2.12	2.00	1.82	83	97
87	2.12	1.94	1.69	1.26	2.24	2.10	1.95	1.55	85	93
88	2.05	1.52	1.47	0.65	2.20	1.70	1.65	0.80	67	78
89	1.66				1.94				30	39
90	1.92	1.52	1.44	1.18	2.08	1.75	1.62	1.40	52	93
91	1.96	1.61	1.44		2.07	1.78	1.63		60	86
92	1.80	1.42	1.04		2.08	1.70	1.34		41	58
93	2.06	1.90	1.60		2.20	2.10	1.92		75	89
94	1.78	1.35			1.97	1.65			41	50
95	1.82	1.41			2.15	1.95			45	54
96	1.62	1.34			1.97	1.83			34	53
97	2.12	2.06	1.92	1.57	2.25	2.22	2.10	1.75	107	119
98	1.92	1.75	1.35		2.15	2.00	1.67		58	76
99	2.02	1.75	1.30		2.22	2.10	1.88		60	72
100	2.08	1.94	1.72	1.46	2.25	2.20	2.05	1.75	87	115
101	1.70	1.81	1.75	1.58	2.21	2.21	2.20	2.03	103	108
102	1.82	1.59			2.20	1.99			52	60

*under heavy load

TABLE I-b Continued

CELL VOLTAGES ON SUCCESSIVE DAYS AND END VOLTAGES TO 1.5 AND 1.3

Test	High Load Voltage After:				Low Load Voltage After:				Hours to*:	
No. T-	1 day	2 days	3 days	4 days	1 day	2 days	3 days	4 days	1.5v	1.3v
103	1.80	1.70	1.37		2.15	2.06	1.70		61	88
104	2.20	1.97	1.85	1.50	2.30	2.20	2.07	1.75	96	105
105	1.42	1.25			1.95	1.80			16	44
106	1.84	1.67	1.33		2.18	2.05	1.84		64	74
107	2.10	1.89	1.43		2.26	2.08	1.68		69	78
108	2.14	1.93	1.81	1.34	2.24	2.16	2.04	1.63	84	99
109	1.25				1.60				0	3
110	2.14	1.98	1.89	1.61	2.25	2.14	2.05	1.80	106	121

*under heavy load

DISCUSSION OF RESULTS

Many variations in cell geometry, composition, and treatment were made during the third quarter in order to improve performance and our understanding of the factors which affect $Mg/HgSO_4$ cell life. While it is desirable to make single changes, it is not usually possible to do so in an actual cell. Comparisons have, therefore, been made by tabulation of related runs; and a broader area of factors has been studied.

CELL GEOMETRY

Anode Variations - 20 grams Sulfur at -63°C

Table II shows the effects of changes in anode thickness and composition. The thicker sheet provides more available Mg, but its rigidity makes it difficult to fit properly to the cathode and prevents expansion as the cathode swells during activation and discharge. These factors may be responsible for the shorter life of the cell with the thicker anode. A thickness of 0.025 inches has been procured as a compromise between a desired excess Mg and flexibility.

Pure Mg appeared to be inferior to the alloy, AZ31B Mg on the basis of one test.

TABLE II

Anode Variations - 20 grams Sulfur at -63°C

Test No.	Anode Thickness	$HgSO_4 \cdot NH_3$ Coord. No.	Hrs. to 1.5v	Hrs. to 1.3v
T-31 & 41	0.016"	2	91	102
T-64	0.040"	2	71	88

TABLE II Continued

Anode Variations - 20 grams Sulfur at -63°C

Test No.	Anode Thickness	$HgSO_4 \cdot NH_3$ Coord. No.	Hrs. to 1.5v	Hrs. to 1.3v
T-60	0.016"	0	106	119
T-66	0.014"*	0	87	94

*Pure maganesium sheet; all other anodes were the alloy AZ31B Mg.

Cathode Design - 20 grams Sulfur at -63°C

The nominal 1-1/8 inch diameter cathode is shown in Table III to be superior to both larger and smaller diameters and has been adopted as standard. Triple cathodes of small diameter were inferior when used in conjunction with either a common anode or with individual anodes.

TABLE III

Cathode Design - 20 grams Sulfur at -63°C

Test No.	Cathode Diam.	$HgSO_4 \cdot NH_3$ Coord. No.	Hrs. to 1.5v	Hrs. to 1.3v	Anode No.	Cathode No.
T-40	1.50"	2	48	72	1	1
T-37 & 41	1.13"	2	91	102	1	1
T-60	1.13"	0	106	119	1	1
T-104	1.00"	0	96	105	1	1
T-65	0.75"	0	63	74	1	3
T-82	0.63"	0	55	59	3	3

Separators

Cells T-60 and T-97 were similar to each other except that the former had only a M-1365 Webril separator, while the latter had both a Webril and a microporous rubber (MPR) separator. The life at -63°C was almost the same for both cells.

	Hrs. to 1.5v	Hrs. to 1.3v
T-60	106	119
T-97	107	119

It is evident that the use of MPR is unnecessary in this type of cell when discharged under the same conditions of temperature and loading. However, it is probable that it will aid in the achievement of wet stand, especially at low temperature, as indicated in the section on "Activated Stand."

EFFECTS OF SULFUR ON $HgSO_4 \cdot 2NH_3$ BOBBIN CELLS

Cells assembled in Table IV-a include variations in $HgSO_4 \cdot 2NH_3$:S: carbon. The quantity of sulfur was varied from 0 to 40 grams, and the ratio of $HgSO_4 \cdot 2NH_3$:C was held at 7:3 by weight. The total cathode weight was maintained at 200 grams. The quantity of sulfur and the life to cut-offs of 1.5 and 1.3 volts at the heavy load are tabulated at two temperature levels. Twenty grams of sulfur yielded the longest life at -63°C. At -73°C, the difference between 10 and 20 grams did not appear to be significant to the 1.5 volt level, but performance to a cut-off of 1.3 volts was substantially improved by 20 grams of sulfur.

TABLE IV-a

Effects of Sulfur on $HgSO_4 \cdot 2NH_3$ Bobbin Cells

Test No.	gms. S	Hrs. to 1.5v	Hrs. to 1.3v	Temp. °C
typical 2nd quarter	0	60	68	-63
T-36	5	67	73	-63
T-33	10	77	--	-63

TABLE IV-a Continued

Effects of Sulfur on $HgSO_4 \cdot 2NH_3$ Bobbin Cells

Test No.	gms. S	Hrs. to 1.5v	Hrs. to 1.3v	Temp. °C
T-35	10	72	78	-63
T-37	20	97	97.5	-63
T-41	20	84	107	-63
T-54	25	71	92	-63
T-44	40	72	97	-63
T-6	0	57	59	-73
T-39	10	68	77	-73
T-42	20	60	85	-73

Non-ammoniated $HgSO_4$ was substituted for the diamine in the cells of Table IV-b. At -63°C, twenty grams of sulfur again provided the longest life.

TABLE IV-b

Effects of Sulfur on $HgSO_4 \cdot 0\,NH_3$ Bobbin Cells

Test No.	gms. S	Hrs. to 1.5v	Hrs. to 1.3v	Temp. °C
T-47	0	56	57	-63
T-76	10	72	80	-63
T-60	20	106	119	-63

EFFECTS OF DEGREE OF COORDINATION OF $HgSO_4$ WITH AMMONIA AT VARIOUS LEVELS OF SULFUR CONTENT AND TEMPERATURE

In Table V the effect of temperature and ammoniation are demonstrated with 25 weight percent KSCN/ammonia electrolyte and without spent electrolyte, special separators, or anode protective coating.

In the absence of sulfur, the degree of coordination seemed to be unimportant at -63°C; but at -73°C, the diamine appeared to be superior to the the quaternary compound.

The addition of 10 grams of sulfur increased the cell life to 1.5 volts by about 20 per cent, but the coordination number had no effect.

At the sulfur level of 20 grams, the non-ammoniated $HgSO_4$ was distinctly superior at the lower temperatures. At +20°C, however, the diamine yielded a much longer life to 1.5 volts than the non-ammoniated type. The discharge curve of the latter was exceptionally flat so that an additional 61 hours were obtained between 1.5 and 1.3 volts. In Table VI, the results of special treatments of cells operated at +20°C will be given.

The life obtained from cell No. T-51 is questionable because it was inferior to that of Cells 20 and 21 which contained no sulfur.

TABLE V

Effects of Degree of Coordination of $HgSO_4$ with Ammonia

Test No. T-	$HgSO_4$ gms.	S gms.	C gms.	Coord. No.	Temp. °C	Hrs. to 1.5v	Hrs. to 1.3v
20 & 21	143	0	62	4	-63	53	--
Typ. 2nd Qtr.	130	0	56	2	-63	60	68
47	126	0	60	0	-63	56	57
33 & 35	133	10	57	2	-63	72	78
76	116	10	60	0	-63	72	80
51	126	20	54	4	-63	38	--
37 & 41	126	20	54	2	-63	91	102
60	106	20	60	0	-63	106	119

TABLE V Continued

Effects of Degree of Coordination of $HgSO_4$ with Ammonia

Test No. T-	$HgSO_4$ gms.	S gms.	C gms.	Coord. No.	Temp. °C	Hrs. to 1.5v	Hrs. to 1.3v
9 & 14	161	0	69	4	-73	37	--
6 & 16	143	0	62	2	-73	52	--
42	126	20	54	2	-73	63	85
61	106	20	60	0	-73	85	102
50	126	20	54	2	+20	49	76
62	106	20	60	0	+20	30	91

Latimer[1] gives aqueous reactions for the mercuric ion with both the thiocyanate ion and with ammonia. The equilibrium constants for these reactions are approximately the same at 2×10^{19} as indicated below.

$$Hg^{++} + 4CNS^- \xrightarrow{Aq} Hg\,(CNS)_4^{=} \quad K \doteq \quad 2 * 10^{+19}$$

$$Hg^{++} + 4NH_3 \xrightarrow{Aq} Hg(NH_3)_4^{++} \quad K \doteq \quad 2 * 10^{+19}$$

The implication of these aqueous data is that the mercury ion of the mercuric sulfate is at least partially coordinated by the thiocyanate ion rather than ammonia when activated with electrolyte at -63°C. Furthermore, if coordination with ammonia has been accomplished prior to this, a transformation to the pseudo halide complex does not take place. This metastable condition appears to exist or be of significance in the presence of sulfur!

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[1]W. L. Latimer, Oxidation Potentials (1952) pp. 180-1.

CELL TESTS AT +20°C

It is not an object of this program that cells should run for 72 hours at +20°C. However, tests were conducted at this temperature for the knowledge which might be gained with respect to corrosion problems and the achievement of wet stand.

The best results, a 76-hour life to 1.5 volts, was obtained in No. T-68 which had the following features:

1. $HgSO_4 \cdot 0\,NH_3$: S : C = 106 : 20 : 60;
2. 50 per cent spent electrolyte from a similar discharged cell, plus 50 per cent of 25 weight per cent KSCN in liquid ammonia;
3. activation at -63°C;
4. the outside of the anode was coated with K-M rubber cement to reduce corrosion.

T-90, which ran 52 hours, was the same except that spent electrolyte was not used.

T-62 had neither spent electrolyte nor a coated anode. It ran only 30 hours.

All of these cells had about the same life to 1.3 volts; namely, over 90 hours.

The electrolyte in Nos. T-91, T-83, and T-88 contained a mixture of $Mg(SCN)_2$ and KSCN. In addition, No. T-83 contained $MgSO_4$ in the electrolyte. Electrolyte (H), containing the higher concentration of $Mg(SCN)_2$ yielded reasonably good results.

Activation of slaked $HgSO_4$ at 20°C was unsuccessful and none of the special anodes worked as well as a sheet of AZ31B Mg wrapped around the outside of the cathode.

The results of test No. T-50, containing $HgSO_4 \cdot 2NH_3$ indicate that this cathode would give good performance if spent electrolyte and a coated anode were used.

A summary of the experiments at 20°C is given in Tables VI and VII.

TABLE VI

Cell Tests at +20°C

Test No.	$HgSO_4 \cdot NH_3$ Coord. #	S gms.	Electrolyte Code*	Activ. Temp.	Hrs. to 1.5v	Hrs. to 1.3v	Special Features
T-38	4	10	A	+20	11	19	Incomplete actv.
T-43	4	20	C	+20	0	--	
T-45	4	20	A	+20	5.5	9.5	Mg tube anode
T-52	2	20	A	-63	33	45	center anode
T-53	2	20	A	-63	35	62	double anode
T-50	2	20	A	-63	49	76	
T-62	0	20	A	-63	30	91	
T-90	0	20	A	-63	52	93	coated anode
T-68	0	20	B	-63	76	92	coated anode
T-91	0	20	H	-63	60	86	coated anode
T-83	0	10	G	-63	49	76	coated anode
T-88	0	10	H	-63	67	78	coated anode

*refer to "Notes and Code to Table I-a."

TABLE VII

Cell Tests at +20°C

Test No.	High Load Voltage after: 1 day	2 days	3 days	4 days	Low Load Voltage after: 1 day	2 days	3 days	4 days
T-50	1.85	1.50	1.35	---	2.00	1.70	1.60	---
T-62	1.74	1.46	1.44	1.15	1.96	1.73	1.65	1.42
T-90	1.92	1.52	1.44	1.18	2.08	1.75	1.62	1.40
T-68	1.98	1.53	1.51	1.20	2.06	1.77	1.66	1.40
T-91	1.96	1.61	1.44	---	2.07	1.78	1.63	---
T-83	2.05	1.50	1.35	---	2.20	1.65	1.60	---
T-88	2.05	1.52	1.47	0.65	2.20	1.70	1.65	0.80

Table VII demonstrates a remarkable similarity in the voltages generated by most of these cells after the first day of discharge.

CATHODE COMPOSITION

TABLE VIII

Variations in the Proportions of $HgSO_4$, Sulfur and Carbon

Test No. T-	$HgSO_4$ gms.	S gms.	C gms.	Acet. Black gms.	Coord. No.	Temp. °C	Hrs. to 1.5v	Hrs. to 1.3v	Coulombs per gram Oxidants
37 & 41	126	20	54	0	2	-63	91	102	466
44	112	40	48	0	2	-63	72	97	355
48	72	36	72	0	2	-63	78	93	534
60	106	20	60	0	0	-63	106	119	628
80	75	39	72	0	0	-63	83	98	544
86	50	50	80	0	0	-63	83	96	620
99	40	60	80	0	0	-63	60	72	451
85	106	20	54	6	0	-63	79	95	468
55	0	30	90	0	-	-63	41	45	968
56	0	30	90	0	-	-63	33	45	775
59	0	42	84	0	-	-63	25	45	431

Variations in the Proportions of $HgSO_4$, Sulfur and Carbon

A mercuric sulfate to carbon ratio of approximately 7 : 3 as employed in tests T-37, T-41, and T-60 produced the longest life to 1.5 volts.

A comparison of T-48 with T-44 shows that an increase in carbon (and a significant decrease in $HgSO_4$) improved the life to 1.5 volts only slightly, but it increased the observed coulombs per gram of oxidants from 355 to 534. Thus, while the watt hours obtained were not increased greatly, the weight of the cathode reactants was substantially reduced. Similarly, T-80 and T-86 exhibited long life and relatively high coulombic output.

The only observed advantage of acetylene black (T-85) was an improvement in electrolyte absorption.

The proportions used in T-99 yielded a pronounced decrease in discharge time to 1.5 volts.

When the $HgSO_4$ was reduced to zero, the cell life was reduced to one half of the required value; but the coulombs per gram of oxidant* increased to an average of almost 900. The results of test No. T-59 indicate that better results might have been obtained by increasing the ratio of C : S.

$HgSO_4 \cdot 0\ NH_3$ Versus Other Oxidants

The test results assembled in Table IX show that the best cathode developed thus far for low temperature discharge is the one containing 106 grams of $HgSO_4$ and 20 grams of sulfur, together with 60 grams of carbon.

*sulfur

TABLE IX

$HgSO_4 \cdot 0\ NH_3$ Versus Other Oxidants

Test No. T-	$HgSO_4$ gms.	S gms.	$Hg(SCN)_2$ gms.	HgS gms.	$PbSO_4$ gms.	Temp. °C	Hrs. to 1.5v	Hrs. to 1.3v
60	106	20	0	0	0	-63	106	119
70	0	20	106	0	0	-63	63	74
77	0	20	0	106	0	-63	35	40
96	0	20	0	0	108	-63	34	53
47	126	0	0	0	0	-63	56	57
71	0	0	0	130	0	-63	21	28
61	106	20	0	0	0	-73	85	102
73	0	20	106	0	0	-73	60	74

meta-Dinitrobenzene

Cell No. T-110 contained the same cathode as T-60, except that 10 grams of m-DNB were added to the former. The cell life at -63°C was 106 hours to 1.5 volts and 121 hours to 1.3 volts. No differences were observed.

Table X demonstrates the performance of m-DNB/C bobbin cells at -63°C.

TABLE X

meta-Dinitrobenzene

Test No. T-	m-DNB grams	Carbon grams	Hrs. to 1.5v	Hrs. to 1.3v
57	30	90	22	57
58*	30	90	0	18

*70-hour activated stand at -63°C prior to discharge

It is evident that m-DNB shows little promise of successful operation in this type of construction.

TABLE XI

Effects of the Addition of Sulfates to the Cathode to Depress the Solubility of $HgSO_4$ at -63°C

(Basic cathode = 106 g. $HgSO_4$ + 20 g. S + 60 g. C)

Test No. T-	Sulfate Additive	Electrolyte Code*	Hrs. to 1.5v	Hrs. to 1.3v
60	None	A	106	119
81	10 g. $MgSO_4$	F	49	57
100	10 g. $(NH_4)_2SO_4$	A	87	115
108	10 g. K_2SO_4	A	84	99

*Refer to "Notes and Code to Table I-a," page 7.

None of the sulfates seemed to be effective in prolonging cell life. $(NH_4)_2SO_4$ was the least detrimental.

ELECTROLYTE STUDIES

The results of electrolyte studies are given in Table XII, (a) through (d). The electrolyte code is explained in "Notes and Code to Table I-a," page 7.

The cathodes reported in Table XII-a were comprised of 106 grams of $HgSO_4 \cdot 0 NH_3$, 20 grams of sulfur, and 60 grams of carbon. In T-81, 10 grams of $MgSO_4$ were added to the above mixture.

At -63°C, an increase in the ratio of "spent" to "new" electrolyte decreased cell life to 1.5 volts from 106 hours with 100 per cent new to 78 hours with 100 per cent spent. Poor results were obtained in T-81 with a $Mg(SCN)_2$ electrolyte saturated with $MgSO_4$ and a cathode which contained excess $MgSO_4$. The sulfate was added to depress the solubility of $HgSO_4$. T-87 yielded 85 hours to 1.5 volts. Half of the electrolyte therein was a 17 weight per cent $Mg(SCN)_2$ solution in liquid NH_3.

An electrolyte containing 50 per cent "spent" decreased life at -73° C, but substantially increased life at +20° C, essentially providing greater than 72 hours over this even wider temperature range. About half of the improvement in T-68 over T-62 was due, probably, to the coating of the back of the anode in T-68 with rubber cement. This is indicated by No. T-90 in which a coated anode was used in conjunction with new electrolyte. T-91 shows that a half and half mixture of new KSCN and synthetic $Mg(SCN)_2$ electrolyte produced a cell life between that of new and spent electrolytes at +20° C.

Although the life to 1.5 volts varied considerably, it should be noted that the voltages at the end of each day were quite similar in all cells.

Excerpt from Table I-b

	High load voltage after:			Low load voltage after:		
	1 day	2 days	3 days	1 day	2 days	3 days
T-62	1.74	1.46	1.44	1.96	1.73	1.65
T-90	1.92	1.52	1.44	2.08	1.75	1.62
T-68	1.98	1.53	1.51	2.06	1.77	1.66
T-91	1.96	1.61	1.44	2.07	1.78	1.63

See Table VI, page 33, for cell variables.

The following chemical analyses have been made, and the results are being evaluated:

1. spent electrolyte from Cell No. T-62
2. gas formed in Cell No. T-62
3. gas formed in Cell No. T-68

In T-85 and T-87, the interaction between spent electrolyte and acetylene black is not significant at -63°C.

The net result of these experiments indicates that considerable benefit can be derived from spent electrolyte at +20°C, but 50 percent spent electrolyte slightly decreased the performance at -63°C and more so at -73°C. Optimum performance over the range +20°C to -73°C is interpolated in the region of 25 percent spent electrolyte.

TABLE XII-a

$HgSO_4$ + 20 grams Sulfur

	Electrolyte								
			Synthetic						
	New %	Spent %	#1 %	#2 %	Code	Cathode Additive	Temp. °C	Hrs. to 1.5v	Hrs. to 1.3v
T-60	100				A		-63	106	119
T-67	50	50			B		-63	101	109
T-74	0	100			D		-63	78	87
T-81			100		F	10 gm. $MgSO_4$	-63	49	57
T-87	50			50	H	6 gm. acet. blk.	-63	85	93
T-61	100				A		-73	85	102
T-72	50	50			B		-73	67	75
T-62	100				A		+20	30	91
T-90	100				A		+20	52	93
T-68	50	50			B		+20	76	92
T-91	50			50	H		+20	60	86

TABLE XII-a Continued

$HgSO_4$ + 20 grams Sulfur

	Electrolyte New %	Electrolyte Spent %	Electrolyte Synthetic #1 %	Electrolyte Synthetic #2 %	Code	Cathode Additive	Temp. °C	Hrs. to 1.5v	Hrs. to 1.3v
T-87	50			50	H	6 gm. acet. blk.	-63	85	93
T-85	100				A	6 gm. acet. blk.	-63	79	95
T-93	electrolyzed KSCN in L. NH_3				I		-63	75	89
T-101	50 Wt. % KSCN in L. NH_3				J		-63	103	108
T-102	10 Wt. % KSCN in L. NH_3				E		-63	52	60

Concentration of KSCN Electrolyte

The following excerpts from Table I-b illustrate the relative performance of KSCN/NH_3 electrolytes in concentrations of 10% (T-102), 25% (T-60), and 50% (T-101). Ten per cent KSCN was unsatisfactory, but both 25% and 50% provided long cell life, although the latter generated voltage at a much lower level during most of the high load portion of the cycle.

Excerpts from Table I-b

Test No. T-	High Load Voltage after: 1 day	2 days	3 days	4 days	Low Load Voltage after: 1 day	2 days	3 days	4 days	Hrs. to 1.5v	Hrs. to 1.3v*
102	1.82	1.59			2.20	1.99			52	60
60	2.15	2.10	1.95	1.55	2.26	2.25	2.15	1.80	106	119
101	1.70	1.81	1.75	1.58	2.21	2.21	2.20	2.03	103	108

See Table XII-a, page 39, for cell variables

*under heavy load

Electrolyzed KSCN

In T-93, the electrolyzed KSCN worked reasonably well, but it did not run as long as T-60 with new electrolyte.

Table XII-b shows that the more concentrated $Mg(SCN)_2$/liquid NH_3 electrolyte, (H), was superior to the more dilute one, (G), which also contained $MgSO_4$.

TABLE XII-b

$HgSO_4$ + 10 grams Sulfur

	Electrolyte							
			Synthetic					
	New %	Spent %	#1 %	#2 %	Code	Temp. °C	Hrs. to 1.5v	Hrs. to 1.3v
T-83	50		50		G	+20	49	76
T-88	50			50	H	+20	67	78

$Hg(SCN)_2$/S cells performed almost equally well at -63°C with either new or 50 per cent spent electrolyte.

TABLE XII-c

$Hg(SCN)_2$ + 20 Grams Sulfur

	Electrolyte							
			Synthetic					
	New %	Spent %	#1 %	#2 %	Code	Temp. °C	Hrs. to 1.5v	Hrs. to 1.3v
T-70	100				A	-63	63	74
T-78	50	50			B	-63	60	70

Pre-treatment of Cathode Mix with 25% KSCN/liquid NH_3

The cathode mix contained in cells T-69 and T-75 was treated with 25 per cent KSCN/liquid NH_3 electrolyte; after which the NH_3 was evaporated and the mixture was pulverized and then used to build the bobbin cathodes. Since the combined weight of the solids was not increased by the treatment, it is assumed that none of the NH_3 coordinated with the $HgSO_4$. This leads to the further assumption that all of the $HgSO_4$ must have combined in some complex form with the KSCN. Subsequent cell tests with this material were not encouraging.

TABLE XII-d

Pre-treatment of Cathode Mix with 25% KSCN/liquid NH_3

		Code	Temp. °C	Hrs. to 1.5v	Hrs. to 1.3v
T-69	liquid NH_3 activation	C	-63	30	45
T-75	activated with 10% KSCN/L. NH_3	E	-63	0	23

REPRODUCIBILITY

With respect to reproducibility, three pairs of cells are listed in Table XIII which differ only with respect to slight variation of anode area. The average variation in life between pairs to 1.5 volts was 9 per cent. Considering the small value of $\Delta v/\Delta t$ (the slope of the voltage time curve), this correlation is felt to be rather good.

TABLE XIII

Outside Anode; Low Temperature Liquid Activation

	Hours to 1.5 VHL	Anode Area cm^2 One Side	Variation in Life
T-18	59	430	11%
T-19	53	362	
T-33	73	337	1%
T-35	72	377	
T-37	97	368	14%
T-41	84	368	

ACTIVATED STAND

Objective II of this program is aimed at limited wet stand to +70°C.

Preliminary investigations included (1) the coating of Mg anodes with lead by vapor deposition, (2) "tinning" the Mg surfaces by a proprietary process, (3) coating the outer anode surface with K-M rubber cement, (4) electrolyte modifications such as "spent" and synthetic $Mg(SCN)_2/NH_3$ solutions, (5) cathodic stabilization through the addition of sulfates, (6) cathode composition, (7) improved separation, (8) active stands under light drain, (9) analyses of spent electrolyte and gaseous cell products, and (10) studies of cell chemistry. The work has not progressed far enough at this writing to warrant detailed evaluation.

The activated stand cell tests are summarized in Table XIV. In order to gain an insight into the relative effects of various factors, the initial wet stands were conducted at -63°C, followed by one stand at +20°C.

Several interesting developments may be found in Table XIV. (a) The application of a light drain, such as 3,000 Ω or about 2/3 mA, increased the discharge life decidedly. (b) The use of a microporous rubber separator, in addition to the standard M-1365 Webril paper, was very beneficial. (c) In T-103, a modest improvement was gained by painting one side of the MPR with K-M rubber cement in the form of 1/4" wide bands at 1/4" intervals. (d) Similar results were obtained in T-106 by coating both sides of the MPR with 1" wide bands of cement on 1/4" spacings. The masking design was offset on the two sides in a pattern that required diffusion to follow a zig-zag course. (e) The longest life to 1.5 volts was obtained in T-107 through the use of a double layer of MPR. (f) Half-spent electrolyte yielded very poor results in T-105.

Some progress is indicated by test No. T-109 in which the wet stand was conducted at 20°C with a 3,000 Ω load, followed by discharge under cyclic load at -63°C.

TABLE XIV

ACTIVATED STAND

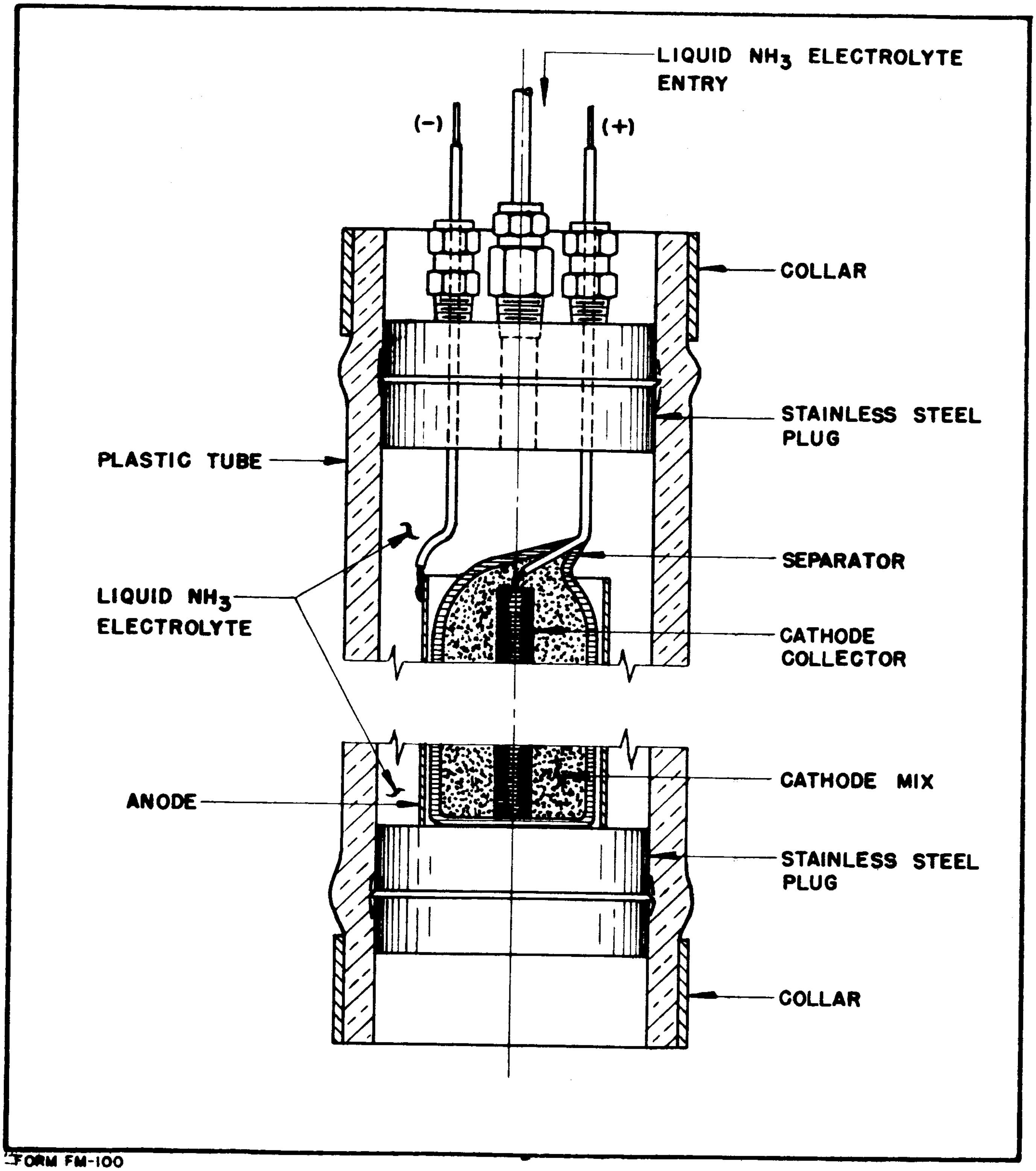
Discharge Temperature = -63°C

Test No. T-	$HgSO_4$ gms	Coord. No.	S gms	C gms	Activated Stand Hrs.	Activated Stand Temp. °C	Activated Stand Load Ω	Discharge Hrs. to 1.5v	Discharge Hrs. to 1.3v	Special Features
46	126	2	20	54	64	-63	o.c.	12	17	cathode only exposed to activated stand
63	120	2	20	60	66	-63	o.c.	10	16	cathode only exposed to activated stand
79	106	0	20	60	66	-63	o.c.	15	20	anodes coated on back with rubber from here on
In the following tests, the complete cells were exposed to activated stand.										
89	106	0	20	60	45	-63	3000	30	39	cyclic load applied for 1 hour after first day's stand
92	106	0	20	60	65	-63	3000	41	58	
105	106	0	20	60	65	-63	2700	16	44	electrolyte was half spent, half new
94	106	0	20	60	65	-63	645	41	50	
98	106	0	20	60	65	-63	3000	58	76	additional microporous rubber separator (MPR)
103	106	0	20	60	65	-63	3000	61	88	one side of MPR partially masked with rubber cement
106	106	0	20	60	65	-63	2700	64	74	both sides of MPR partially masked with rubber cement
107	106	0	20	60	65	-63	2700	69	78	double layer of MPR
95	50	0	50	80	65	-63	3000	45	54	
109	106	0	20	60	65	+20	3000	0	3	ran 75 hours to 0.80 volts

TEST HARDWARE

Two sizes of Pyrex test tubes were employed as cell cases for low temperature tests during the third quarter. The one size is 1.8 inches inside diameter by 16 inches long; the other, 2.5 inches inside diameter by 20 inches long. The longer tube was used for greater depth in the cooling bath. In most tests, a plastic liner was inserted in the test tube to reduce the volume by about 20 $inches^3$. These tubes are convenient to use and permit observation and modification to cells during operation in the presence of case material.

Another type of test chamber, No. A-624, Figure I, page 48, was used for tests at -73°C and at +20°C. This vehicle makes use of disposable, cross-linked polyethylene pipe and re-usable stainless steel end plugs. Preliminary hydraulic and pneumatic tests conducted on this container indicated that it could withstand pressures in excess of 1,000 pounds per square inch at room temperature. The versatility of this plastic pipe makes changing the cell length an easy task.



A-624 TEST VEHICLE

FIGURE 1

REFRIGERATION

One of our mechanical refrigeration units was redesigned and rebuilt to provide a continuous operating temperature of -63°C.

A liquid CO_2 refrigeration unit with forced circulation has been operated successfully at -73°C.

A mechanical refrigerator capable of maintaining a temperature of -90°C is scheduled for delivery in April.

FUTURE WORK

Bring the electrode and electrolyte studies to a logical conclusion.

Continue the effort towards wet stand.

Conduct lower temperature cell tests towards the goal of -90°C.